Rational Design of Dithienylethenes with Photoelectrochromic Properties

by

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Abstract

1,2-Dithienylethene compounds (DTEs) reversibly interconvert between two isomeric forms, referred to as the colourless (ring-open isomer) and coloured (ring-closed isomer). This interconversion can be achieved through photochemical, electrochemical and thermal means. The photochemical toggling of DTEs is well characterized in the literature. However, their electrochromic behaviour is seldom reported and almost all known examples degrade through electropolymerisation. The fully electroactive DTEs are unstable in the coloured form at room temperature and undergo ring-opening in the dark. Depending on the application, DTEs may require a “single time use” (biological application / imaging) or must undergo extensive cycling (ophthalmics, smart windows). The goal of this work was to find the structural demands that allow integration of three desirable features, photo-, electrochemical and thermal stability.

The first part of this thesis addresses the synthetic manipulation of the DTE core capable of catalytic oxidative ring-opening reactions. Key functional groups were appended in the $\alpha$-positions of the electroactive DTE framework. These groups were carefully chosen in the context of thermal stability of the coloured-form and the mitigation of the undesired electropolymerisation. These substituents range from electron donating (through induction) methyl and $t$-butyl, to electron withdrawing fluorine atoms and electron rich thiophene rings. It was found that the DTEs studied presented an additive driving force, $\pi$-$\pi$ stacking, for the undesired thermal ring-opening in the dark, a first observation among these type of compounds.

The second part of the thesis is concerned with the mechanism of the ring-closing reaction triggered by the reduction of the uncoloured form. A new hypothesis regarding the mechanism of the process is presented. The preliminary studies suggest that the intermediate for the ring-closing reaction is the doubly reduced form of the ring-open isomer rather than the mono-reduced form as previously thought.

Keywords: 1,2-Dithienylethenes; ring-open and ring closed-isomers; photo and electrochromic, electropolymerization, thermal ring-opening.
To my husband, Dan.
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<tr>
<td>°C</td>
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<td>+I</td>
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</tr>
<tr>
<td>M. p</td>
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<td>n-BuLi</td>
<td>normal-butyl lithium</td>
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<tr>
<td>NBu₄PF₆</td>
<td>tetrabutylammonium hexafluorophosphate</td>
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<td>N-chlorosuccinimide</td>
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<td>nanometre</td>
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<td>nuclear magnetic resonance</td>
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<td>NVS</td>
<td>night vision safety</td>
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<td>P</td>
<td>parallel</td>
</tr>
<tr>
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<td>para substituted</td>
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<td>[1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane</td>
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<td>photoelectrochromic devices</td>
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<td>phenyl</td>
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<td>polyoxometalates</td>
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<tr>
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<td>ring-open</td>
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<tr>
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<td>standard calomel electrode</td>
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<td>standard deviation</td>
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<td>half life</td>
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<tr>
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<td>transparent conductor layer</td>
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<td>TLC</td>
<td>thin layer chromatography</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
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<td>ultraviolet–visible</td>
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<tr>
<td>V</td>
<td>Volt</td>
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<tr>
<td>W</td>
<td>Watt</td>
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<td>working electrode</td>
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<tr>
<td>d</td>
<td>chemical shift</td>
</tr>
<tr>
<td>DH</td>
<td>change in enthalpy</td>
</tr>
<tr>
<td>I</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>wavelength at the absorption maximum</td>
</tr>
<tr>
<td>$\mu$A</td>
<td>microamper</td>
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1. Introduction

Colour is the visual sensation that is caused by differing qualities (hue, tint, brightness or intensity) of the light reflected or emitted by certain materials or substances. The role of colour in nature and even in our socio-economic environment is too complex to be defined here and not within the scope of this thesis. Due to the fact that colours are so important in our daily lives, their use from art to technology has become a topic of growing interest for many authors. Furthermore, the change in colour of a certain substance or device on demand is being employed in different technologies that are already marketable. The two types of colour changing (chromism) discussed in this thesis are photochromism and electrochromism. The reader has to be aware that other types of chromism exist (thermochromism, solvatochromism, halochromism) with various potential applications, and they have been already reviewed in literature.

The first type of colour change discussed here is photochromism. It is the property of absorbing and filtering light on demand by exposing the device to a source of light (the most convenient being the sunlight). The second colour change discussed is electrochromism, where absorbing and filtering light on command is done using electricity.

1.1. Applications for Photochromic and Electrochromic Technologies

Photochromic materials change colour upon absorption of light, as a result of an isomerization between two forms: typically one isomer is colourless and the other coloured. In electrochromic technology the optical properties of the material are varied in response to a change in the oxidation state. If the colour changes when the material is oxidized, the colouration is said to be anodic; if the material changes colour when reduced the colouration is said to be cathodic. Many substances possess photo- or
electrochromic properties, but few have ideal properties. For example, photochromic materials used in ophthalmic lenses must be resistant to photodegradation and have a relatively fast response to UV stimulus. On the other hand, if electrochromics are used in smart windows, they are expected to be energy efficient, to have high durability, and lastly to be affordable, more so for electrochromics rather than photochromics (500$/sqm).4

1.2. Marketed Photochromic and Electrochromic Devices and Other Emerging Technologies

So far to the best of my knowledge, only three devices are already commercialized: photochromic lenses (commercialized by Transitions™ and Radenstock), NVS Mirrors (commercialized by Gentex) and electrochromic windows (commercialized by Sage Electrochromics and EControl-Glas). These types of technologies have been developed for two reasons: (1) the photochromic lenses are very convenient for people requiring prescription glasses and the electrochromic devices are developed to reduce glare (automotive industry) and to reduce air-conditioning costs (smart windows). In the next section, there is a succinct explanation of the mechanisms of darkening and fading of colour and the architectural requirements for such devices.

In this thesis, the technology that combines the properties of photochromics and electrochromics is referred as photoelectrochromic (PEC). One of the steps (colouring or fading) is triggered by irradiation with light and the reverse step is triggered by applying an electric potential. Traditionally PECs were regarded as photovoltaic powered electrochromic devices. The photoelectrochromics are superior to the above mentioned technologies as they will take advantage of both processes.

1.3. Thesis Overview

The goal of this research was to design and synthesize a dithienylethene (DTE) molecule that would have the desirable properties to be used in PEC devices. The most robust DTEs are compounds that consist of a perfluorocyclopentene ring that is disubstituted with thiophene rings (Scheme 1-1). The arrangement of three alternating
double bonds, one from the cyclopentene moiety and one from each of the two thiophenes, forms a π orbital framework that facilitates a conrotatory electrocyclic reaction upon exposure to UV light. This form is called ring–open isomer. The photochemical reaction affords the other isomer and its main features are the newly formed six membered ring and the planarity that allows the extended conjugation (Scheme 1-1). This form is called ring–closed isomer. By irradiation with visible light, the ring–closed isomer undergoes the conrotatory cycloreversion affording the ring–open isomer.

The α positions of the thiophene rings are substituted with various groups (R groups). Depending on the structure of these R groups, DTEs are also electrochromic. Unlike the photochemistry which is bidirectional for DTEs, the electrochemistry is mainly unidirectional. That means that only one of the isomers can be obtained by applying an electrical potential.

Scheme 1.1. General photochemical reaction that affords the toggling between the two forms: ring–open and ring–closed isomers.

Chapter 2 of this thesis is a summary of the photo-electrochromic properties of DTEs as well as the characterization method used in the field and the shortcomings of this class of compounds.

Given the complexity of the research goals, the work in this thesis was split into two parts:

1. Chapters 3 and 4 addresses the unidirectional, ring–opening reaction driven by application of an oxidative potential. This work is necessary
because there is a need for a systematic study of structure–property relationship, so one will be able to design a fully electrochromic and photochromic DTE not by trial and error, but rather by informed decisions. To date, it is relatively easy for someone to design a photochromic DTE: depending on the application one would require the use of the DTE for a very extensive period of time (ophthalmics, automotive industry) or even for a single time use (biological application / imaging). On the other hand, the electrochemical behaviour and fatigue (electrodegradation) of DTE(s) are scarcely reported.

2. Chapter 5 addresses the logical design of a DTE that can be toggled between the two forms either with photochemical or electrochemical means as desired, and novel insights into the mechanism of ring–closing driven by electrochemical reduction is presented.

1.3.1. **Photochromic devices**

The major application of photochromic materials is in ophthalmic lenses, although other applications are being envisioned, such as optical switches, optical filters and memory devices. Although there are many compounds that possess quite remarkable photochromic properties, usually three important classes are regarded as potential candidates for the applications mentioned above: naphthopyrans, spironaphthoxazines and diarylethenes. The first two classes of compounds: naphthopyrans, and spironaphthoxazines are already used in the ophthalmic industry. Although the exact structures of the compounds used in photochromic lenses (such as Transitions™) are not fully known, Scheme 1-2 depicts the basic molecular architecture of such compounds. A common aspect of the three compounds presented in the Scheme 1-2 is that the photochromism is due to a rearrangement of the bonds from a cyclic structure (closed forms, therefore the suffix bolded “c” is used in the labelling of such compounds) to the ring–open isomer (hence the bolded “o”). Throughout this thesis, this type of labelling of the structural isomers will be commonly employed. Compounds 1.1c and 1.2c are colourless because they are comprised of two aromatic moieties separated by sp³ hybridized tetrahedral carbon atoms, that isolates them
electronically. The electronic absorption spectra of the ring–closed (RC) forms consists of $\pi-\pi^*$ transitions in the UV region.

![Diagram of structural changes between two isomers](image)

**Scheme 1.2.** Structural changes between the two isomers as a result of light irradiation or thermal influence for: naphthopyran (1.1), spironaphthoxazine (1.2) and diarylethene (1.3).

If compounds 1.1c and 1.2c (both colourless) are irradiated with UV light they undergo an electrocyclic ring–opening of the pyran or oxazine rings. Thus are formed the coloured ring–open (RO) isomers 1.1o and 1.2o, usually named merocyanines. The ring–open isomers are coloured due to the now extended conjugation through the planar backbone. Compounds 1.1 and 1.2 belong to the T–type photochromic dyes which means that the back reaction (ring–closing) occurs in the dark. These T–type photochromic dyes, where both phenomena (colourizing and fading) are a result of a dynamic equilibrium between the forward photochemical colourizing reaction and the reverse back thermal fading reaction, are already marketed in the form of ophthalmics. Photochromic lenses have come a long way since they were first introduced on the
market: usually it takes around two minutes for the lenses to completely change from light stage to the dark stage, which is a huge advance compared to the initial darkening times. A big improvement was achieved with the new photochromic lenses that are basically clear compared to the older versions that still possessed a tint in the colourless state. There are two major disadvantages of the photochromic lenses: (1) they do not get darker inside vehicles as the windshield absorbs most of the UV radiation, changing the spectrum and intensity of light for which the ophthalmic lenses were designed and (2) the fading reaction is very slow.

Unlike napthopyrans and spironaphthoxazines, diarylethenes (such as compound 1.3) are P−type photochromics (thermally irreversible). The ring-open form 1.3o is colourless due to a lack of extended conjugation, although the isomer is cross-conjugated. Upon irradiation with UV-light, the open form undergoes a conrotatory 6π-electrocyclic reaction and forms the coloured isomer 1.3c. The ring-closed isomer is coloured due to extended linear conjugation through the rigid backbone. The reverse photochemical reaction of fading (ring-opening) can be photochemically induced by selectively exciting the coloured ring-closed isomer with visible light. Due to its high bistability (generally both isomers are stable in the dark even at elevated temperatures) many diarylethenes are not ideal candidates for photochromic lenses, but rather for optoelectronic devices. The two isomers of the diarylethenes, although not yet incorporated in a device, have not only different absorption spectra, but also quite different physical and chemical properties (redox potentials, refractive indices, optical rotation, magnetic interactions).

1.3.2. Electrochromic Devices

Electrochromics are materials that change colour in response to a change in oxidation state caused by a redox reaction, which occurs when an electrical potential is applied. Electrochromic devices are coloured and faded when desired within seconds of applying the potential. Thus, the colouring and fading processes are independent of the environmental factors: lighting and temperature. Such control is needed, but it comes at a greater cost of manufacturing, because most devices have a somewhat more complicated architecture when compared to their photochromic counterparts. The electrochromic technologies have the potential to be used in various applications such
as smart windows used in buildings, automotive industry and aircrafts, sunglasses, or camouflage gear.

An electrochromic device (Figure 1.1) usually consists of several layers. A typical device contains a first layer, which is the transparent support layer (glass), second is the transparent conductor layer (TCL, that usually is either ITO, indium tin oxide or FTO, fluorine doped tin oxide), third layer (deep blue) is the cathodically electroactive layer, fourth layer is the ion conductor layer, fifth layer is the ion storage layer or the anodic complementary layer and another TCL and finally the back support layer.

![Figure 1.1. Basic design of an electrochromic multilayered device where layers (1) and (7) are glass, (2) and (6) are the transparent conductive layers, (3) and (5) are the electrochromic layers and (4) is the ion conductive layer. Arrows show the movement of electrons and ions through the device.](image)

**Solid Oxide Electrochromic Device**

Solid oxide electrochromic devices are based on the cathodically colouring of tungsten oxide WO₃. The colour of pure WO₃ (W oxidation state is VI) is pale yellow. When the oxide is deposited as a thin film it looks almost colourless. When the W^{VI} is
electrochemically reduced to $W^{V}$, electrochromism takes place due to intervalence charge transfer between $W^{VI}$ and $W^{V}$. As a result of the reduction process, a build up of negative charge within the film occurs, therefore the device must contain small and highly mobile positive ions ($\text{Li}^+$, $\text{H}^+$) that will intercalate in the now mixed tungsten oxide lattice ($W^{VI}$ and $W^{V}$) in order to neutralize it.\textsuperscript{13} The formal reaction is presented in Scheme 1-3.

\[
\text{WO}_3 + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_xW_{(1-x)}^{VI}W_x^ VO_3
\]

Scheme 1.3. Formal reaction for the reduction of $\text{WO}_3$.

Reversibility was reported to be around $10^4$-$10^7$ cycles\textsuperscript{14} depending upon the type of device and conditions. SAGE Electrochromics, Inc. already is commercializing electrochromic windows for exterior applications with a warranty given by the company of 10 years. The materials themselves are not very expensive, although the manufacturing process requires a sophisticated multilayer deposition and vapour deposition.\textsuperscript{4}

**NVS Mirrors Marketed by Gentex**

The electrochromic devices marketed by Gentex are based on viologens (4,4' -bispyridinium salts). The mirrors are called NVS (night vision safety) mirrors and their composition is protected by patents. Although it is possible to speculate that the NVS mirror contain two complementary electroactive chemical species: 1) a cathodically colouring species – viologen (changes colour when reduced) 2) an anodically colouring species – thiazine or a phenylene diamine (changes colour when oxidized).\textsuperscript{14} Viologens are 4,4'-bispyridinium salts that have a well studied electrochromic behaviour.
There are three redox states for the typical viologen species (Scheme 1-4). The first state is a dication and is colourless, but changes its colour when it is monoreduced to form the monoradical cation. The colour of the monoradical cation is due to the charge transfer between the two nitrogen atoms formally charged with +1 and respectively 0. When the mirror is switched on, the species migrate to their respective electrodes. Once the dual electrochromic colouration process has begun, the products (now coloured species) diffuse away from their respective electrodes and meet in the solution, where electron transfer reaction takes place and the original uncharged species are reformed. This type of ECD is used only in small sized devices due its requirement for a continuous flow of current for the recolouring of the electroactive species and therefore is not energy efficient.

**Promising Electrochromic Technologies**

Although not yet marketed as an electrochromic device, π-conjugated aromatic polymers and metal coordination complexes might be good alternatives to the more expensive devices based on transition metal oxides. The benefits in the case of polymers are quite numerous and just to name a few: mechanical flexibility, ease of colour tuning, polychromism and one of the more important factors is the low-cost processing. This section contains a very brief description of the colouration mechanisms for the two classes of electrochromics with a few very important examples.

**Metal Coordination Complexes**

There are quite a few examples of electrochromic metal coordination complexes. One of the most well known and largely studied one is Prussian Blue (generic name).\(^\text{15}\) Unlike other metal oxides (WO\(_3\)) its electrochromism is anodically driven: if reduced it turns from deep blue to colourless (reaction (1), Scheme 1-5), if it is fully oxidized it turns

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**Scheme 1.4.** The redox states of viologen.
from deep blue to yellow. The blue colour of the Prussian Blue is due to the intervalence charge transfer between Fe$^{\text{II}}$ and Fe$^{\text{III}}$. Once again to achieve the neutrality of the devices ingress (for reduction) and outgress (for oxidation) of the counter-ion is required. Prussian Blue is mainly used as a complementary anodic colourizing layer next to cathodically colourizing electrochromic WO$_3$.\textsuperscript{16}

\[
\text{[Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^\text{-} + e^- \rightarrow \text{[Fe}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6]^{2-} \quad \text{(1)}
\]

\[
\text{blue} \quad \text{colourless}
\]

\[
\text{[Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^\text{-} \rightarrow \text{[Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6] + e^- \quad \text{(2)}
\]

\[
\text{blue} \quad \text{yellow}
\]

**Scheme 1.5.** Electrochromic behaviour of Prussian Blue.

**Electrochromic Polymers**

Electrochemical oxidation of aromatic conjugated polymers has as an end result the formation of the bipolaron bands.\textsuperscript{17} A bipolaron is the part of a conjugated polymer that contains two positive charges. The colour of the polymers is a function of the optical band gap $E_g$ (highest occupied $\pi$ electron band = valence band and lowest unoccupied band = conduction band for the neutral state). For the oxidized or reduced form, the colour is due to the energy difference between the bipolaron band and conduction band.

Polythiophenes (PT) are easily synthesized and processed. This polymer in its neutral state is red coloured and when oxidized it is pale blue, almost colourless. In its neutral state the red colour is due to a strong $\pi-\pi^*$ interband transition. When it is partially oxidized it forms radical cations (polarons) and has a mixed structure between the regular aromatic thiophene and a quinoidal structure. At this stage the $\pi-\pi^*$ interband transition takes place to a smaller extent and new electronic transitions of lower energy can occur, hence the lighter red. Nevertheless, it is quite difficult to obtain homogeneous PT films because of its insolubility and various side reactions. For this reason PT has not been incorporated in marketable devices so far; although better versions were developed. A polymer with remarkable electronic and electrochromic properties is poly(3,4 ethylene dioxythiophene) (PEDOT).\textsuperscript{17,18}
Although electrochromic polymers offer better processability, facile colour tunability and multiple coloured states in the same film (polyelectrochromic) than their inorganic or molecular counterparts, large electrochromic devices are not on the market yet. The field of electrochromic polymers research is growing and better versions are reported regularly. It is only a matter of time until the electrochromic polymers will become marketable. So far there is no clear winner between the inorganic and organic electrochromic devices. On one hand, the inorganic devices show very good stability, but the engineering is expensive, caused by the difficulty to precisely deposit the multilayers within the device. On the other side, the organic based EC devices are already commercialized (Gentex mirrors) and surprisingly, the devices are based on small organic molecules (viologen and phenylene diamine). So far the electrochromic polymers have great potential due to their mechanical flexibility, and ease in colour-tuning via structural control, along with the low-cost processing. It is interesting to note that some of the drawbacks of the EC polymers from 15 years ago: low cycle-life stability, difficulty in finding a suitable and compatible material for the counter electrode (one EC polymer has to get coloured when oxidized the other one has to change colour when reduced)\textsuperscript{18} some of them are solved.\textsuperscript{19} 

\textbf{Figure 1.2.} Chemical structures (bottom) of (a) neutral PT, (b) small degree of oxidation of the polymer (polaron) and (c) higher degree of oxidation (bipolaron) and the allowed electronic transitions for each state (top).
**Liquid Crystal Based Devices**

A rival to the above-mentioned electrochromic technologies is now the mature field of the liquid crystal devices. The liquid crystal (LC) is incorporated in a polymer matrix and sandwiched between two transparent electrodes. When the device is the ON state, the liquid crystal molecules align and the device is clear and light passes through. When the power is switched OFF the liquid crystal molecules are randomly oriented, scattering light hence the device is opaque. A French company Saint-Gobain Glass already commercializes these types of smart windows. They require continuous power consumption for the clear state and also they show some photodegradation.

Furthermore, the transparent state still shows some haze. When compared to ECD, LC based devices are easily manufactured, but from the point of energy efficiency they are inferior due to the fact that the transparent state requires continuous energy consumption unlike the ECD that require energy only to get to the darker state.

**1.3.3. Photoelectrochromic Devices – Dual Mode Devices**

Initially photoelectrochromic devices (PECD) devices were defined as hybrids of electrochromics (EC) and a source of renewable energy - dye-sensitized solar cells. But pertinent to this thesis, a photoelectrochomic technology is referred to any type of device where its colouration / decolouration processes can be achieved with both stimuli (light and electricity), thus including with the photovoltaic electrochromic devices also the polyoxometalates and dithienylethenes containing technologies. Photoelectrochromic devices (PECD) are superior to the ECD because they will significantly reduce the amount of electricity consumed for example by air conditioning (if used as smart windows).

**Photovoltaic Based Design**

The first dual mode photochromic and electrochromic devices contain tungstenate films (WO₃) incorporated into the architecture of a photovoltaic electrochemical cell. The basic design of a such photovoltaic cell contains: the anode (transparent semiconductor) is coated with a photovoltaic film (ruthenium-polypyridine sensitized polycrystalline titanium oxide) and the cathode (transparent semiconductor) is covered with the electrochromic layer of WO₃ (Figure 1.3). The photovoltaic film - dye
sensitized semiconductor, when exposed to sunlight, absorbs photons of the right energy (sufficient energy to excite the dye). In this process the photoexcited dye is oxidized and the electrons are placed into the conduction band of TiO$_2$ particles. The electrons move through the TiO$_2$ particle to the anode (doped SnO$_2$) and from here to the external circuit. The electrons are passing through the external circuit and the WO$_3$ film is reduced at the other electrode (colouration mechanism explained previously). In order to maintain charge compensation of the WO$_3$ layer, Li$^+$ ions from the electrolyte migrate into the WO$_3$ film. If the device is not irradiated, the charged WO$_3$ film expels the Li$^+$ ions and the electrons pass through the external circuit and fading takes place. The blue colour of the device can be maintained if the connection between the electrodes is interrupted.

![Diagram of a photoelectrochromic device](image)

**Figure 1.3.** On the left is a diagram of a photoelectrochromic device in the dark and in the bleached state. Electrolyte contains LiI dissolved in propylene carbonate at a certain concentration. On the right is the diagram of the same photoelectrochromic device that is being irradiated; electrons are flowing on the external circuit (direction is shown by the arrow). The curvy arrows inside of the device show the two processes: Li$^+$ being intercalated into the partially reduced WO$_3$ film (note the charged - blue colour of the WO$_3$ film) and I$^-$ reducing the oxidized dye.

Although there are advancements in the area of photoelectrochromics, there are no marketed products yet. There are still some problems regarding their stability. One important factor is the desorption of the dye from TiO$_2$ into the electrolyte (although some dyes perform better than others). Some reports present the degradation of WO$_3$.
in the electrolyte: LiI–I₂-polycarbonate, although there are reports that this degradation is not observed. Because these types of devices have so much potential, it is expected that a marketable photoelectrochromic technology should be eventually developed.

**Polyoxometalates (POM) Based Devices**

Polyoxometalates (POM) are inorganic polyatomic ions that contain transition metal oxyanions linked together by shared oxygen atoms to form a large three-dimensional framework. One such POM that has already incorporated in an electrochromic devices is (NH₄)₁₄[NaP₉W₃₀O₁₁₀]. This particular POM has a complex structure: cyclic assembly of five PW₆O₂₂⁻³ units and Na⁺ ion in the center of the cluster. In its neutral state the POM is colourless, and absorbs only in UV region due to oxygen-to-metal (O→M) ligand-to-metal charge transfer (LMCT). Nevertheless, they can change colour when reduced or by UV-irradiation under certain conditions. From the point of view of photochemistry, in the presence of counterions that can donate a proton (pyridinium) the irradiation of POM crystals by UV light results in a coloured blue species. The colouration mechanism, although quite complicated, can be explained by formation of the charge transfer species I in Scheme 1-6. As a result of the UV-irradiation a charged transfer species is formed by the electron transfer from alkylammonium cations to the excited state of POM and the simultaneous proton transfer between the alkyl ammonium to the oxygen atom. On the other hand, when the POM, is reduced electrons are placed on the empty d orbitals of the metal, d¹ electrons facilitate the absorption of visible light through intervalence charge transfer among metal centers and d-d transitions.

![Scheme 1.6. Charge transfer species of the POM(s) with alkyl ammonium cations.](image)

Device containing photo and electrochromic POM(s) have been already fabricated. A schematic representation of a such device is presented in Figure 1.4. This type of device presents great benefits: it does not require vacuum deposition and
the fabrication process is simpler: the multilayer formation is done with the polymer polyethyleneimine and polystyrene by dipping the substrate repeatedly into aqueous solutions containing poly(4-vinylpyridine) or POM. This type of device shows no degradation even after 1500 cycles (photochemical testing). However the photochemical darkening does not have the same efficiency as the electrochemical darkening (note stage II in the diagram is lighter blue when compared to the dark stage IV, Figure 1.4.). Furthermore, both colouration stages (electrochromic and photochromic steps) have a low optical contrast. Some hybrid devices containing an organic component (such as viologen that has high optical contrast) and POM are being tested.28

Figure 1.4. On the right: schematic representation of a device based on a transparent negatively charged POM embedded in a matrix of poly(4-vinylpyridine) and polyethyleneimine. The device contains also polystyrene but not shown for clarity. On the left the colour change associated with each of electrochromic and photochromic stage.

A Device Incorporating a Dithienylethene (DTE)

One can speculate that the engineering aspects of the multilayer ECD and PECD are quite difficult regardless of the electrochromic material (inorganic or organic). On the other hand, the sandwich type devices containing the LC are much easier to manufacture. But so far ECD and PECD devices have a higher potential to be used in commercial devices (smart windows and ophthalmics) unlike LC devices that are mainly
used as privacy walls in conference rooms. Thinking one step ahead, one can speculate that the best device will be the one that has:

1. a simple architecture (LC type),
2. the durability of the inorganic electrochromic devices (WO$_3$ based devices),
3. tunability and ease of processing of the polymer based ECD,
4. and the energy efficiency comparable to that of the PECD.

A very interesting approach to such type of technology was presented by Gorodetsky et al. where he designed and synthesized an organic molecule 1.4$^{2+}$ that belongs to the dithienylethenes (DTE) class (Scheme 1-7). This particular DTE shows extraordinary electrochromic and photochromic properties. It can undergo darkening (colour change from pale yellow to dark blue) when irradiated with sunlight and the same colour change can be obtained if the DTE is reduced electrochemically.

Scheme 1.7. DTE with dual electrochromic and photochromic behavior: stages I and II represent the photochromic transformations, stage III represents the thermal ring-opening in the dark; stage IV is the reduction process and stage V is the catalytic oxidation. Counteranions (PF$_6^-$) are omitted for clarity.

The system can undergo fading if it is irradiated with visible light or if it is oxidized. Thus this compound has dual photochromic and electrochromic behavior
making it an excellent candidate to be the active ingredient in a full electrochromic and photochromic device. The device containing compound $1.4^{2+}$ (Scheme 1-7) will meet many criteria for the marketed product. First of all, the darkening will be automatic: if the sun is shining on the window or the glasses, they will change colour almost instantaneously without human interaction. This step does not require electrical power input, as the device is activated by the light. This darkening process will lower energy consumption even more by reducing the energy needed to cool down a room. In general the persistence of colour for this class of compounds can range from weeks to years. Thus DTEs will bring the benefits of photochromics if they are incorporated in the ECD. On the other hand, if fading is required the device containing a DTE (of the type of compound $1.4^{2+}$), an oxidation potential can be applied: the ring–closed isomer would be oxidized and will undergo a spontaneous ring–opening reaction, thus forming the colourless ring-open isomer. Due to the number of reactions: photochemical, electrochemical and even an undesired and unexpected spontaneous ring–opening (in the dark) this type of molecule can undergo, a more detailed explanation is necessary and it will be discussed in Chapter 2.

1.4. Summary

Photochromic lenses are widely marketed and accepted worldwide. On the other hand, ECD are still considered to be expensive and sometimes reliability is being questioned. There is no question that lately in the context of global warming and depletion of some of the traditional energy sources that the energy saving methods will be welcomed. ECD and PECD if used as windows will minimize the consumption of energy during summer time for cooling by blocking the UV-Vis radiation.

So far the ECD based on $\text{WO}_3$ are already marketed. The fact that they are not prone to degradation (10 years warranty given by the manufacturer) are making them quite attractive for a more wider use. On the other hand, the process of manufacturing these devices is more complicated and expensive as they require the deposition of five layers of precise thickness. Another issue of certain importance is that usually the only colour it presents is blue. A very promising alternative to the inorganic based ECD is the polymer based devices. The electrochromic polymers offer easier processability and a
wide colour range that can be tuned by facile synthesis. A drawback to the polymer based devices is that they do not posses yet the same stability as their inorganic counterparts.

PECD (photoelectrochromic devices) are better alternatives to the ECD as they tend to use a lower amount of energy and provide a better control without human interaction. PECD are not marketable yet. However the reason and this can be first attributed to the number of cycles that one such device performs without degradation, about 150. The lack of colour tunability (only shades of blue are available) and high cost of mass production might be also good reasons for these classes of PECD not being commercialized.

But compared to inorganic electrochromic technologies that approach 40 years since the first reports and soon will reach maturity, PECD are still to be developed in order to be considered for use. Among PECD the DTE based technology stands out as being the most versatile from the point of view of ease of designing devices because there is no need for costly layer depositions. DTE molecules also posses the advantage of easy colour tuning through synthetically means. The energy for colourizing step will require minimal power consumption as it is done automatically by sun irradiation.
2. **Introduction to Properties, Characterization Methods and Degradation Pathways for Photoelectrochromic Dithienylethenes**

The field of photochromic dithienylethenes (DTE(s)) is well matured, but to the best of my knowledge compounds $1.4^{2+}$ and $2.1^{2+}$ are the only two reported examples able to toggle between two isomers either photochemically or electrochemically, as desired (Scheme 2.1). However these two compounds fall short in three ways:

1. pronounced photodegradation,
2. electrochemically induced degradation (electropolymerization), and
3. the coloured state is not stable in the dark at room temperature, thus requiring a constant application of potential in order to maintain the coloured state which is energy inefficient.
The behaviour of these two compounds (1.4\textsuperscript{2+} and 2.1\textsuperscript{2+}), both desired and undesired (decomposition) is complex. To make things even more complicated, each of the two isomers have different decomposition pathways. The next discussion is meant to introduce the molecular structural requirements of a full electrochromic and photochromic DTE, their unique photo and electrochemical properties (both desired and undesired) and methods used to characterize them throughout this work.

2.1. Photochromic Behavior of DTE(s)

The photochromic isomerisation (6\pi, conrotatory, electrocyclic) reaction is the structural transformation that is responsible for the colour changes of these type of compounds. The next discussion represents an introduction to the background theory of the photochromism of DTEs. Upon irradiation with UV light, the colourless ring–open...
isomer undergoes photochemically induced $6\pi$, conrotatory, electrocyclic reaction to form the coloured ring–closed form (Scheme 2.2). By this photoreaction, the ring–closed isomer is formed, which presents extended conjugation that runs along the rigid backbone of the DTE. The result of this change in structure is best noted in the UV-Vis spectrum where a new band is detected. Pertinent to this thesis, substituents at the positions 2 and 2’ are called internal groups ($R_i$) and substituents at positions 5 and 5’ are called external groups ($R_e$).

![Scheme 2.2. General photochromic reactions of DTE(s). On the left is the ring open isomer that upon irradiation with UV light undergoes $6\pi$ electrocyclic ring closure reaction forming the ring–closed form. The ring–closed isomer if irradiated with visible light undergoes the ring–opening reaction.](image)

2.1.1. Mechanism for Photochemical Ring–Closing and Opening Reactions

To emphasize the stereospecific nature of the ring closure, the frontier molecular orbitals (only HOMO and LUMO) are presented in Figure 2.1. For this purpose, the hexatriene ($2Z,4Z,6Z$)-octa-$2,4,6$-triene, which is the simplest molecular framework that a DTE can be reduced to is shown. When the ring–open isomer is irradiated with UV-light, an electron is promoted form HOMO to LUMO. Due to symmetry considerations ($\pi$ orbital symmetry), ring–closing can occur only in a conrotatory fashion. The conrotatory ring closure can occur clockwise or counterclockwise direction with equal probability, therefore, both stereoisomers RR and SS are obtained in equal amounts.
The ring–open isomers are usually colourless, due to only cross-conjugation and absorb in the UV region of the spectrum (continuous line in Figure 2.2). Upon irradiation of the ring–open isomer with UV-light, the absorption band in the UV region decreases, while the absorption band in the visible region increases. As a result, the photochromic system changes from a colourless to a coloured form. Figure 2.2 illustrates how the change takes place as function of irradiation time. The first spectrum (solid black line) represents the absorption spectrum of a solution containing only the ring–open isomer. After 10 seconds of irradiation of the solution with an UV-lamp with 365 nm, a new absorption band appears in the visible region; this new absorption band is due to the formation of the ring–closed isomer. Upon further irradiation with 365 nm light, the concentration of the ring–closed isomer increases.
Figure 2.2. Overlapped absorption spectra of a representative DTE containing solution (CH₃CN) that is irradiated with 365 nm light. Solid black line is the absorption spectrum for pure ring-open isomer and the dashed line spectra contain a mixture of both forms.

It is important to note that the photochemical transformation (from ring–open to ring–closed isomer) is not quantitative. After a certain period of time, an equilibrium between the two forms is reached and the ratio of ring–closed to the ring–open form does not change. There is an overlap in the absorption spectra of the two isomers, which is the reason for the formation of a chemical equilibrium between the two isomers. The ring–closed isomers has two electronic transitions, S₀–S₁ centered in the visible region and S₀–S₂ centered in the UV region. Because the electronic transition S₀–S₂ of the ring–closed form usually overlaps with the S₀–S₁ transition of the ring–open isomer the photochemical cycloreversion is competitive with the ring–closing reaction. This equilibrium established between the two forms is referred to as the photostationary state (PSS) and it can be calculated with the Equation 2-1.
The mechanism of ring-opening is also conrotatory, allowed due to symmetry considerations, and takes place when a PSS mixture is irradiated with visible light (usually only the ring-closed isomer absorbs visible light).\textsuperscript{31}

\subsection*{2.1.2. Photodegradation of DTE(s)}

DTEs take advantage of a photochemical reaction, rearrangement (6-π-electrocyclization) in order to toggle between the two isomers. But at the same time, unfortunately some irreversible photochemical processes accompany the desired isomerization. The interconversion between two forms is called cycling. Compounds that can undergo numerous ring-closing and opening cycles, without photodegradation, are referred to as photofatigue resistant. At a first glance, Table 2.1 reveals that there are two factors dictating the photostability: the molecular architecture and the environment in which the testing was done. Compound \textbf{2.2} is the most stable DTE reported. Compound \textbf{1.3} shows extremely different behaviour depending on environment, from $10^4$ cycles in the crystalline state to only hundreds of cycles in dissolved state. In the next discussion, the photodegradation as function of molecular structure and environment of cycling will be addressed briefly.

\begin{equation}
\text{PSS} = \frac{[\text{RC}]_{\text{at equilibrium}}}{[\text{RO}]_{\text{initial}}} \times 100 \quad \text{eq 2-1}
\end{equation}
Table 2.1. The number of photochemical cycles for few representative DTEs as function of structure and environment of cycling (2.2, 2.3, 1.3, 2.4 and 2.1<sup>z</sup>).

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>Medium</th>
<th>Crystal</th>
<th>Solvent</th>
<th>Higher Viscosity Medium - Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>&lt;1.3 X 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>200</td>
<td>&gt; 850</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>800</td>
<td>200</td>
<td>10&lt;sup&gt;4&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1500</td>
</tr>
<tr>
<td>2.1&lt;sup&gt;z&lt;/sup&gt;</td>
<td>NA but almost complete degradation after 24 hours of continuous irradiation</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Different Photodegradation Pathways for Both Isomers

DTEs are usually regarded as stable compounds from the point of photodegradation. But some of the compounds are more stable than others and one would like to use the latter in a device. The questions are:

- Which of the two photoisomers photodegrades?
- What is the cause for the photodegradation from the molecular architectural point of view?
- Can this decomposition pathway can be avoided?

The major byproducts from photodegradation have been isolated and characterized, and a mechanism for their formation proposed. Scheme 2.3 gives the general structures of the byproducts resulting from prolonged exposure of the individual isomers to UV light (254 nm).

\[ \text{Scheme 2.3. Photodegradation products of the two isomers.} \]

When explaining the formation of the byproducts from the ring–open isomer, the primary cause is the presence of the H atom in position three of the thiophene that undergoes a series of sigmatropic shifts. The proposed mechanism involves one $6\pi$ electrocyclic ring closure (different from the one that yields the desired ring–closed isomer), two sigmatropic shifts and, in the end, the loss of an HF molecule forming the
photochemical byproduct \(2.5^{2+}\) (Scheme 2.4). One way to prevent this degradation is to block that position with a \(\text{CH}_3\) group.

Scheme 2.4. Proposed mechanism for the formation of compound \(2.5^{2+}\).

The ring–closed isomer also photodegrades and a general mechanism\(^\text{37}\) was proposed and it is given is Scheme 2.5. Unlike its photoisomer, whose photodegradation can be impeded by blocking the positions that trigger the photodegradation, the ring–closed isomer is just photodegradable due to excess UV light.\(^\text{39}\)
Photochemical Stability as Function of Medium of Cycling

The compound most stable to photodegradation is 2.2 (Table 2.1).\textsuperscript{32} The reason for its particular stability is given by the fact that this compound is a benzothiophene derivative, thus having blocked the positions prone to photoreactions (Scheme 2.4). What is surprising about its stability is that the cycling was done even in the presence of oxygen. It is known that organic molecules react with singlet oxygen in a reaction called photooxidation, this being one the degradation routes for organic molecules, dyes and polymers. Professor Irie proved that benzothiophene DTEs have a lower reactivity towards singlet oxygen and also the main photochemical pathway of decomposition (Scheme 2.6) cannot be generated from this type of compound.\textsuperscript{7} On the other hand, compound 1.3 does not have the same photostability.\textsuperscript{33} Under the same conditions (oxygenated solvent), it has only 200 stable photochemical cycles. It is believed that this is due to the three factors enumerated above: 1) decomposition of ring–open isomer, 2) decomposition of the closed form and 3) photooxidation. When one of the factors is eliminated (the cycling is done in absence of oxygen) compound 1.3 can be cycled 800 times, thus proving that oxygen indeed is reacting with the compound. When comparing the photostability of compound 2.4 (methyl groups in position 4 and 4’) with compound 1.3 (hydrogen atoms in positions 4 and 4’) the former is more stable. Upon 850 cycles compound 2.4 shows no degradation whereas compound 1.3 shows a decline in absorbance and formation of decomposition compounds. A more interesting change

*Scheme 2.5.* Proposed mechanism for the photodegradation of ring–closed isomer.
regarding the photostability of compound 1.3 is when the photochemical cycling is done in solid state (crystal). The stability is drastically improved to $10^4$ cycles. Once the molecule is “locked” and does not have the same degree of freedom to rotate or to collide with the neighbouring molecules, it does not photodegrade and undergoes only the desired $6\pi$ electrocyclization reaction. It is worthy to mention that many DTEs (such as compound 1.4o$^{2+}$) do not undergo the photochemical ring-closing reaction in the solid state (crystal) and in order to be used in a device the compounds should be dissolved in a polymer medium. The polymer matrix will mimic both environments: keeping the molecule “locked”, but at the same time it will allow some collisions with the neighbouring molecules. For compound 2.4 testing was performed in a polymer matrix to investigate if the photochromism is preserved in such environment.\textsuperscript{34} It was found that compound 2.4 can be cycled 1500 times until the film-medium starts to degrade. Given the fact that today the plastic industry has developed so much and by the incorporation of UV blockers into plastics the life of the plastics can significantly extend their lifetime, one can speculate that the photodegradation can be drastically changed if the right amount of tuning is done to the medium of environment.\textsuperscript{39}

\subsection*{2.2. Thermal Stability of the Ring–Closed Isomer in the Dark}

Usually the ring–closed isomers of DTEs are mainly known for their remarkable stability in the dark. The following section contains a very brief overview of the thermal stability in the dark of the coloured form, a short enumeration of the factors that trigger the thermal back cycloreversion and the mechanism. For example, compound 1.3c (Table 2.3) has a half life of 1900 years at a temperature of 30 °C,\textsuperscript{40} at the opposite end there is compound 2.1c$^{2+}$ with a half life of less than 30 minutes at the same temperature.\textsuperscript{29} The thermal ring–opening in the dark is due to both steric and electronic factors: bulky internal groups such as 2-methyl-thiophene impose a certain strain on the 2-2’ $\sigma$ C-C bond; the strong external EWG groups (eg. pyridiniums) decrease the electron density on the same $\sigma$ C-C bond. The combination of these two factors results in the instability of the ring–closed isomer in the dark.
2.2.1. **Thermal Characterization of the Ring–Closed Isomers in the Dark**

The thermal stability of the ring–closed isomers of diarylethenes is related to three very important factors (1) aromatic stabilization, (2) steric and (3) electronic effects. The next discussion is a brief literature review on the stability of the ring–closed isomer in the dark as a function of substituent structure:

1) Aromatic stabilization energy of the aryl groups (Figure 2.4).

When the aryl groups have low aromatic stabilization energies (such as thiophene and furan), the energy difference ($\Delta H$) between the two isomers becomes small and the energy barrier in the thermal cycloreversion (dark) reaction becomes larger, hence the ring–closed form is “thermally stable”.\(^{41}\) On the other hand when the aryl group has a high aromatic stabilization energy (e.g. benzene) $\Delta H$ is quite big and the energy barrier for the thermal cycloreversion is smaller hence the ring–closed isomer is unstable in the dark and is considered “thermally unstable”.

![Diagram showing different isomers and their energy differences](image)

**Figure 2.3.** Half lives at 80 °C and calculated $\Delta H$ for three representative DTEs, where the rearomatization is the driving force for the thermal cycloreversion.\(^8\)

2) Steric destabilization of the cyclohexadiene ring.

When the volume of the internal group is increased from methyl 1.3c,\(^7\) to ethyl 2.6c,\(^{42}\) to isopropyl 2.8c\(^{43}\) the stability of the ring–closed isomer is decreased and the reaction rate for the thermal cycloreversion in the dark changes from
thousands of years to months (Table 2.2). Usually the reason is accepted to be the increase in the bond length of the photochemically generated $\sigma$ C–C bond, hence it is a weaker bond.

**Table 2.2.** Half life of four representative DTEs where the stability of the ring-closed isomer is accepted to be a function of the steric bulk of the internal groups.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Half Life</th>
<th>Temperature</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3c</td>
<td>22 days</td>
<td>100 °C</td>
<td>decalin</td>
</tr>
<tr>
<td></td>
<td>1900 years</td>
<td>30 °C</td>
<td></td>
</tr>
<tr>
<td>2.6c</td>
<td>40 h</td>
<td>100 °C</td>
<td>toluene</td>
</tr>
<tr>
<td></td>
<td>64 years</td>
<td>30 °C</td>
<td></td>
</tr>
<tr>
<td>2.7c</td>
<td>29 h</td>
<td>100 °C</td>
<td>toluene</td>
</tr>
<tr>
<td></td>
<td>38 years</td>
<td>30 °C</td>
<td></td>
</tr>
<tr>
<td>2.8c</td>
<td>30 min</td>
<td>100 °C</td>
<td>decalin</td>
</tr>
<tr>
<td></td>
<td>91 days</td>
<td>30 °C</td>
<td></td>
</tr>
</tbody>
</table>

Note: half life for compound 2.7c\(^{44}\) for all the other compounds the reference is given in the text.

3. Electronic influence of various groups (both internal and external groups).

- Heteroatoms as internal groups typically result in a decrease in the stability of the cyclic form in the dark, thus they do increase the rate of thermal cycloreversion in the dark. Table 2.3 presents the half lives for compounds 2.9c, 2.10c and 2.11c.\(^{45}\) Compound 2.9c (methoxy as internal group) shows a decrease in the stability in the dark, but is not
as pronounced as 2.10c (OEt as internal group). Therefore compound 2.11c follows the same trend. Also the steric effects play a role as expected in the series presented in Table 2.2.

**Table 2.3.** Half lives of representative DTE(s) where the internal group is a heteroatom.

<table>
<thead>
<tr>
<th>compound</th>
<th>half life</th>
<th>temperature</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3c</td>
<td>1900 years</td>
<td>30 °C</td>
<td>decalin</td>
</tr>
<tr>
<td>2.9c</td>
<td>420 years</td>
<td>30 °C</td>
<td>decalin</td>
</tr>
<tr>
<td>2.10c</td>
<td>65 years</td>
<td>30 °C</td>
<td>decalin</td>
</tr>
<tr>
<td>2.11c</td>
<td>7 years</td>
<td>30 °C</td>
<td>decalin</td>
</tr>
</tbody>
</table>

- The influence of EWG as internal and external groups, upon the half lives of DTEs is presented below. EWG as external substituents decrease the stability of the ring–closed form in the dark by decreasing the electron density at the photochemically generated σ bond (Table 2.4) Compound 2.13c has a very modest half life (at 60 °C) of less than 4 minutes. Compounds 2.14c and 2.15c follow the same trend. The half life of compound 2.12 (CN as internal susbtituents) was not reported, but it was mentioned that the ring–opening in the dark was not seen after one day.
The purpose of the overview presented above is to outline that compound 1.3c is the most stable DTE in the dark and any structural modification results in a decrease in the stability of the ring-closed form in the dark. The above mentioned factors all contribute to the destabilization of the cyclohexadiene motif of the ring-closed isomer but what is also of interest is the mechanism of the thermal-dark reaction. The next section presents is a short discussion on the mechanism of the dark cycloreversion.

### 2.2.2. Mechanism of the Thermal Cycloreversion in the Dark

There are numerous reports regarding the thermal stability of the ring-closed isomer in the dark with very well characterized kinetic values. Irie’s review from 2000 presents a comprehensive list of compounds and trends. Overall, the thermal cycloreversion reaction (in the dark) is fitted to first order reaction kinetics. However, there are not many reports regarding the mechanism. That was until relatively recently,
when an important study regarding the mechanism of the cycloreversion in the dark was conducted in the crystal and in solution (toluene) of compound 2.6c. The solution study probed the kinetics of the thermal cycloreversion in the dark, and revealed that the reaction does not produce any byproducts, only the ring–open isomer. By heating a crystal of pure ring–closed isomer and monitoring the process of ring-opening by X-ray crystallography it was revealed that the reaction is conrotatory. Due to symmetry orbital considerations if the thermal cycloreversion is a Woodward-Hoffman type electrocyclic reaction, the ring–opening reaction must be disrotatory: in order to correlate the symmetry of the HOMO of the starting material (cyclohexadiene) with that of the HOMO of the product (hexatriene), thus leading to a E,Z-hexatriene, which is not possible due to steric hindrance. Furthermore, the X–ray analysis of a crystal containing only ring–closed isomer that was heated and monitored revealed a Z,Z- hexatriene (Scheme 2.6) as the single form for the ring–open isomer. Thus the thermal ring–opening is not an electrocyclic/concerted reaction, but rather a reaction that involves an intermediate, most likely a biradical, followed by a rearrangement.
2.3. Electrochromic Properties of DTE Molecules

The ring–opening and closing reactions can be triggered photochemically as described. The same transformation can be often achieved by electrochemical means. In order to understand the electrochromic properties of DTEs, one has to first understand the electrochemical behaviour of both isomers, which is different (the reason will be explained below) and how do they respond to electron transfer reactions.

2.3.1. Electrochemical Behaviour of DTEs

The redox potentials of organic molecules are dictated by the relative energies of their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). The electrochemical potential at which a molecule is oxidized (loses an electron) is proportional to the energy of the HOMO. On the other hand, the
electrochemical potential at which a molecule is reduced (accepts electrons) is proportional to the energy of the LUMO.

The oxidation potential of the ring–open isomer is dictated by the two thiophene rings, hence its oxidation potential is over +1 V and is accompanied by electropolymerization. The oxidation potential of the ring–closed form occurs at lower potential (less positive by as much as 500 mV) when compared to the ring–open isomer due to the fact that the HOMO of the ring–closed isomer is higher in energy then the HOMO of the ring–open isomer. On the other hand, because the ring–closed isomers of DTEs have smaller HOMO-LUMO energy gaps in comparison to the corresponding ring–open isomers, the reduction potentials of the ring–closed isomers occur at less negative potentials. From a very simplified point of view, the redox potential of the ring–closed form can be viewed as a conjugated polyene when compared to the ring–open isomer (assuming that the pendant external and internal groups do not have a strong effect) (Scheme 2.7).

![Scheme 2.7](image)

**Scheme 2.7.** The photo and electrochemical switching between the two isomers leads to reversible structural (geometry) and electronic changes (HOMO-LUMO gap redox potential). Note the smaller HOMO-LUMO gap in the case of the ring–closed isomer.

### 2.3.2. *Introduction to Electrochromic DTEs*

It is important to note that the vast majority of the DTEs molecules possess unidirectional electrochromism. The majority of the DTEs can undergo the isomerization electrochemically only when they are oxidized. Compounds **2.16o** undergoes only
ring–closing when oxidized. Compound 2.17c undergoes only ring–opening when oxidized (Scheme 2.8).

Only a few DTEs show electrochromism when reduced.\(^50,51\) Compound 2.18o\(^{2+}\) is one of the few DTEs that when reduced undergoes ring–closing (Scheme 2.9).

The reason for their electrochromic behaviour is not still completely understood. Initially the electrochromic behaviour was attributed to the molecular architecture if the DTE has internal alkyl groups (usually CH\(_3\)) it will undergo oxidative ring–closing, if the DTE possess aromatic groups as internal groups (thiophene, benzene) it will undergo oxidative ring–opening (Scheme 2.8). Regarding the ring–closing triggered by the electrochemical reduction, only the DTEs with pyridinium groups as external groups are undergoing the isomerizations.
Having all this information regarding the unidirectional electrochromism Gorodetsky et al. synthesized a fully electrochromic and photochormic DTE system. There was a single viable choice in choosing the external and internal groups:

1. the external groups are pyridinium moieties to allow the reductive ring–closing reaction, and
2. internal groups are aromatic moieties to allow the oxidative ring–opening process to occur.

To the best of my knowledge, so far there are only two DTEs, 1.4<sup>2+</sup> and 2.1<sup>2+</sup> (Scheme 2.10) that are fully electrochromic. The ring–closing takes place as a result of the reduction and the ring–opening reactions can be triggered by oxidation. The same isomerisation can be achieved also by photochemical means.<sup>29</sup>

![Scheme 2.10. Photochromic and electrochromic reactions for compounds 2.1<sup>2+</sup> and 1.4<sup>2+</sup>.](image)

### 2.3.3. Cyclic Voltammetry (CV) as Analytical Technique in Probing the Isomerization of DTE as Response to a Change in the Applied Potential

At this stage, the reader will benefit from a very brief overview of the most utilized voltammetric technique, cyclic voltammetry (CV). The basic principle of a voltammetric
technique is the application of a potential to an electrode, that is immersed in a solution containing the analyte of interest and monitoring the resulting current. In voltammetric techniques, the scanning of the potential is done in one direction; either to more positive or to more negative potentials. In cyclic voltammetry the scanning of the potential is done in both directions. During a CV experiment, the species formed during the forward scan are studied by analyzing their behaviour on the return scan. A typical experiment (Figure 2.4) uses three electrodes: a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). All three electrodes are immersed in the solution to be analyzed and connected to the potentiostat. The potential of the WE is adjusted externally, therefore both processes (oxidation and reduction) can be achieved on its surface. Usually the working electrode is made out of a chemically inert conductive material such as platinum. The RE (such as Ag/AgCl or SCE) maintains a invariant potential under the conditions of the experiment. The potential is measured between the RE and WE and the current is measured between the WE and the CE. A CE is employed to allow for accurate measurements to be made between the working and reference electrodes. The CE is used to ensure that the current runs between itself and WE. The solution that contains the analyte has to contain also the supporting electrolyte. The supporting electrolyte (NBu4PF6 was used in these studies) has to be inert and has the role of maintaining a homogeneous electric field.52
Figure 2.4. (a) Schematic representation of a cyclic voltammogram setup (A = amperemeter, CE = counter electrode, WE = working electrode, RE = reference electrode, V = voltmeter) (b) A typical three-electrode cell filled with solvent and electrolyte (always at least 100 times more concentrated than the analyte); the CE is separated from the bulk of the solution by a glass tube with a fritted ending.

Important parameters of a CV experiment are: potential range, initial potential $E_i$, initial sweep direction, scan rate $\nu$ (mV /s ), final potential $E_f$, peak currents $I_{p,a}$ and $I_{p,c}$, peak potentials $E_{p,a}$ and $E_{p,c}$, half wave potential $E_{1/2}$ and zero current line (Figure 2.5). All these parameters are explained briefly below. The potential range is scanned between the initial potential and final potential at a fixed rate. However once the final potential is reached (forward scan), the scan is reversed and the voltage is swept back to the initial potential (backward scan). Initial sweep direction can be either in anodic or cathodic direction (see the direction of the arrow on each CV graph). The scan rate linearly is the linear ramping of the potential of the WE potential versus time and can be calculated from the slope of the line, applied potential vs time (Figure 2.5(a)). A zero current has to be chosen (that is the baseline) that accounts for the capacitive current. The next step is to analyze the cathodic and anodic currents and potentials as shown in Scheme 2.5(c). The half wave potential $E_{p/2}$ is calculated by formula $\frac{1}{2} (E_{p,a} + E_{p,c})$. If a cyclic voltammogram is reversible (the requirements for a full reversible cyclic voltammogram will be further discussed bellow) the formal potential is equal (approximated to be equal) to the $E_{p/2}$. 

40
Figure 2.5. (a) Cyclic voltammogram triangular potential sweep waveforms; potential range 0 V-1.75 V; sweep rate = 300 mV/s; two sweeps performed (b) cyclic voltammogram of an electroactive analyte (c) zoom in the CV: anodic (oxidation) peak potential ($E_{pox} = 0.39$ V) cathodic (reduction) peak potential ($E_{pred} = 0.32$ V).

Figure 2.5(b) represents the cyclic voltammogram of an analyte that has a reversible oxidation at 0.35 V and one irreversible oxidation at 1.49 V. The CV starts at the initial potential of 0 V and the potential is swept anodically (in the positive direction) until the maximum potential of 1.75 V. Once the potential reaches the maximum desired potential, it is swept back with the same sweep rate. The current peaks are described by peak potentials ($E_{pox}$ and $E_{pred}$ in Figure 2.5(c)). The redox couple at 0.35 V, is said to be “reversible” when the ratio of the peak currents passed at oxidation ($I_{pox}$) and reduction ($I_{pred}$) equals unity (see Equations 2-2 and 2-3).
Fully reversible electrochemical reactions are described by Nernst Equation 2-2 and \( E_{\text{pox}} \) and \( E_{\text{pred}} \) should be separated by a difference of 0.057 V for monelectronic process. Furthermore, for a fully reversible cyclic voltammogram, \( E_{p/2} \) has to be independent on the scan rate and \( I_p \) has to be proportional to \( \nu^{1/2} \) (scan rate). In the case described in Figure 2.6 b \( I_{\text{pox}}/I_{\text{pred}} = 1 \), but the difference \( E_{\text{pox}} - E_{\text{pred}} = 0.39 - 0.32 \) V = 0.07 V. At a first glance, expected value of 0.057 V for a reversible CV and the experimental value of 0.07 V for the difference of peak potentials suggests that the case described is not fully reversible. However, this particular CV was run in an organic solvent that has a higher resistivity compared to water and it is well know that in such systems the peaks can be separated with as much as 0.1 V and still be considered fully reversible. In order to assess if a redox couple is reversible or not, one has to be cautious and to know previous reported values.

The advantage of cyclic voltammetry is that it allows us to observe an electrochemical reaction in real time, thus it gives us access to mechanistic information. Useful information can be gathered by analyzing the irreversible waves, at least in the case of DTE(s). In the CV depicted above, Figure 2.5(b) from the reversible redox couple (0.35 V), one can say that whatever is being oxidized on the forward scan is stable enough on the CV time scale to be reduced on the back sweep.

EC Irreversible Electrochemical Reactions

The more intriguing question is regarding the species that is being oxidized at the more anodic potential of 1.49 V in Figure 2.5(b). Once the species is oxidized, if the redox couple is reversible, one should be able to see the reduction of the species produced and this is not the case. A possibility is that the oxidized species is unstable and undergoes a reaction to another species that has a different redox behaviour or might not be electroactive in the given potential range. This type of mechanism is called
EC (Electrochemical Chemical) because in the initial electrochemical step, the analyte (A) is being oxidized and for the sake of simplicity the oxidation is one-electronic to $A^+$. This newly formed species is unstable and undergoes the chemical transformation to species $B^+$ (chemical step), hence the name EC mechanism. $B^+$ is not responsive on the potential of the experiment (Scheme 2.11).

$$\begin{align*}
A & \xrightarrow{k_{\text{oxid}}} A^+ + e^- \\
A^+ & \xrightarrow{k_c} B^+
\end{align*}$$

*Scheme 2.11.* General reaction scheme of an irreversible EC reaction ($k_c > k_{\text{red}}$).

**ECE Class Irreversible Electrochemical Reactions**

There are a multitude of examples of irreversible CVs and reaction mechanisms associated with them, but the ones pertinent to the research in this thesis are EC (presented above) and ECE which are going to be described below. An ECE type reaction (Scheme 2.12) is similar to an EC reaction, except for the fact that the product formed in first step (electrochemically) undergoes a chemical reaction forming new species that is also electrochemically active in the CV. So if the analyte A is being oxidized, it forms the oxidized species $A^+$, which is not stable and cyclizes to the more stable species $B^+$. The newly formed species $B^+$ can be reduced and the peak associated with this process can be monitored in the CV.
Next will be presented the two types of ECE reactions that the fully electrochromic DTE(s) are undergoing in order to be toggled between the two isomers. The first one is the irreversible reduction of the ring-open isomer, thus yielding the cyclic form and the second one is electrochemical ring-opening reactions of some DTEs that are catalytic. The reader has to be aware certain DTE(s) can undergo ring-closing reactions through oxidation of the ring-open isomer, but the mechanism is beyond the scope of this thesis and is not discussed here.  

2.3.4. **Electrochemical Ring-Closing of DTE(s) through Reduction of the Ring-Open Isomer – ECE Mechanism**

The easiest way to understand the behaviour of a fully electrochromic DTE is to analyze the CV of compound 1.4$^{2+}$ (Figure 2.6). With a solid black line is plotted the CV acquired for the ring-open isomer (1.4o$^{2+}$) and with a dashed line is plotted the CV of the ring-closed isomer obtained photochemically.
Figure 2.6. Cyclic voltammograms of compounds 1.4o$^{2+}$ (solid line) and 1.4c$^{2+}$ (dashed line). With green is emphasized the formation of the ring–closed isomer. With pink and a star is emphasized the ring–opening reaction during oxidation of the ring–closed isomer. The graph is modified from reference 50 with permission from Wiley.

The sweep starts from 0 V and is swept anodically. The first notable peak on the first sweep is probably the oxidation of the thiophene moieties at about 2.0 V. By sweeping in the cathodic direction an irreversible wave is seen at -1 V. At this point, the ring–open isomer is reduced monoelectronically. This step is the electrochemical (E) step. This species is unstable and undergoes a cyclization reaction, mechanism depicted with curved arrows (Scheme 2.13), this is the chemically irreversible (C) step. Thus the coloured ring–closed isomer is formed which is in its reduced form. The presence of the ring–closed isomer is noted by the presence of a small peak on the return scan. Its presence its emphasized with a green circle (oxidation of the radical cation of the ring–closed isomer), this being the second E step (electrochemical step).
Scheme 2.13. Typical electrochemical ring closing reaction of a DTE 1.4$^{2+}$ through a reduction step that follows an ECE type mechanism (photochemical reaction conditions and thermal stability are given in blue). Counterions PF$_6^-$ are omitted for clarity. Equations of the ECE of the ring closing reaction $k_{\text{red}}$, $k_{\text{ox}}$, $k_c = \text{reaction constant for cyclization}$.29

The electrochemically driven ring–closing isomerisation can be summarized:

1. the reduction of ring–open species (1.4o$^{2+}$) to the radical cation species (1.4o$^{*+}$),
2. the cyclization of the unstable radical cation species (1.4o$^{+*}$) to the more stable radical cation (1.4c$^{*+}$), and
3. the oxidation of the radical cation species ($1.4c^{\cdash}$) to the ring-closed isomer ($1.4c^{2+}$).

2.3.5. **Electrochemical Ring–Opening of DTEs through Oxidation of the Ring–Closed Isomer – ECE Type Mechanism**

The oxidative ring–opening reaction takes place also through an ECE mechanism (Scheme 2.14). The electrochemical ring–opening reactions of DTEs are known to be catalytic. This catalytic effect occurs because the ring–open isomer has an oxidation potential that is more positive than the oxidation potential of the ring–closed isomer. Compound $1.4c^{2+}$ undergoes such a type of reaction due to the presence of an aromatic substituent as an internal group. The electrochemically triggered ring–opening reaction can be monitored with the aid of CV. When the ring–closed form ($1.4c^{2+}$) is oxidized (dashed line Figure 2.6) at a potential of 1.5 V (pink-asterix in Figure 2.6) there is a very small peak barely noticeable above the baseline current. The ring–closed isomer is being oxidized to the radical cation isomer ($1.4c^{\cdash}$), this is the first E step. The radical cation ring–closed isomer undergoes cycloreversion at the electrode and forms the radical cation of the ring–open isomer ($1.4o^{\cdash}$) (a chemically irreversible step). The radical cation of the ring–open isomer can oxidize a neighbouring molecule of the ring–closed form (third step E and induces a catalytic ring–opening cascade).
Scheme 2.14 Oxidative ring-opening reaction of compound 1.4c\textsuperscript{2+}, the photochemical conditions for the isomerization and the thermal stability of the ring-closed are given in blue.

A schematic diagram of this type of transformation is presented in Scheme 2.15. With blue is depicted the molecule of the ring-closed isomer that is being oxidized at the electrode and is undergoing the cycloreversion forming the more stable ring-open radical cation. The newly formed ring-open radical cation can migrate to the other electrode to be reduced, but it is more probable that it will oxidize a neighbouring ring-closed molecule (shown in red) thus making this process a catalytic cycle.
Scheme 2.15. Schematic mechanism of the catalytic ring-opening reaction through oxidation. PF$_6^-$ counteranions are now shown for clarity. With blue is the molecule that is being oxidized at the electrode; with red is the molecule that is being oxidized by previous oxidized molecule at the electrode, hence the catalytic ring-opening reaction.

2.3.6. Electrochemical degradation of DTEs

So far DTEs such as compounds 1.4$^{2+}$ and 2.1$^{2+}$ undergo ring-closing triggered by a negative potential applied to the ring-open isomer and a ring-opening reaction when a positive potential is applied to the ring-closed form. From the point of view of the structure, this is due to the presence of EWG groups (pyridinium) as external groups and
at least one aromatic group as internal group. Scheme 2.16 presents the full photoelectrochromic cycle and in the middle is the photochemical transformation, on top is the electrochemical ring–closing reaction and on the bottom are presented the steps necessary for the electrocatalytic oxidative ring–opening. Decomposition takes place in both of the electrochemically triggered isomerisations together with the desired reactions of ring–closing or ring–opening. Unlike the photochemical degradation of the both isomers that has been well documented and reported, the electrochemical degradation is believed to be due to electropolymerization. In the next two subchapters the electrochemical degradation will be discussed form the point of view of applied potential.
Scheme 2.16. Steps I) and II) are the photochemical isomerizations, III) thermal cycloreversion, IV) reduction of the 1.4o2+ to 1.4c*•, IV') cyclization of the 1.4o2+• to 1.4c*•, IV'') oxidation of the 1.4c*• to 1.4c2+, V) oxidation of the 1.4c2+ to 1.4c3+, V') ring-opening of the 1.4c3+ to the 1.4o3+ and V'') catalytic reduction of the 1.4o3+ to the 1.4o2+.

Electrochemical degradation during reduction step

When compound 1.4o2+ is reduced to the radical cation 1.4o2•+, it undergoes cyclization to the ring–closed radical cation (1.4c*•). The yield of this reaction is under 25%. This molecule could not be used in a useful device because of the substantial
degradation after the first reduction step. Although the degradation compounds were not characterized, it was noted that an insoluble black precipitate was formed, thus implying that maybe a polymerization type reaction is also taking place. It is known that viologen molecules form dimer structures. Given the particular structure of the DTE one can only speculate about the structure of the insoluble black precipitate polymer. In Scheme 2.17 if the radical is shown in the right position, it yields the desired reaction (path a), but through resonance (path b) one can place the radical α to the nitrogen and a dimerization will be possible. Overall the degradation during the reduction is maybe due to the coupling of the pyridium rings rather than the reduction of thiophene rings. The reductive electropolymerization of the thiophene, although known, is less likely and can be achieved only in certain conditions. Both isomers (open and closed forms) have similar electrodegradation pathways when reduced, but the extent of the decomposition was not assigned so far.
**Scheme 2.17.** Possible decomposition when a negative potential is applied (path b) and desired coupling (path a).

**Electrochemical Degradation During Oxidation Step**

When oxidized, the ring–closed isomer 1.4c^{2+} undergoes the desired ring–opening, but this reaction is accompanied by the anodic electropolymerization of thiophene rings. It is well known that both α and β positions of the thiophene rings are susceptible to electropolymerization. The relative reactivity of the α and β positions is...
about 95:5 in the case of the monomer, but once the polymer chain increases in length this ratio changes and the probability of $\alpha$ to $\beta$ linkage increases.\textsuperscript{58} Compound 1.4 has four positions suitable for electropolymerization, highlighted with a grey circle (Scheme 2.17). Although not all four positions can be electropolymerized, due to steric repulsions, electrodegradation is inevitable and a crosslinked polymer as the one from Scheme 2.18 can be formed.

Scheme 2.18. Possible degradation during oxidation step. Pyridinium groups are abbreviated Py$^+$ and counterion (PF$_6^-$) are omitted for simplicity.

2.4. Elucidation of Electrochromic Behaviour by DFT Calculations

The ring–closing in the reduction step and ring–opening in the oxidation step are possible because the thermal barrier for the cyclization / ring–opening is very low in the
reduced, respectively oxidized form of the DTEs. So far DFT (Density Functional Theory) calculations were done for molecules 2.16o, 2.16c, 2.17o, 2.17c,\textsuperscript{59} and pyridinium derivative 2.9o\textsuperscript{2+} and 2.9c\textsuperscript{2+} (its structure in Scheme 2.19).\textsuperscript{51}

1. \textit{Ring-closing triggered by oxidation} – compound 2.16o once oxidized forms compound 2.16o\textsuperscript{•+}, which spontaneously isomerizes to form compound 2.16c\textsuperscript{•+}. The driving force for the oxidative cyclization is the larger stabilization of the radical cation for the closed isomer, $\Delta H(2.16c^{+\bullet}) < \Delta H(2.16o^{+\bullet})$.

2. \textit{Ring-opening triggered by oxidation} – when compound 2.17c is oxidized the radical cation formed 2.17c\textsuperscript{•+} is less stabilized than the open form 2.17o\textsuperscript{•+}, hence the cycloreversion is thermodynamically spontaneous, $\Delta H(2.17c^{+\bullet}) > \Delta H(2.17o^{+\bullet})$.

3. \textit{Ring-closing triggered by reduction} – when compound 2.19o\textsuperscript{2+} (bispyridinium) is electrochemical reduced, a radical cation is formed, 2.19o\textsuperscript{•}, that is less stabilized than its ring-closed isomer 2.19c\textsuperscript{•+}, $\Delta H(2.19c^{+\bullet}) < \Delta H(2.19o^{+\bullet})$. 
Scheme 2.19. Energy diagram of calculated total energies for both isomers and their radical cations (for three representative compounds: 2.6, 2.7 and 2.9) formed either oxidation (case a and b) or by reduction (case c). The value of total energies are not given in the scheme because their were calculated with different hybrid functionals B3LYP for and a) and b) and PBE0 for c).
2.5. Summary

Due to their response to both light and electricity, DTEs are good candidates to be incorporated in photoelectrochromic devices. The benefit from the point of view of the design of the device is quite notable. The need for multiple layer devices is diminished, as the same molecule of DTE will be able to be oxidized or reduced; hence no ion storage layer or complementary redox layer would be needed. Therefore this type of device would be superior to the inorganic based devices. One more advantage is the ability to fine-tune the DTE colour by choosing the appropriate internal and external groups. By using a mixture of various DTEs with different absorption spectra, a grey colour can be obtained. This is a very desired quality in the photochromics and electrochromics where blue (WO$_3$ or PEDOT based devices) is now prevalent. The colour tuning and easy synthesis is making DTEs good opponents to polymers. But the most important aspect might be the energy efficiency: DTEs require only sunlight in order to achieve the coloured state and do not require continuous potential in order to stay coloured for a long period of time.

Although two examples of full photochromic and electrochromic DTEs were reported (1.4$^{2+}$ and 2.1$^{2+}$) a device containing these molecules was not developed yet due to a lack of stability of these two compounds (Scheme 2.20).
Scheme 2.20. Top – photochemical and electrochemical desired isomerization reactions of compound 1.42+. Below are summarized the different decomposition pathways for both isomers.
3. **Investigation of Catalytic Oxidative Ring–Opening of Diarylethenes**

In this chapter is presented the logical design, synthesis and characterization of the molecules presented in Table 3.1, the reasoning in choosing them is discussed in Chapter 3.1. The characterization includes the photochemical behaviour (UV-Vis spectra, PSS), electrochemical behaviour and thermal stability of the ring–closed forms. Furthermore, DFT calculations have been done in order to establish if there is a correlation between the thermal stability and the difference in total energy of both isomers.

3.1. **Overview of Chapter 3 and Research Objectives**

The goal of the work discussed in this chapter is to determine the relationship between the structure, the electrochemical behaviour of both isomers and the ring–closed form stability in the dark in the context of DTEs that are undergoing electrochemical oxidative ring–opening. In order to achieve this goal, synthesis, kinetic thermal studies (for the thermal cycloreversion), electrochemical studies and DFT calculations were employed.

The molecules synthesized and characterized in this chapter are presented in Table 3.1. The synthesis of compound 2.17 and 3.1 was published previously. The electrochemical behaviour was published only for compound 2.17. The thermal stability of the ring–closed form was studied in decane at four different temperatures. The electrochemical behaviour and photochemical properties were studied in two solvents (CH$_3$CN and CH$_2$Cl$_2$, where the solubility allowed it).
Table 3-1. List of compounds synthesized and characterized in Chapter 3 (2.17 and 3.1)\textsuperscript{9} characterization, and a brief overview of some important characteristics: PSS and \( t_{1/2} \) at 60 °C

<table>
<thead>
<tr>
<th>entry</th>
<th>RO isomer</th>
<th>synthesis</th>
<th>photochemistry</th>
<th>electrochemistry</th>
<th>DFT calculations</th>
<th>( t_{1/2} ) 60 °C</th>
<th>RC in the dark</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17o</td>
<td></td>
<td>80 %</td>
<td>lit</td>
<td>lit</td>
<td>lit</td>
<td>1 day</td>
<td></td>
</tr>
<tr>
<td>3.1o</td>
<td></td>
<td>73 %</td>
<td>84 %</td>
<td>✓</td>
<td>✓</td>
<td>1.5 days</td>
<td></td>
</tr>
<tr>
<td>3.2o</td>
<td>✓</td>
<td>84 %</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4.8 h</td>
<td></td>
</tr>
<tr>
<td>3.3o</td>
<td>✓</td>
<td>70 %</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>4 days</td>
<td></td>
</tr>
<tr>
<td>3.4o</td>
<td>✓</td>
<td>62 %</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>1 hour</td>
<td></td>
</tr>
</tbody>
</table>

The reason behind the selection of these candidates was a somewhat complicated task as multiple factors had to be taken into consideration. One can envision many structural modifications that will mitigate one of the degradation paths discussed in Chapter 2, but each may affect the other properties in a negative way. In
Scheme 3-1 is a short overview of the common degradation pathways for compound 2.17 (a known photochromic and electrochromic DTE), pertinent to each isomer.

![Scheme 3-1](image)

**Scheme 3.1.** Overview for the degradation of compound 2.17.

Compound 2.17 is one of the very few examples of DTEs that is undergoing catalytic oxidative cycloreversion. Compound 2.17 was used as a template in designing the presented DTEs (Table 3.1). The factors that have to be taken into consideration are:

1. The synthetic modifications are somewhat limited by the single requirement of the DTEs that are undergoing oxidative catalytic ring-opening: an aromatic internal group must be present in position two of the central thiophene (Figure 3.1(a)).

2. The first problem to solve was the electrochemical degradation. The polythiophene class of compounds is quite mature as there are numerous published reports regarding the successful polymerization of thiophene. But pertinent to this work and of more importance are the examples where the electropolymerization is hindered. It is known that α substituted thiophene cannot
be easily electropolymerized (Figure 3.1(b)). Therefore, it is a safe choice to block the \( \alpha \) positions. From now on the groups present on the outer \( \alpha \) positions of the terthiophene 5,5" are referred as R groups. The choice of selection of the moieties (R groups) used to block these electropolymerizable positions is a more challenging task (Figure 3.1(c)) and it will be explained fully within the following text.

3. The stability of the ring–closed form is influenced by both steric and electronic factors. By blocking of \( \alpha \) positions (with various R groups) one has to take into consideration:

- bulky internal groups weaken the (photochemically generated) \( \sigma \) bond, and
- both electron donating groups (EDG) and electron withdrawing groups (EWG) speed up the cycloreversion in the dark (Figure 3.1(d)).

The initial goal of this research was to synthesize a DTE compound that would be photochemically, electrochemically and thermally stable (ring–closed form) and ready to be used in a device. Therefore the knowledge of the structure–property relationship in organic molecules (DTEs) is the first task required in achieving the main goal. The \( \alpha \) substitution of thiophenes, with various R groups would modulate all the three key elements of DTE(s): photo-, electro- and thermal stability. Given the DTE design constrains imposed by the structural requirements and the known implications of the potential blocking groups R, two methods for tuning the behaviour of the molecules were used. The first is to investigate the effect of the substituents from electron donating to electron withdrawing and the second is to observe the effect of extending the conjugation. The best way to assess this issue is to carefully inspect a Hammett constant table for substituents. The Hammett constant \( \alpha \), is a measure of the total polar effect exerted by a certain substituent (Table 3.2), relative to a hydrogen substituent on a particular reaction. The values for \( \alpha \) are positive for EWG and negative for EDG. Furthermore, the Hammett constant for substituents is usually given only for meta and para positions as ortho can show complications due to the steric demand of different functional groups. For \( \alpha \) substituted thiophenes one can use the \( \alpha \) values (Hammett constants) published for \( p \)-substituted benzenes.
The requirement for a DTE molecule to undergo catalytic oxidative ring-opening is presented in figure (a) aromatic internal groups. The most reactive positions are circled in figure (b). Mitigation of electrodegradation can be done by blocking of the α positions as presented in Figure (c) with various groups labelled generically R. On the other hand the protecting group R will influence the stability of the ring–closed form in the dark by weakening the σ C–C bond as circled in Figure (d).

It is useful to mention the Charton size parameter (Es) for different functional groups that takes into account only the steric size of the substituent and not the electronic influence. The size parameter is useful in the context of thermal stability of the ring–closed isomer in the dark.
Table 3.2. Selected Hammett $\sigma$ para constants and Charton values

<table>
<thead>
<tr>
<th>entry</th>
<th>compound</th>
<th>substituent</th>
<th>Hammett$^a$ $\sigma$</th>
<th>Charton (Es)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.17</td>
<td>H</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>$\text{CH}_3$</td>
<td>-0.04</td>
<td>0.52</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>$\text{t-Bu}$</td>
<td>-0.20</td>
<td>1.24</td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
<td>F</td>
<td>0.06</td>
<td>0.27</td>
</tr>
<tr>
<td>5</td>
<td>3.4</td>
<td>Ph</td>
<td>-0.01</td>
<td>2.15</td>
</tr>
</tbody>
</table>

$a)$ the $\sigma$ values for para substituted benzene

Compound 2.17, $R = H$, was synthesized following the literature procedure to be used as a standard.$^9$ The reasoning for synthesis of compound 3.1, $R = \text{CH}_3$ is presented below:

1. its synthesis is facile,$^9$
2. from the point of view of photochemical properties, it will probably possess similar characteristics as compound 2.17,
3. from the perspective of electrodegradation, one can expect a decrease of electropolymerization due to the blocking of the $\sigma$ C-H positions with the very stable C–C bonds, and
4. from the point of view of the thermal stability of ring–closed form in the dark:
   - the $\text{CH}_3$ group has an electron donating effect, (see the smaller negative value in the Hammet table) and the inductive effects are diluted with distance, so likely the photochemically generated, $\sigma$ bond will not be affected much by its presence, and
   - the $\text{CH}_3$ group from a steric point of view (Charton value $\text{Es} = 0.52$) is average, towards smaller, hence the effect towards the stability of the ring–closed form in the dark was speculated to be minimal.

The properties of compound 3.1 will dictate the synthesis of future compounds. If 3.1c spontaneously reverts at room temperature to the ring–open form, the project of blocking the electropolymerizable positions with alkyl groups will be deemed unusable, but if it will have acceptable stability the next logical step will be to increase the bulk of
the R group, and this is the reasoning for using t-Bu as blocking groups (compound 3.2). The full reasoning of choosing t-Bu groups is presented in the next discussion:

1. Separating, if possible, the steric factor from the electronic influence that dictate the stability of the ring–closed form:
   • From electronic point of view, the t-Bu group has the same electron donating effect, +I effect as CH\(_3\), albeit a higher \(\sigma\) value of -0.2. If compound 3.2c has a shorter half life it will be attributed mainly to the steric factor.
   • Steric point of view: one of the most sterically demanding alkyl groups is t-Bu with an \(E_s = 1.24\).

2. By choosing t-Bu as a blocking group, not only are the \(\alpha\) positions blocked, but also the \(\beta\) positions are less likely to electropolymerize, being masked by the bulky t-Bu group through space.

In the quest for finding an answer to the question: Is there a correlation between the R group and thermal stability of the ring–closed form? Compound 3.3 (\(R = F\)) is the right candidate in order to separate, the electronic influence from the steric aspects. Comparing Charlton values from Table 3.2 one can notice that F has the size between H and methyl groups: \(E_s (H) = 0.00 < E_s (F) = 0.24 < E_s (CH_3) = 0.52\). Therefore one can expect that the sterics will have a minimal influence on the cycloreversion. On the other hand fluorine has an overall effect of an EWG: see the positive \(\sigma\) value of 0.06. Although caution has to be taken as fluorine presents two opposite electronic effects: being the most electronegative element it acts as an EWG through inductive effects (-I) but it also possesses non bonding electrons that can be pushed through resonance, thus making it an EDG having a +M effect (mesomeric effect).

Compound 3.4 is the only compound with different internal and external groups presented in this series. It was noted that increasing the length of the conjugation substituents (external substituents) decreased both the efficiency of the photochemical ring–closing and ring–opening reactions. But the decrease in efficiency (quantum yield) of the ring–opening reaction is much more severe and eventually with the right amount of structural tuning it can be completely suppressed.\(^{11, 65, 65b}\) This is important in the context of the PSS, as there is a dynamic equilibrium between the two isomers due to
the overlap in their absorption spectra. By suppressing the photochemical ring-opening reaction, a solution of pure coloured form (100 % of the ring-closed form, obtained photochemically) would be formed, thus requiring a lower amount of the active ingredient in the devices. Synthesizing compound 3.4 allows for the relationship between the extended conjugation and the half life of the ring-closed isomer to be evaluated. Nevertheless, one can synthesize a DTE with an extended conjugation that can form 100 % of the ring-closed form due to the inhibition of the photochemically driven ring-opening reaction, but if the ring-closed isomer is thermally unstable then this will not be a useful candidate.

In the above explained rationale for synthesizing the compounds presented in this chapter, the derivatives substituted with stronger EDG (NH$_2$, OMe) and EWG (CN, NO$_2$) were deliberately not included. This will be a first choice for any systematic study that is looking to find the relationship between the molecular structure and various properties of the substance. Nevertheless in the context of the DTEs present in this chapter:

1. Certain substituted DTEs (mainly NH$_2$ substituted) are very difficult to synthesize and handle in the open atmosphere because they spontaneously degrade.\textsuperscript{66}
2. Cyano substituted DTEs might complicate the electrochemical behaviour. Certain cyano substituted oligothiophenes do not have perfect reversible reduction peaks as noticed in their cyclic voltammograms.\textsuperscript{67} This is one of the reasons for using electrochemically silent (in the given potential range) functional groups R.

3.2. Synthesis of DTEs Terthiophene Derivatives

3.2.1. Introduction

Typically the DTEs are synthesized by a double substitution between a lithiated derivative formed \textit{in situ} and octafluorocyclopentene (Scheme 3-2). The yield of this type of reaction is quite modest, usually lower than 50% as part of octafluorocyclopentene is undergoing only monosubstitution. Nevertheless this is a robust synthetic route that can yield gram quantities of desired material.
3.2.2. Synthesis of Compounds 2.17o and 3.1o

Compounds 2.17o and 3.1o were synthesized according to literature procedures with similar yields (Scheme 3-3). The first step is a Kumada coupling of the organomagnesium compounds formed in situ with 2,3,5-tribromothiophene. The second step is a metal-halogen exchange of the 3'-bromoterthiophene derivatives with n-BuLi followed by treatment with perfluorocyclopentene. Compounds 2.17o and 3.1o were characterized by 1H and 13C NMR spectroscopy and compared to the previously reported spectra. The synthesis of compound 2.17o was scaled-up without problems to obtain 10 g (22 %). Although the synthesis of compound 3.1o was previously published, its photochemical and electrochemical properties were not reported.

3.2.3. Synthesis of Compound 3.2o

Synthesis of compound 3.2o was done by careful monitoring of a Friedel–Crafts alkylation of compound 2.17o (Scheme 3-4). Although the Friedel–Crafts alkylation
reaction is not very selective in this case, the product is obtained in an acceptable yield (24 %) as a yellow powder with a melting point of 234 – 236 °C.

**Scheme 3.4.** Synthesis of compound 3.2o.

From the reaction mixture, five major compounds were isolated. Figure 3.2 represents the TLC plate of the reaction mixture and the top spot, labelled spot 1 is the desired compound, which turns green upon irradiation with UV light (365 nm). The other compounds spots 2–4 were analyzed by $^1$H NMR spectroscopy and revealed a tri-, di- and monotertbutylated compounds, mainly in the $\alpha$ positions of the thiophene rings. In order to obtain compound 3.2o purification was repeated three times by flash chromatography. $^1$H NMR spectroscopy revealed four peaks in the aromatic region (two doublets, two doublets overlapped in one peak and one singlet) and two peaks [2 X C(CH$_3$)$_3$] in the alkyl region, as expected. $^{13}$C NMR spectroscopy revealed 16 peaks out of 19 (molecule is symmetrical).
3.2.4. **Synthesis of Compound 3.3o**

The synthesis of compound 3.3o was achieved in two steps: initially the tetrabromination of compound 2.17o is performed and followed by the Br-Li exchange *in situ* followed by an electrophilic flourination with N-fluorobenzenesulfonimide (Scheme 3-5). Compound 3.3o was obtained with a modest yield, of 9 % (for the second step) as a yellow powder.

*Figure 3.2.* TLC representation of the Friedel–Crafts alkylation reaction (silica gel plate, eluent hexanes).
Scheme 3.5. Synthesis of compound 3.30.

The compound was characterized by $^1$H NMR spectroscopy (coupled and uncoupled with $^{19}$F) four doublets (uncoupled $^1$H-$^{19}$F) NMR spectrum and one singlet (Figure 3.3 top). The $^{13}$C NMR spectrum revealed only 12 peaks out of the expected 17 peaks. The mass spectrum is in accordance with the desired compound. $^{19}$F NMR spectrum of compound 3.30 revealed four signals (Figure 3.3 bottom).
The lithiation of the tetrabrominated compound 3.70 was achieved in a low yield. Although other synthetic routes can be envisioned for compound 3.3o, this route is relatively fast and yields acceptable amounts of the compound. The best way to perform the lithiation is “to titrate” the solution of compound 3.70 with a solution of n-BuLi making sure that traces of mono-bromo or dibromo- compounds are not visible on TLC plate and only the tetralithiated species is in solution. Otherwise the purification is quite difficult as
the bromo-compounds have the same RF(s) (retention factor) as the fluorinated versions (Figure 3.4(b)).

![Chemical structures and TLC separations]

**Figure 3.4.** (a) TLC of the bromination reaction of compound **2.17o** (silica TLC plate, eluent hexanes) (b) TLC representation of the reaction mixture obtained after the treatment with with N-fluorobenzenesulfonimide of the tetralithiated species of compound **3.7o**.

The bromination of compound **2.17o** under the given conditions is a clean reaction, yet not taken to completion, meaning that it affords mainly the desired compound **3.7o** with a yield of 60 % and for the most part the rest being unreacted starting material (**2.17**). Although by a careful examination of the TLC plate during the
reaction one can see the formation of the mono-, di-, tri- and tetrabrominated compounds with minimal decomposition (Figure 3.4 a). Stacked $^1$H NMR spectra of compounds 3.7o, 3.8o, and 3.9o are presented in Figure 3.5. The top $^1$H NMR spectrum is consistent with the structure of the proposed product, compound 3.7o that is a symmetrical $\alpha$-tetrabrominated terthiophene DTE due to its four doublets and one singlet. The central $^1$H NMR spectrum is consistent with compound 3.8o that is a symmetrical $\alpha$-bisubstituted terthiophene DTE. There are three doublet of doublets that represent the splitting of the protons from the thiophene cycle that are not undergoing bromination. The two doublets are consistent with the protons from the monobrominated thiophene cycle, also the coupling pattern is in agreement with two ortho protons. 2D NMR spectroscopy and the single crystal X-ray crystallography of compound 3.8o are consistent with an $\alpha$-external-disubstituted-terthiophene DTE. In Figure 3.6 are assigned the $^1$H NMR peaks for compound 3.8o. Regarding the bottom $^1$H NMR spectrum from Figure 3.5 it belongs to compound 3.9o which is expected for an $\alpha$ monosubstituted terthiophene DTE: asymmetrical, hence 12 signals are seen (there is a partial overlap of a doublet of doublet with a doublet). Significant peaks are the two singlets belonging to the protons from the central thiophene, the two ortho-doublets belonging to the mono-substituted thiophene cycle from the molecule.
Figure 3.5. Partial stacked spectra of compounds 3.9o (bottom), 3.8o (central) and 3.7o (top). The spectra were acquired in CDCl₃ and on a 400 MHz instrument.
3.2.5. **Synthesis of Compound 3.4o**

Compound 3.4o synthesis was achieved by a Kumada coupling of the *in situ* formed organomagnesium compound of 2-bromothiophene and compound 3.8o (Scheme 3-6). Compound 3.4o was obtained as a yellow powder.

*Figure 3.6.* Assigned $^1$H NMR peaks for compound 3.8o and molecular structure of compound 3.8o in crystal (thermal ellipsoids drawn at 20 % probability level).
Scheme 3.6. Synthesis of compound 3.4o.

Compound 3.4o was characterized with the aid of $^1$H and $^{13}$C NMR spectroscopy. In Figure 3.7 is presented the $^1$H NMR spectrum and an expansion of the aromatic region. All nine signals (18 protons) are accounted for and the coupling pattern is consistent with the desired compound 3.4o. The compound is symmetrical, has one singlet due to the proton from the central thiophene, two doublets and six doublets of doublets belonging to the most outer and internal thiophene cycles.
Figure 3.7. Structure of compound 3.4o with the peak assignment. $^1$H NMR spectrum of compound 3.4o full spectrum (bottom), partial spectrum (top). Spectrum was acquired on a 400 MHz instrument and in CDCl$_3$ as a solvent.
3.2.6. *Determining the Half Lives for the Thermal Cycloreversion in the Dark for the Compounds 2.17c, 3.1c, 3.2c, 3.3c and 3.4c*

Rearomaticity is invoked to explain the thermal stability of the ring–closed isomers among the different classes of the diarylethene family of compounds: dithienyl ethenes (DTEs) and difuryl ethenes are more stable (less aromatic) than diphenylethenes (the latter one being the more aromatic one).\(^8\) However rearomaticity was never used to explain the different thermal behaviour in the same class of compounds. In the same class of compounds, mainly the DTEs (pertinent to this work), steric and electronic reasons are invoked to explain this behaviour. Given the fact that any modification brought to the “parent compound” 1.3c results in a decrease in the half life of the thermal cycloreversion in the dark of the new compound, one would have expected that all the DTEs presented in this work will be more unstable in the dark compared to compound 2.17c as mentioned above.

The thermal cycloreversion can be evaluated by monitoring the decrease in absorbance of this isomer as function of time and temperature (Figure 3.8).

The thermal cycloreversion reactions of the ring–closed isomers were monitored by UV-vis absorption spectroscopy at four different temperatures: 40, 50, 60 and 80 °C. The absorbance of the ring–closed isomers can be used instead of the concentration values in kinetics studies because both values are linearly related through the Beer–Lambert law of absorbance. Stock solutions of each ring–open isomer were prepared in anhydrous and deoxygenated decane (1 x 10\(^{-6}\) M) that was then used to prepare triplicate samples in quartz cuvettes (1 cm path length). Decane was chosen as a solvent for solubility reasons and to its high boiling point. The samples were irradiated with UV light at room temperature (365 nm) until no increase in the absorbance of the ring–closed form was noticed. Once the PSS state was achieved, the three cuvettes were inserted in the UV-Vis instrument equipped with a temperature controlled multi-cell chamber. The maximal absorbance wavelengths were recorded every minute as a function of temperature. Thermal cycloreversion in the dark was marked by a decrease in the maximal visible absorbance wavelengths of the ring–closed form (Figure 3.8). All the results presented in Figure 3.8 can be fitted to a straight line (\(\ln[A]\) vs. time (s) gives
a straight line with a slope of \(-k = \) the first order rate constant). All the thermal cycloreversions were considered to follow first order reaction kinetics.

Compound 3.2c when heated to 80°C does not follow a first order reaction, as the natural logarithm of absorbance vs time graph looks more of curve than a straight line. This might signify a change of mechanism or an addition of another mechanism with the increase in temperature that takes in the same time with the regular cycloreversion in the dark mechanism. In Table 3.3 are given the rate equations for each compound at each temperature and the \(R^2\) values.
Figure 3.8. Normalized ring-opening reactions for compounds 2.17c, 3.1c, 3.2c, 3.3c and 3.4c in decane as monitored by UV-Vis spectroscopy, using fixed wavelengths corresponding to the decrease of the maximum visible absorption intensity of each compound (625, 636, 636, 617, 657 nm) at four different temperatures (40, 50, 60 and 80°C).
Table 3.3. Tabulated equations of the straight lines (first order kinetics) and the $R^2$ values, that were fitted to the monitored ring–opening reactions for compounds 2.17c, 3.1c, 3.2c, 3.3c and 3.4c in decane and in the dark at four temperatures. The software used is Excel.

<table>
<thead>
<tr>
<th>compound</th>
<th>temperature</th>
<th>equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17c</td>
<td>40 °C</td>
<td>ln($A/A_o$) = -6E-07t - 0.0008</td>
<td>0.99266</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>ln($A/A_o$) = -2E-06t - 0.0026</td>
<td>0.99266</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>ln($A/A_o$) = -8E-06t - 0.0003</td>
<td>0.99989</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>ln($A/A_o$) = -8E-05t - 0.0046</td>
<td>0.99985</td>
</tr>
<tr>
<td>3.1c</td>
<td>40 °C</td>
<td>ln($A/A_o$) = -7E-07t - 0.004</td>
<td>0.86885</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>ln($A/A_o$) = -1E-06t - 0.0091</td>
<td>0.92783</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>ln($A/A_o$) = -5E-06t - 0.0086</td>
<td>0.98451</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>ln($A/A_o$) = -5E-05t - 0.0046</td>
<td>0.99916</td>
</tr>
<tr>
<td>3.2c</td>
<td>40 °C</td>
<td>ln($A/A_o$) = -4E-06t - 0.0134</td>
<td>0.97532</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>ln($A/A_o$) = -1E-05t - 0.0023</td>
<td>0.99897</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>ln($A/A_o$) = -4E-05t - 0.0084</td>
<td>0.99939</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>ln($A/A_o$) = -3E-04t - 0.0719</td>
<td>0.98703</td>
</tr>
<tr>
<td>3.3c</td>
<td>40 °C</td>
<td>ln($A/A_o$) = -2E-07t - 0.0033</td>
<td>0.73116</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>ln($A/A_o$) = -6E-07t - 0.006</td>
<td>0.9163</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>ln($A/A_o$) = -2E-06t - 0.0028</td>
<td>0.99317</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>ln($A/A_o$) = -3E-05t - 0.0032</td>
<td>0.99913</td>
</tr>
<tr>
<td>3.4c</td>
<td>40 °C</td>
<td>ln($A/A_o$) = -2E-06t - 0.0023</td>
<td>0.99805</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>ln($A/A_o$) = -7E-06t - 0.0037</td>
<td>0.9997</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>ln($A/A_o$) = -2E-05t - 0.0031</td>
<td>0.99994</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>ln($A/A_o$) = -2E-04t - 0.0054</td>
<td>0.99984</td>
</tr>
</tbody>
</table>

The half life of a first order reaction is given by the formula $t_{1/2} = \ln(2) / k$. The slope of the graph A vs t is $-k$ as mentioned, hence having the equations for the linear fit can be calculated the half life and the results are given is Table 3.4.
Table 3.4.  a) Tabulated half lives values at four different temperatures for compounds 2.17c, 3.1c, 3.2c, 3.3c and 3.4c in decane and in the dark.

<table>
<thead>
<tr>
<th>compound</th>
<th>( t_{1/2} ) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 °C</td>
</tr>
<tr>
<td>2.17c</td>
<td>326 ± 55.2</td>
</tr>
<tr>
<td>3.1c</td>
<td>278.64 ± 40</td>
</tr>
<tr>
<td>3.2c</td>
<td>48.24 ± 0</td>
</tr>
<tr>
<td>3.3c</td>
<td>840 ± 192</td>
</tr>
<tr>
<td>3.4c</td>
<td>96 ± 0</td>
</tr>
</tbody>
</table>

Note: There was a certain variation in the half lives of the 3 cuvettes (experiment done in triplicates) hence the average is reported ± the standard deviation. Some cuvettes do not present any deviation hence the ± 0.

b) Normalized half lives of all compounds to the fastest (compound 3.3c at 60 °C) for comparison reason.

<table>
<thead>
<tr>
<th>entry</th>
<th>normalized half lives</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17o</td>
<td>0.263</td>
</tr>
<tr>
<td>3.4o</td>
<td>0.01</td>
</tr>
<tr>
<td>3.1o</td>
<td>0.427</td>
</tr>
<tr>
<td>3.2o</td>
<td>0.04</td>
</tr>
<tr>
<td>3.3o</td>
<td>1</td>
</tr>
</tbody>
</table>

From the half life values of the reactions, the activation energy can be calculated using the Arrhenius equation. Furthermore, by using Eyring equation one can calculate the entropy and enthalpy of activation. The Arrhenius equation (eq 3.1) is an empirical relationship that defines the temperature dependence of a chemical reaction rate. By plotting \( \ln(k) \) versus 1/T (temperature in K) a straight line is the result (eq 3.2). The
activation energy barrier for a reaction is determined from the slope of the line. Also the pre-exponential factor $A$ is determined from the graph.

$$k = A \ e^{-E_a/RT} \quad \begin{cases} \text{$k =$ rate constant (s$^{-1}$)} \\ \text{$A =$ pre-exponential factor (s$^{-1}$)} \\ \text{$E_a =$ activation energy barrier (J/mol)} \\ \text{$R =$ universal gas constant (8.3144462 J/mol-K)} \\ \text{$T =$ temperature (K)} \end{cases} \quad \text{eq 3-1}$$

$$\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A) \quad \text{eq 3-2}$$

The Eyring equation (eq 3-3) resembles the Arrhenius equation but is based on the transition state model of chemical reactions. A linear relationship is achieved by constructing the plot of the mathematical transformation of Eyring equation, which is presented as equation 3-4 ($\ln(k / T)$ vs $1 / T$). From the slope of the line, the enthalpy of activation is calculated and from the intercept, the entropy of activation can be calculated.

$$k = k_B T \ e^{\Delta G^+ / h}$$

$$\begin{cases} \text{$k_B =$ Boltzamann's constant (1.38 \cdot 10^{-23} \text{ J/K})} \\ \text{$h =$ Plank's constant (6.62 \times 10^{-33} \text{ Js})} \\ \text{$\Delta G^+ =$ Gibbs energy of activation} \end{cases} \quad \text{eq 3-3}$$

$$\ln \left( \frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{R} \frac{1}{T} + \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad \text{eq 3-4}$$

$\Delta H^\ddagger =$ enthalpy of activation
$\Delta S^\ddagger =$ entropy of activation
Figure 3.9. (a) Comparative Arrhenius plot and (b) comparative Eyring plot for the thermal cycloreversion reactions for all five compounds (2.17c, 3.1c, 3.2c, 3.3c, and 3.4c) in decane. The equations for the linear fit and the $R^2$ values are given on the graph together with the legend.

In Table 3.5 are presented the kinetic values derived from the Arrhenius and Eyring plots as calculated from their respective plots (Figure 3.9).
Table 3.5. Kinetic characterization data for the thermal cycloreversion in the dark of compounds 3.2c, 3.4c, 2.17c, 3.1c and 3.3c (arranged in ascending order regarding thermal stability in the dark) in decane and the half lives at 80 °C.

<table>
<thead>
<tr>
<th>compound</th>
<th>R</th>
<th>Ea / kJ mol⁻¹</th>
<th>ΔH‡ / kJ mol⁻¹</th>
<th>ΔS‡ / J mol⁻¹</th>
<th>t₁/₂ 80 °C</th>
<th>A (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2c</td>
<td>t-Bu</td>
<td>93.44</td>
<td>98.42</td>
<td>-34.64</td>
<td>39 min</td>
<td>2.8 x 10¹¹</td>
</tr>
<tr>
<td>3.4c</td>
<td>thiophene / H</td>
<td>105.3</td>
<td>102.6</td>
<td>-26.50</td>
<td>57 min</td>
<td>7.4 x 10¹¹</td>
</tr>
<tr>
<td>2.17c</td>
<td>H</td>
<td>113.3</td>
<td>110.6</td>
<td>-11.11</td>
<td>2.4 h</td>
<td>4.7 x 10¹²</td>
</tr>
<tr>
<td>3.1c</td>
<td>CH₃</td>
<td>103.1</td>
<td>100.4</td>
<td>-45.20</td>
<td>3.8 h</td>
<td>7.8 x 10¹⁰</td>
</tr>
<tr>
<td>3.3c</td>
<td>F</td>
<td>115.9</td>
<td>113.2</td>
<td>-13.01</td>
<td>6.4 h</td>
<td>3.7 x 10¹²</td>
</tr>
</tbody>
</table>

It is known that the weaker bonds are, the more easily bonds break. Therefore, the ring–opening reactions breaking weak bonds in reactants generally have low ΔH‡–values.⁶⁸

One would have expected that the activation energy values (Ea) to follow the same trend as the half lives: the larger the half life, the higher the activation energy (Figure 3.10). This is true for the thermal cycloreversion in the dark for compound 3.3c that has highest half life 6.4 h at 80 °C and the highest activation energy 115.9 kJ mol⁻¹. On the other hand, if comparing only the activation energies for the thermal cycloreversion in the dark for compounds 2.17c (113.3 kJ mol⁻¹) and compound 3.1c (103.1 kJ mol⁻¹) leads to a conclusion that the fastest ring–opening is the case of 3.1c. This is not the case as the experimental value of half live for 3.1c is higher than the case of compound 2.17c: 3.8 hours and 2.4 hours, respectively. This misleading assumption happened because it was assumed that both compounds have the same preexponential factors (A factor) see equation 3-1 and obviously this is not the case. Therefore it is better to compare the half lives rather than activation energy values. With the exception of compound 3.1c (grey in Table 3.5) the trend is true for the rest of compounds (Figure 3.10).
Figure 3.10. The general trend regarding the half lives at 80 °C versus Ea and ΔH‡ for the ring–closed isomers: the larger the half life the higher the Ea.

3.2.7. Concluding Remarks Regarding the Thermal Kinetic Values in the Dark for the Cylcoreversion

The kinetic data revealed that the rate of thermal cycloreversion in the dark increases in the order: 3.3c < 3.1c < 2.17c < 3.4c < 3.2c. The cycloreversion of compound 3.3c being the slowest, the reaction in the dark almost doubles for compound 3.1c, is four times faster for compound 2.17c, it is ten times faster for compound 3.4c and it is 25 times faster for compound 3.2c.

It is known that both EDG and EWG both stabilize the diradicals. Because the transition state of the thermal cycloreversion in the dark resembles a diradical, one can speculate also that any structural modification of compound 2.17c will have as a result
the decrease in stability of the ring–closed isomer. This is not the case as both compounds 3.1c (α CH₃ substituted) and 3.3c (α fluorine substituted) are more stable in the dark compared to compound 2.17c. In view of the results regarding the thermal stabilities of the coloured forms only speculations can be employed at this time to explain the somewhat unexpected results:

1. The thermal cycloreversion in the dark of compound 3.3c is the slowest because the R group, fluorine atom, is a relatively small group in comparison to hydrogen, so the influence of steric factor is minimal. The electronic factor plays a certain role, but at this stage it is very hard to assess its impact.

2. The thermal cycloreversion in the dark for compound 3.1c once again is slower when compared to the parent compound 2.17c. Although the steric and electronic effects are known to be working in favour of a faster thermal cycloreversion in the dark.

3. Unlike compounds 3.3c and 3.1c, compound 3.2c ring–opens the fastest in the dark. The electronic factor of the t-Bu group is the same type to that of the Me group (Table 3.2, Hammet factor). The only difference is in the substantial volume occupied by t-Bu group so the steric effect plays a major role in the thermal cycloreversion in the dark. On the other hand t-Bu group is not attached to the carbon atoms involved in the rehybridization and the thiophene spacer is used in each derivative presented in this work, so one would not have estimated such a big change in the half life. It is known that the preferred conformer of 1,3,5-trineopentanylbenezene is the one on the right, where all the neopentyl groups are lying on the same face of the benzene ring (Scheme 3-7). In this case the attractive forces, van der Waals forces are outweighing the repulsive forces. A reasonable speculation can be done regarding the thermal cycloreversion of compound 3.2c in the dark: 3.2o isomer is more stabilized because the alkyl groups attract each other and this phenomenon acts as a different driving force for the thermal cycloreversion in the dark.
4. The cycloreversion in the dark for compound 3.4c can be compared only to the standard compound 2.17c as it is asymmetric (different internal and external groups). As expected its cycloreversion is faster in the dark probably due to a better stabilization of the diradical formed in the transition state.

So far no speculations were presented regarding the thermal stability in the dark of compounds 3.1c and 3.3c as no literature precedents were found. The next discussion Chapter 3.3 and Chapter 3.4 is looking to find the answers for the somewhat unexpected behaviour of these compounds. In the field of DTEs it is well known that there is a correlation between the calculated energy difference with DFT method between the isomers, ΔE(E_{RC} − E_{RO}) and the stability of the ring closed isomer in the dark.59 In Chapter 3.3 this aspect will be addressed. In Chapter 3.4 one very important structural difference between the compounds reported is discussed: how the internal aromatic (thiophene) rings affect the stability by being involved in π–π stacking. At this point the reader will benefit from a very brief introduction of DFT calculations regarding DTEs.

### 3.3. DFT B3LYP Calculations for Compounds 2.17, 3.1, 3.2, 3.3 and 3.4 and Their Respective Radical Cations

Calculations for the total energies for ring–open and closed isomers were done because:
1. The difference in enthalpy between the two isomers can be correlated with the thermal stability. The smaller the difference in $\Delta H$ (eq 3-5), the more stable the ring–closed isomer is in the dark at room temperature. This trend is best observed by examining the values for the five DTEs presented in Table 3.6. The same relationship between the experimentally determined half lives and calculated $\Delta H$ is presented in Figure 3.11. There are many factors that determine the thermal stability of the ring–closed isomer in the dark: aromatic stabilization energy of the aryl groups, electron withdrawing substituents at the aryl groups (electronics) and steric hindrance of the substituents at the reactive carbons (sterics). They were discussed the thermal stability chapter of this thesis (Chapter 2.2).

$$\Delta H = E_{RC} - E_{RO}$$  \hspace{1cm} \text{eq 3-5}

$$\Delta H = E_{RC}^{+\cdot} - E_{RO}^{+\cdot}$$  \hspace{1cm} \text{eq 3-6}

2. One can determine the direction of the electrochemical isomerisation by calculating the energy difference between the radical cation of the ring–closed isomer and the radical cation of the ring–open isomer (eq 3-6). Overall if this difference is positive the oxidative cycloreversion is allowed and if this difference is negative oxidative cyclization is allowed.\textsuperscript{59}
Table 3.6. Experimentally determined thermal stability at 60 °C of the ring-closed isomer and the calculated relative energy difference ($\Delta H = E_{RC} - E_{RO}$) at B3LYP/6-31G* level for compounds 1.3, 2.9, 2.15, 2.18, 2.14.

<table>
<thead>
<tr>
<th>entry</th>
<th>$\Delta H$ calculated (kcal/mol)</th>
<th>$t_{1/2}$ @ 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3c</td>
<td>13.2</td>
<td>21 years</td>
</tr>
<tr>
<td>2.9c</td>
<td>14.1</td>
<td>3.66 years</td>
</tr>
<tr>
<td>2.15c</td>
<td>21.3</td>
<td>573 min</td>
</tr>
<tr>
<td>2.18c</td>
<td>21.9</td>
<td>247 min</td>
</tr>
<tr>
<td>2.14c</td>
<td>22.7</td>
<td>3.3 min</td>
</tr>
</tbody>
</table>
3.3.1. Basic Aspects of DFT Calculations Regarding DTE(s)

DFT (Density Functional Theory) is a computational method that can calculate different properties of a molecule: (UV-Vis spectrum, NMR chemical shifts, enthalpy) by determining the electron density for the molecule rather than relying solely on solving wave function for each electron (as in ab initio methods).\(^{72}\) The DFT method used in this thesis is B3LYP (Becke, 3-parameter, Lee-Yang-Parr)\(^{73}\) because this is the standard literature for calculating the energy of diarylethenes.\(^{71}\) The purpose of the calculations presented in this thesis is not to develop or improve new methodology for calculating the energy of diarylethenes, but rather using the already published methodology to solve certain problems, or to look for correlations such as thermal stability of the ring-closed isomer as function of the R substituent (Figure 3.1). All the calculations used in this thesis are done with the basis set of 6-31G*. A basis set describes the functions of the orbitals. The geometry of the molecule was first optimized DFT-B3LYP and then the total energy calculated. For neutral molecules, restricted formalism was used and for radical cations, unrestricted formalism was employed (UB3LYP). The calculations were submitted on Westgrid, which is a HCP (high computing power) facility mainly for the use of researchers from Western-Canada. The calculations for neutral molecules required 3-4 hours and for radical cations around 4-5 hours. The software used to do the calculations is Gaussian 09.\(^{74}\)
Procedure for Drawing the DTE Molecules

Gaussview is the graphical interface of Gaussian 09. All molecules were drawn in Gaussview. Although this interface resembles Chemdraw (software used to create chemical structures), a higher degree of confidence and knowledge is required (at least regarding DTEs).

The factors that were taken into account when drawing the ring–open isomer (Figure 3.12) are:

1. terthiophene was drawn in an all trans conformation,\textsuperscript{75} with thiophene rings not coplanar with an angle $\sim$10-20 ° out of plane (Figure 3.12),\textsuperscript{76}

2. the molecule is not symmetrical, the two dihedral angles $\alpha_1$ and $\alpha_2$ are slightly different (Figure 3.12).\textsuperscript{71} These angles increase and get closer in value as the internal substituents become bulkier (such as the case of a thiophene ring as internal substituent),

3. all the ring–open isomers were drawn in the antiparallel (AP) conformer (Figure 3.12) as this is the conformer that is undergoing the photochemical ring closing reaction and also for consistency reasons.

DTEs exist in two conformers: parallel and antiparallel. The antiparallel conformation enables the photochemical ring–closing whereas the parallel does not. The two conformers are usually present in solution in equal proportions (at least for compound 1.3o and the majority of DTEs that have CH$_3$ groups as internal groups) and they are due to the ability of each thiophene ring to rotate about the carbon-carbon single bond. The parallel (P) has mirror symmetry and the antiparallel (AP) has a C$_2$ symmetry (Figure 3.12 b).the above a) and b) and c) points are in good agreement with the single crystal X-ray structure for compound 2.17o.\textsuperscript{54}
Figure 3.12. (a) The antiparallel (AP) conformer of compound 2.17, dihedral angles $\alpha_1$ and $\alpha_2$ (51.7° and 41.3°) (top) and bottom terthiophene unit with the out of plane angle $\beta$ of 20°. (b) Antiparallel (C$_2$ axis symmetry) and parallel (mirror plane symmetry) conformers for compound 1.3, the structures were optimized with Gaussian, B3LYP, 6-31-G$^*$. 

For the ring–closed isomer, drawing the molecules in Gaussview was simpler because this isomer does not possess as many degrees of freedom: once again in the terthiophene unit the thiophene cycles were all trans, and the difference between the dihedral angles $\alpha_1$ and $\alpha_2$ is minimal.

DFT Calculations for Compounds 2.16 and 2.17

The calculations project started by repeating the calculations for two compounds 2.16 and 2.17 as neutral molecules and radical cations. These two molecules were chosen because the calculations were published before, and because they are representative of the DTEs that are undergoing (a) oxidative cyclization (2.16) hence $\Delta H$
\[ \Delta H = E_{RC}^{\bullet\bullet} - E_{RO}^{\bullet\bullet} < 0 \]

and (b) oxidative cycloreversion (2.17)

The literature calculations were done with G03 (Gaussian 03) and the ones reported in this thesis with G09. To the best of my knowledge, no modifications to the hybrid functional B3LYP was implemented between the two versions of the software in order to affect the final results hence, given the fact I used the same functional and the same basis set (6-31G*), the values can be compared.

In Table 3.7 are presented the reported calculated total energy values and the ones calculated in this work. Although not quite identical they are very close. The energy values are given in 1 a.u = 1 Hartree. Hartree is an atomic unit (a.u) of energy and one Hartree = 627.5 kcal/mol.
Table 3.7. Total energies for the neutral molecules (RB3LYP) and radical cations (UB3LYP) of both isomers (a.u) and difference in energy (ΔE). On top are the structures for compounds 2.16 and 2.17.

<table>
<thead>
<tr>
<th>Compound</th>
<th>corrected total energy (a.u)</th>
<th>ΔE(C-O) kcal/mol</th>
<th>corrected total energy (a.u)</th>
<th>ΔE(••-••) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ring open isomer</td>
<td>ring closed isomer</td>
<td>ring open isomer radical cation</td>
<td>ring closed isomer radical cation</td>
</tr>
<tr>
<td>2.6</td>
<td>-3076.314470</td>
<td>-3076.296699</td>
<td>+11.51</td>
<td>-3076.069224</td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>-3076.314456</td>
<td>-3076.296696</td>
<td>+11.14</td>
<td>-3076.069962</td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.17</td>
<td>-4101.261222</td>
<td>-4101.218712</td>
<td>+26.67</td>
<td>-4101.027948</td>
</tr>
<tr>
<td>literature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.17</td>
<td>-4101.261235</td>
<td>-4101.22016</td>
<td>+25.77</td>
<td>-4101.02745</td>
</tr>
<tr>
<td>this work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.2. *DFT Calculations of the Ring–Open Isomers*

Geometry optimization is the procedure that attempts to find the configuration of minimum energy of a molecule. That means that the atoms in the molecule will be “moved” until the lowest energy is found. Although the goal is to find the global minimum sometimes a local minimum will be found. This is the reason that multiple configurations (four configurations) for the ring–open isomers were submitted to be optimized. The way these structures were chosen was as follows:
1. all the compounds were drawn in antiparallel conformer,
2. the thiophene units were drawn in all trans conformation and out of plane, and
3. the dihedral angles $\alpha_1$ and $\alpha_2$ were drawn equal to 55°, 60°, 65°, and 70°, the distance $\delta$ between the reactive carbon atoms was not modified.

The values before optimization, as submitted for calculations are on the left and on the right are the values optimized with DFT B3LYP 6-31 G* for all the ring–open isomers (Tables 3-8 (2.17o), 3-9 (3.1o), 3-10 (3.2o), 3-11 (3.3o) and 3-12 (3.4o)). On the right of the table there are three values for the energy of the molecule:

1. total energy of molecule. By default all the calculations are done at 298 K, and reported here is this energy at this particular temperature.
2. ZPC (Zero Point Correction) or sometimes encountered as ZPE (Zero Point Energy) is the calculated energy at 0 K. Even at this temperature there are still vibrations persisting. It is not included in the reported energy at point 1), because one needs to calculate the vibrations of the molecule which is a separate calculation that follows the optimization step.
3. total corrected energy. The ZPC is added to the total energy (the energy mentioned at point 1)

**DFT Calculation of 2.17o**

Table 3.8 summarizes some of the geometrical values before the optimization (dihedral angles $\alpha_1$, $\alpha_2$ and the distance $\delta$ between the reactive carbon atoms) and the geometrical values and energy obtained after optimization for four different cases (when dihedral angle is varied from 55° – 70°. It appears that regardless of how the dihedral angles are varied the optimized values are almost identical (both geometrical values and energy values).
Table 3.8. Geometrical values and total energy of compound 2.17o (DFT B3LYP 6-31G*).

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
<th>total energy (a.u.)</th>
<th>ZPC (Hartree/particle)</th>
<th>ZPC corrected total energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 = \alpha_2$ (°)</td>
<td>$\delta$ (Å)</td>
<td>$\alpha_1$ (°)</td>
<td>$\alpha_2$ (°)</td>
<td>$\delta$ (Å)</td>
</tr>
<tr>
<td>55.00</td>
<td>3.423</td>
<td>63.53</td>
<td>62.84</td>
<td>3.980</td>
</tr>
<tr>
<td>60.00</td>
<td>3.596</td>
<td>63.52</td>
<td>62.89</td>
<td>3.980</td>
</tr>
<tr>
<td>65.00</td>
<td>3.767</td>
<td>63.54</td>
<td>62.85</td>
<td>3.980</td>
</tr>
<tr>
<td>70.00</td>
<td>3.934</td>
<td>63.52</td>
<td>62.83</td>
<td>3.979</td>
</tr>
</tbody>
</table>

**DFT calculations of 3.1o**

Table 3.9 gives the values before and after optimization for compound 3.1o. Once again the values are almost equal for the optimized structures.
Table 3.9. Geometrical values and total energy of compound 3.1o (DFT B3LYP 6-31G*).

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 = \alpha_2$ (°)</td>
<td>$\alpha_1$ (°)</td>
</tr>
<tr>
<td>55.00</td>
<td>3.284</td>
</tr>
<tr>
<td>60.00</td>
<td>3.468</td>
</tr>
<tr>
<td>65.00</td>
<td>3.641</td>
</tr>
<tr>
<td>70.00</td>
<td>3.814</td>
</tr>
</tbody>
</table>

DFT Calculations of 3.2o

Table 3.10 gives the geometrical values before optimization and after optimization (geometrical and total Energy values) for compound 3.2o. Once again there is no difference between the three calculated values.
Table 3.10. Geometrical values and total energy of compound 3.20 (DFT B3LYP 6-31G*)

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 = \alpha_2$ (°)</td>
<td>$\delta$ (Å)</td>
</tr>
<tr>
<td>55.00</td>
<td>3.160</td>
</tr>
<tr>
<td>60.00</td>
<td>3.344</td>
</tr>
<tr>
<td>65.00</td>
<td>3.524</td>
</tr>
</tbody>
</table>

DFT calculations of 3.30

Table 3.11 contains the values before and after optimization for compound 3.30 and as expected there is no big difference between the calculations.
Table 3.11. Geometrical values and total energy for compound 3.3o (DFT B3LYP 6-31G*).

![Chemical structure of compound 3.3o]

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 = \alpha_2$ ($^\circ$)</td>
<td>$\delta$ (Å)</td>
</tr>
<tr>
<td>55.00</td>
<td>3.306</td>
</tr>
<tr>
<td>60.00</td>
<td>3.485</td>
</tr>
<tr>
<td>65.00</td>
<td>3.662</td>
</tr>
<tr>
<td>70.00</td>
<td>3.835</td>
</tr>
</tbody>
</table>

DFT Calculations of 3.4o

Table 3.12 gives the geometrical values and the energy for compound 3.4o. The calculations are consistent and they are not dependent upon the structure submitted for calculations, as the optimized structure has the same general molecular geometry and total energy as in the case as previous calculations 2.17o, 3.1o, 3.2o and 3.3o.
Table 3.12. Geometrical values and total energy for compound 3.4o (DFT B3LYP 6-31G*)

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1 = \alpha_2$ (°)</td>
<td>$\Delta$ (Å)</td>
</tr>
<tr>
<td>55.00</td>
<td>3.46</td>
</tr>
<tr>
<td>60.00</td>
<td>3.641</td>
</tr>
<tr>
<td>65.00</td>
<td>3.811</td>
</tr>
<tr>
<td>70.00</td>
<td>3.97</td>
</tr>
</tbody>
</table>

3.3.3. DFT Calculations for the Ring–Closed Isomers

For the ring–closed isomers only one calculation was done (for each compound). Table 3.13 summarizes the significant geometrical parameters before and after optimization and the calculated energies. The last column of the table contains the corrected total energy. From the geometry point of view: all the ring–closed isomers are not perfectly planar as they have the two dihedral angles $\alpha_1$ and $\alpha_2$ in average 6°.
Table 3.13. Geometrical values and total energy for ring–closed isomers (DFT B3LYP 6-31G*).

<table>
<thead>
<tr>
<th>before optimization</th>
<th>after optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α₁ (°)</td>
</tr>
<tr>
<td>2.17c</td>
<td>8.47</td>
</tr>
<tr>
<td>3.1o</td>
<td>12.35</td>
</tr>
<tr>
<td>3.2o</td>
<td>12.35</td>
</tr>
<tr>
<td>3.3o</td>
<td>12.34</td>
</tr>
<tr>
<td>3.4o</td>
<td>8.30</td>
</tr>
</tbody>
</table>
Although the expectation was to see an increase in $\delta$ (lengthening of the photogenerated $\sigma$ bond) as function of a substituent (R) there is a minimal difference the bond varying between 1.582–1.584 Å. Nevertheless the length of the calculated $\sigma$ bond for the terthiophene DTEs series can be placed in the context of the previous calculations: $\sigma_{(\text{Me})} = 1.584 > \sigma_{(\text{Et})} = 1.557 > \sigma_{(\text{iPr})} = 1.578 > \sigma_{(\text{terthiophene series})} = 1.583 > \sigma_{(\text{tBu})} = 1.604$ Å (Figure 3.13).

![Figure 3.13. Comparative $\sigma$ bond lengths as calculated by DFT-B3LYP as function of internal substituent for significant DTE(s), pertinent to this work.](image)

According to the calculations, the length of the $\sigma$ bond photochemically generated for the terthiophene DTEs series is very close in value to the one presented by compound 2.8c (isopropyl internal group) (Figure 3.13). Compound 2.8c has a half life at 40 °C of 21 days. On the other hand the compounds presented in this work have half lives between 4 – 35 days. Hence in the terthiophene DTE series the same correlation between the calculated $\sigma$ bond length and half lives: the longer (weaker) $\sigma$ bond the faster the cycloreversion in the dark. Unfortunately, the results regarding the bond length ($\sigma$ bond) cannot explain the different rates of the cycloreversion in the dark within the compounds presented in this work (2.17c, 3.1c, 3.2c, 3.3c and 3.4c).
Figure 3.14. Relationship between the $\sigma$ bond length photochemically generated (calculated at DFT level, B3LYP) versus the log of half lives for compounds already published.

3.3.4. DFT Calculations for the Radical Cations

The calculations for the radical cations for ring-opened and closed isomers were done using UB3LYP method with a basis set of 6-31-G*. Once the optimized values (coordinates) for the neutral molecules were obtained, they were resubmitted for optimization with a change of charge and multiplicity. For neutral molecule the charge is 0 and multiplicity is 1 and for radical cation the charge is 1 and multiplicity 2. In Table 3.14 are given the total energy values.
Table 3.14. Total energy values for the radical cations of 2.17c, 3.1c, 3.2c, 3.3c and 3.4c.

<table>
<thead>
<tr>
<th>entry</th>
<th>total energy (a.u.)</th>
<th>ZPC (Hartree/particle)</th>
<th>ZPC corrected total energy (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7a **+</td>
<td>-4101.380374</td>
<td>0.352429</td>
<td>-4101.027951</td>
</tr>
<tr>
<td>2.7c **+</td>
<td>-4101.354711</td>
<td>0.353848</td>
<td>-4101.000863</td>
</tr>
<tr>
<td>3.1a **+</td>
<td>-4258.668816</td>
<td>0.463174</td>
<td>-4258.205442</td>
</tr>
<tr>
<td>3.1c **+</td>
<td>4258.643268</td>
<td>0.464709</td>
<td>4259.107977</td>
</tr>
<tr>
<td>3.2a **+</td>
<td>-4498.263336</td>
<td>0.31998</td>
<td>-4101.261236</td>
</tr>
<tr>
<td>3.2c **+</td>
<td>-4730.404226</td>
<td>0.805294</td>
<td>-4729.598932</td>
</tr>
<tr>
<td>3.3a **+</td>
<td>-4498.263336</td>
<td>0.31998</td>
<td>-4497.943356</td>
</tr>
<tr>
<td>3.3c **+</td>
<td>-4498.237732</td>
<td>0.321347</td>
<td>-4497.916385</td>
</tr>
<tr>
<td>3.4a **+</td>
<td>-5205.023419</td>
<td>0.446719</td>
<td>-5204.5767</td>
</tr>
<tr>
<td>3.4c **+</td>
<td>-5204.99838</td>
<td>0.447918</td>
<td>-5204.550462</td>
</tr>
</tbody>
</table>

3.3.5. Trends from the DFT Calculations

Table 3.15 has the values for difference in total energy between neutral isomers $\Delta E(E_{RC} - E_{RO})$ and the difference in energy between the oxidized species (radical cations) $\Delta E(E_{RC^+} - E_{RO^+})$. The difference in energy between the two isomers $\Delta E(E_{RC} - E_{RO})$ was calculated and found to be very close for all the compounds 25-26 kcal / mol. The following discussion is divided into two parts putting the results in the frame of previous results and comparing the results in the series.
Table 3.15. Overview of calculated energies for the neutral molecules and their respective radical cations for compounds 2.17, 3.1, 3.2, 3.3 and 3.4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>corrected total energy (a.u) ring-open isomer</th>
<th>ΔE(E_{RC}^{+} - E_{RO}) kcal/mol</th>
<th>corrected total energy (a.u) ring-closed isomer radical cation</th>
<th>ΔE(E_{RC}^{+} - E_{RO}^{+}) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17</td>
<td>-4101.261235</td>
<td>25.78</td>
<td>-4101.02745</td>
<td>16.68</td>
</tr>
<tr>
<td>3.1</td>
<td>-4258.428075</td>
<td>26.04</td>
<td>-4258.20544</td>
<td>16.87</td>
</tr>
<tr>
<td>3.2</td>
<td>-4729.845185</td>
<td>26.03</td>
<td>-4729.625947</td>
<td>16.95</td>
</tr>
<tr>
<td>3.3</td>
<td>-4498.180887</td>
<td>25.55</td>
<td>-4497.943355</td>
<td>16.92</td>
</tr>
<tr>
<td>3.4</td>
<td>-5204.797485</td>
<td>25.80</td>
<td>-5204.576699</td>
<td>16.46</td>
</tr>
</tbody>
</table>

Comparing the difference in energy between ΔE(E_{RC}^{+} - E_{RO}^{+}) of this particular series the terthiophene derivatives does not fit into the previous series (see Table 3.16). This is due probably to the difference in structure of internal groups (methyl group versus substituted thiophene ring).
Table 3.16. Updated series, containing also the terthiophene series, for the correlation between the calculated $\Delta H$ and the experimental determined half life of the ring–closed isomer in the dark at 60 °C.

<table>
<thead>
<tr>
<th>entry</th>
<th>$\Delta H$ calculated (kcal/mol)</th>
<th>$t_{1/2}$ @ 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3c</td>
<td>13.2</td>
<td>21 years</td>
</tr>
<tr>
<td>2.9c</td>
<td>14.1</td>
<td>3.66 years</td>
</tr>
<tr>
<td>2.15c</td>
<td>21.3</td>
<td>573 min</td>
</tr>
<tr>
<td>2.18c</td>
<td>21.9</td>
<td>247 min</td>
</tr>
<tr>
<td>2.14c</td>
<td>22.7</td>
<td>3.3 min</td>
</tr>
<tr>
<td>2.17</td>
<td>$R_{int} = R_{ext} = H$</td>
<td>1 day</td>
</tr>
<tr>
<td>3.1</td>
<td>$-/- = CH_3$</td>
<td>1.5 days</td>
</tr>
<tr>
<td>3.2</td>
<td>$-/- = \text{fBu}$</td>
<td>3.8 hours</td>
</tr>
<tr>
<td>3.3</td>
<td>$-/- = F$</td>
<td>4 days</td>
</tr>
<tr>
<td>3.4</td>
<td>$R_{int} = H$</td>
<td>$R_{ext} = \text{thiophene}$</td>
</tr>
</tbody>
</table>

The outcome of DFT calculations regarding the terthiophene series, cannot be placed in the same series with the already published results. According to the difference in energy between the two isomers, which is around 26 kcal / mol, it will mean that
cycloreversion at 60 °C in the dark should take place within minutes. And the experimental results are in contradiction with the calculated values, as the ring-closed isomers are quite stable in the dark at this particular temperature. The goal of this project was to correlate the experimentally determined half lives with the DFT calculated difference in energy between the two isomers. Unfortunately, this cannot be done as the calculated values for energy do not match the experimental data for the thermal cycloreversion in the dark. This can be due to four reasons:

1. a better calculation method is required for DTE with aromatic internal group, although so far DFT was the standard in calculating the energies for DTEs, and/or

2. looking at the bigger picture, in the end the difference in half lives for the DTEs presented in this work is quite minimal (5 days for compound 3.3c to 1 day for compound 2.17c at 60 °C) and an exact correlation with the calculated energy is not feasible. So far DFT calculations were proven useful in explaining half lives of 21 years at 60 °C for compound 1.3c versus 3.6 years for compound 3.14c, and this difference is quite substantial and/or

3. the comparison is not fair, as the compounds presented in this thesis differ substantially from the structural point of view. The internal aromatic rings might affect substantially the calculated values for the total energy.

4. solvent was not taken into account when the calculations were performed.

It is of interest that the distance $\delta$ between the reactive carbons in the ring–open isomers (Table 3.8 for compound 2.17o) and the half lives of the ring–closed isomers in the dark. The shorter the calculated distance $\delta$ in the ring–open isomer the more stable the ring-closed isomer is in the dark (Table 3.17).
Table 3.17. Values for calculated $\delta$ (Å) for the ring–open isomers as function of half lives of lives of thermal cycloreversion of the ring–closed forms in the dark.

<table>
<thead>
<tr>
<th>entry</th>
<th>$R_{ext/int}$</th>
<th>$\delta$ (Å) (RO)</th>
<th>$t_{1/2}$ 60 °C (RC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3o</td>
<td>F</td>
<td>3.823</td>
<td>4 days</td>
</tr>
<tr>
<td>3.1o</td>
<td>CH$_3$</td>
<td>3.871</td>
<td>1.5 days</td>
</tr>
<tr>
<td>2.17o</td>
<td>H</td>
<td>3.908</td>
<td>1 day</td>
</tr>
<tr>
<td>3.4o</td>
<td>thiophene / H</td>
<td>3.883</td>
<td>9.6 hours</td>
</tr>
<tr>
<td>3.2o</td>
<td>t-Bu</td>
<td>3.925</td>
<td>3.8 hours</td>
</tr>
</tbody>
</table>

By plotting the DFT calculated distance between the reactive carbons (for ring–open isomers) versus the respective half lives value (ring–closed forms), one can notice that: the shorter the calculated distance between the reactive carbon atoms, the larger the half lives (Figure 3.15). Compound 2.17, the parent compound does not follow the trend. However, caution needs to be taken as there are insufficient points and also the difference in the calculated distance between the reactive Carbon atoms is quite small. One speculation can be done in order to explain the trend. The transition state for the dark ring–opening involves a biradical intermediate. Probably, the transition state resembles the ring–open form. The distance between the radicals ($\delta'$) (in the transition state) might be similar to the calculated distance $\delta$ in the ring–open isomer. The shorter the distance $\delta'$, the easier for the molecule to recombine (radical coupling) back to the ring–closed form. This assumption can be verified by performing calculations for the transition states.
Figure 3.15. Relationship between the half lives values and the calculated distance between the reactive carbon atoms for compounds 2.17, 3.1, 3.2, 3.3 and 3.4.

3.4. $^1$H NMR Spectra for Compounds 2.17, 3.1, 3.2, 3.3 and 3.4 and $\pi$-$\pi'$ Stacking

It is interesting to note that the chemical shift of the hydrogen atoms of the central thiophene (singlet) and the two doublets (triplets in the case of compound 3.3o) belonging to the internal thiophene ring are more upfield than expected for the entire series. These upfield chemical shifts of the above mentioned hydrogen atoms are due to $\pi$-$\pi'$ stacking between the central thiophene ring of one of the terthiophene arms and the internal thiophene cycle of the other terthiophene unit (Figure 3.16 top). Aromatic $\pi$-$\pi'$ stacking interactions are defined as the attractive interactions that occur between the dipoles of aromatic rings.
Figure 3.16. (top) Optimized geometry (DFT / B3LYP) for compound 2.17 showing the \( \pi-\pi \) stacking. The reported chemical shifts for both isomers were obtained in CDCl\(_3\) on a 400 MHz instrument. (bottom) Stack of partial \(^1\)H NMR spectra of compounds 2.17o, 3.1o, 3.2o, 3.3o and 3.7o. All spectra are acquired in CDCl\(_3\) on a 400 MHz instrument. Marked with a star is the singlet - the proton from the central thiophene ring.

An expected chemical shift for these types of aromatic protons will be a chemical shift greater or equal to 7 ppm, similar to the ones possessed by the compound 3.10.
from Scheme 3-7, a byproduct formed in the reaction of 3'-bromo-5,5-dimethylterthiophene and perflurocyclopentene.


In Figure 3.9 are overlapped partial $^1$H NMR spectra for compound 3.10 and compound 3.10.

Figure 3.17. Overlapped partial spectra of compound 3.10 (top) and half switch 3.10 bottom, the inset is the aliphatic region. Spectra were acquired in CDCl$_3$ as a solvent and on a 400 MHz instrument.

3.4.1. $^1$H NMR Chemical Shifts and Aromaticity Considerations of Monosubstituted $T$ of $\alpha,\alpha'$-Disubstituted Terthiophenes

Before the discussion regarding the trends of the compounds presented in this thesis the reader will benefit from a short intro regarding the chemical shifts of the
substituted terthiophenes. The chemical shift of thiophene, α monosubstituted thiophene and α−α′-disubstituted terthiophenes are presented in Figure 3.18.77

![Chemical Shifts for Thiophenes](image)

**Figure 3.18.** Top row: are presented the chemical shifts (ppm) for thiophene and of α monosubstituted thiophenes derivatives (pertinent to this work). The multiplicity of the peaks is ignored and only the middle of the signal is reported. Central row: chemical shift for α disubstituted thiophenes.77 Bottom row: is the chemical structure of compound 3.10 and the assigned chemical shifts.

All α protons of the monosubstituted thiophene are shifted upfield in comparison to the α proton of thiophene (Figure 3.18). The trend is valid for the entire series regarding all the protons. It is well known that EDG are shielding hence the upfield shift. The most shielded protons are the ones belonging to the 2-fluorothiophene. Usually F is regarded as an electron withdrawing group (EWG) due to the fact that is the most electronegative element, but when F is part of a delocalized system (such as thiophene) F has a +M (electromeric effect) hence it is able to push the pair of nonbonding electrons through resonance. On the other hand, the difference in chemical shift (upfield shift)
might be due to a loss in aromatic character of the $\alpha$ monosubstituted thiophenes when compared to thiophene, a more double bond like character. Overall aromaticity is the ability of sustaining an aromatic ring current. Nevertheless, aromaticity is a very complex issue and is quite difficult to quantify this property.\textsuperscript{78} However is has been noted that the aromaticity of monosubstituted benzene and monosubstituted thiophene derivatives hardly changes upon substitution.\textsuperscript{79} Although aromaticity and the chemical shifts are closely related, is not fair to say that a shift upfield means loss of aromaticity. It is safe to say that although the $\alpha$ chemical shifts of the protons of the monosubstituted thiophenes present a slight upfield shift, it is due to the electron donating effect of the substituting group rather than loss of aromaticity. Overall it is expected of monosubstituted thiophenes to present upfield shifts for all H atoms if substituted by alkyl groups or halogens. Terthiophene derivatives present the same trend regarding the chemical shifts: the H atoms on the outer thiophenes behave the same as the $\alpha$ monosubstituted thiophenes. It is important to note that the H atoms from the central thiophene unit has almost same chemical shift for all the $\alpha$ disubstituted terthiophenes 6.95 ppm compounds from second row Figure 3.10. Furthermore the substitution of position 3’ of the terthiophene with an electron deficient double bond (perfluoro-cyclopentadiene) does not influence the chemical shift of the neighbouring proton (7 ppm).

3.4.2. \textit{Comparative $^1$H NMR Spectroscopy Data for the Ring–Open Isomers Presented in This Work}

The $\pi–\pi$ stacking is important because it influences the molecule’s orientation. For the work presented in this thesis the stacking is relevant for two reasons:\{Peters, 2003 #98\}

1. Influences the efficiency of the photochemical ring–closing reaction. The ring–open form must be oriented in the proper conformation (AP) in order to undergo the photochemical isomerization. Only the AP conformer undergoes the photochemical ring–closing reaction.

2. This stacking might be a driving force for the ring–opening reactions (photochemical and thermal dark ring–opening). In general it is accepted that the ring–opening reaction has as a driving force the rearomatization. By combining the two driving forces the rearomatization and $\pi–\pi$ stacking the result will be a
decrease in the stability of the ring-closed isomer. The reader has to be aware that the stability of the ring-closed isomer is related in literature to three important factors: rearomatization, steric factor and electronic factor. In the next part of this thesis will be discussed if any trends regarding the \( \pi-\pi \) stacking can be extrapolated from the \( ^1\text{H} \) NMR spectroscopy results.

In Table 3.18 are tabulated the chemical shifts for compounds \textbf{2.17o}, \textbf{3.4o}, \textbf{3.1o}, \textbf{3.2o}, and \textbf{3.3o}. Regarding the ring-open isomers, the chemical shifts of the singlets (Hc) are almost equal for all compounds. On the other hand the doublets Hd and He (internal thiophene) also part of the \( \pi-\pi \) stacking system show a higher degree of variation. For example compound \textbf{3.3o} has the most upfield signals which might be a sign of better \( \pi-\pi \) stacking or this is just the influence of the F atom. Hence it is quite difficult to assess the amount of \( \pi-\pi \) stacking only from the \( ^1\text{H} \) NMR spectral data. As expected compounds \textbf{2.17o} and \textbf{3.4o} have almost identical chemical shifts for Hc (\( \delta = 6.35 \text{ ppm} \)) and the same distance between the same proton and the shielding top thiophene ring. This is due to the fact that both compounds have the same internal substituents: unsubstituted thiophene ring. Compound \textbf{3.1o} has the most upfield chemical shift for Hc of 6.31 ppm and larger calculated distance between Hc and the top shielding thiophene when compared to standard compound \textbf{2.17o}. Compound \textbf{3.2o} has a similar chemical shift for Hc (6.36 ppm) to compound \textbf{2.17o} and the largest distance between Hc and the top thiophene ring. At this stage one cannot speculate about the extent of the \( \pi-\pi \) stacking without factoring out the electronic effects of the R substituents. This can be done by substracting the chemical shifts for the ring-closed isomers.
Table 3.18. The chemical shifts for compounds 2.17, 3.1, 3.2, 3.3, 3.4 and 3.7 both isomers (on top is the legend of labeling the protons). All the spectra were acquired on a 400 MHz instrument and in CDCl₃ as solvent.

<table>
<thead>
<tr>
<th>R_ext</th>
<th>R_int</th>
<th>Ha</th>
<th>Hb</th>
<th>Hc</th>
<th>Hd</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17o</td>
<td>H</td>
<td>7.00</td>
<td>7.05</td>
<td>6.35</td>
<td>6.69</td>
<td>6.80</td>
</tr>
<tr>
<td>2.17c</td>
<td>&quot;</td>
<td>7.07</td>
<td>7.28</td>
<td>6.52</td>
<td>7.30</td>
<td>6.93</td>
</tr>
<tr>
<td>3.4o</td>
<td>thiophene</td>
<td>7.06</td>
<td>6.96</td>
<td>6.35</td>
<td>6.71</td>
<td>7.18</td>
</tr>
<tr>
<td>3.4c</td>
<td>&quot;</td>
<td>a)</td>
<td>6.49</td>
<td>a)</td>
<td>a)</td>
<td>6.83</td>
</tr>
<tr>
<td>3.1o</td>
<td>CH₃</td>
<td>6.63</td>
<td>6.84</td>
<td>6.31</td>
<td>6.45</td>
<td>6.43</td>
</tr>
<tr>
<td>3.1c</td>
<td>&quot;</td>
<td>6.67</td>
<td>7.01</td>
<td>6.40</td>
<td>7.15</td>
<td>6.50</td>
</tr>
<tr>
<td>3.2o</td>
<td>tBu</td>
<td>6.68</td>
<td>6.83</td>
<td>6.36</td>
<td>6.43 b)</td>
<td>6.43 b)</td>
</tr>
<tr>
<td>3.2c</td>
<td>&quot;</td>
<td>6.74</td>
<td>7.02</td>
<td>6.39</td>
<td>7.15</td>
<td>6.55</td>
</tr>
<tr>
<td>3.3o</td>
<td>F</td>
<td>6.69</td>
<td>6.41</td>
<td>6.44</td>
<td>6.28</td>
<td>6.22</td>
</tr>
<tr>
<td>3.3c</td>
<td>&quot;</td>
<td>6.47</td>
<td>6.89</td>
<td>6.38</td>
<td>6.95</td>
<td>6.22</td>
</tr>
</tbody>
</table>

Note: a) chemical shifts were not assigned due to overlap; certain chemical shifts are reported equal b) signals overlap for the ring–open isomer; c) signal overlap for the ring–open and ring–closed isomer

One cannot quantify the increase or decrease of π-π stacking just by inspecting the ¹H NMR spectra of compounds 2.17o, 3.1o, 3.2o, 3.3o, 3.4o and 3.7o without taking into consideration the influence of substituents F, CH₃, t-Bu, as compared to H. The following discussion considers the calculated distances between the hydrogen atom from the central thiophene to the shielding thiophene unit, Figure 3.19.
Figure 3.19. The geometry of the compounds as obtained by DFT optimization at B3LYP/6-31g* level (only compound 2.17o is shown here). R stands for different substituents: H compound 2.17o, CH₃ compound 3.1o, t-Bu compound 3.3o, F for compound 3.4o. The dashed double headed line represents the distance between the H atom and the top shielding thiophene unit.

In Table 3.19 are given the calculated distances between Hc and the top shielding thiophene unit. Given the fact the DTE compounds are not exactly symmetrical (see DFT calculations Chapter 3.3) there are two values: d and d’ and in the table is presented the average value.

Table 3.19. The calculated (DFT / B3LYP) average distance d (Å) between the proton Hc and the top shielding thiophene and the chemical shift of proton Hc (value obtained in CDCl₃ as solvent and on a 400 MHz instrument).

<table>
<thead>
<tr>
<th>entry</th>
<th>R(Int)</th>
<th>d (Å)</th>
<th>t₁/₂ (60 °C)</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17o</td>
<td>H</td>
<td>3.528</td>
<td>25.2</td>
<td>6.35</td>
</tr>
<tr>
<td>3.4o</td>
<td>thiophene/</td>
<td>3.530</td>
<td>9.6</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1o</td>
<td>CH₃</td>
<td>3.604</td>
<td>41</td>
<td>6.31</td>
</tr>
<tr>
<td>3.2o</td>
<td>t-Bu</td>
<td>3.619</td>
<td>3.85</td>
<td>6.36</td>
</tr>
<tr>
<td>3.3o</td>
<td>F</td>
<td>3.594</td>
<td>96</td>
<td>6.44</td>
</tr>
</tbody>
</table>

By plotting the DFT calculated the distances (d) between the proton Hc and top shielding thiophene ring (for the ring–open form) and the respective half lives at 60 °C there is an apparent trend for compounds 3.1, 3.2 and 3.3 (Figure 3.20). The shorter the calculated distance (d), the more stable the ring–closed isomer in the dark. This trend was not further explored because difference in distance for the three compounds above
mentioned, is minimal ranging from 3.594 Å to 3.604 Å. One can also conclude that the calculated distance \(d\) is also related with the amount the \(\pi-\pi\) stacking. The shorter the distance, the more \(\pi-\pi\) stacking the respective compound presents. Therefore the descending order of extent of \(\pi-\pi\) stacking is: \(3.3\text{o}, 3.1\text{o} \) and \(3.2\text{o}\). In the next section of this thesis, \(^1\text{H} \text{NMR spectra analysis of these compounds, the trend regarding the stacking seems to be exactly the opposite. Nevertheless, the reader has to be aware of this observation.}

\[
\begin{align*}
\text{Figure 3.20.} & \quad \text{Relationship between the calculated distance } d \text{ (between proton Hc and top shielding thiophene ring) and the respective half lives, at 60 °C for compounds 2.17, 3.1, 3.2, 3.3 and 3.4.} \\
\end{align*}
\]

As a comparison the “dimer” of thiophene was calculated to have a distance between the two thiophene cycles of 4 Å (Figure 3.21).\(^\text{80}\) So the values for distance \(d\) for the compounds \(2.17\text{o}, 3.1\text{o}, 3.2\text{o}, 3.3\text{o} \) and \(3.4\text{o}\) are in the given range of \(\pi-\pi\) stacking. Furthermore the substituents (both EDG and EWG) are regarded as increasing the extent of \(\pi-\pi\) stacking (both in the case of benzene and thiophene).\(^\text{81}\) Although the
calculated distance $d$ for the compounds presented in this work is somewhat affected by the steric bulk and is increasing with the increase of the volume of substituent.

![Figure 3.21](image)

**Figure 3.21.** The calculated distance (DFT) in $\pi-\pi$ stacking for two geometries of a thiophene dimer.

3.4.3. **Comparative $^1H$ NMR Spectroscopy Data for the Ring-Closed Isomers Presented in This Work**

Due to $\pi-\pi$ stacking, the singlet, Hc belonging to the ring–open isomer is shifted downfield when the compound is undergoing photochemical ring–closing. The difference in chemical shifts ($\Delta\delta$) are given in Figure 3.22. As a rule the singlet Hc in the ring–open isomer is a proton in an aromatic environment and upon photoisomerization is becoming a proton bound to double bond, but the $\Delta\delta$ (RO-RC) is a downfield one. The only compound that does not follow this rule is compound 3.3 where the shift is an upfield one. One can speculate that the $\Delta\delta$ becomes smaller with the decrease in $\pi-\pi$ stacking. The amount of $\pi-\pi$ stacking could not be determined from the chemical shifts of the ring–opened isomers due to the electronic influence of the R group. By subtracting the chemical shift of the ring–closed form form the ring–opened isomer the electronic influence of the R group might by cancelled.
As mentioned the $\pi-\pi$ stacking is important because it might be an additive driving force towards the thermal ring-opening in the dark. The values for the $\Delta\delta$ (ppm) for Hc are tabulated (Table 3.20) in order to see the trends if any.
Table 3.20. The values for chemical shifts for Hc, the difference $\Delta\delta$ (ppm) and the respective half lives at 60 °C, are arranged below from the largest negative value to the positive value of $\Delta\delta$.

<table>
<thead>
<tr>
<th>compound</th>
<th>R</th>
<th>$\delta$ (ppm)</th>
<th>$\Delta\delta$ (ppm)</th>
<th>$t_{1/2}$ (60 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hc (RO)</td>
<td>Hc (RC)</td>
<td>Hc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\delta$</td>
<td>$\delta$ (RO $-\delta$ RC)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ppm)</td>
<td>(ppm)</td>
<td>Hc</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\delta_{RO} - \delta_{RC})$</td>
<td></td>
</tr>
<tr>
<td>2.17o</td>
<td>H</td>
<td>6.35</td>
<td>6.52</td>
<td>-0.17</td>
</tr>
<tr>
<td>3.4o</td>
<td>thiophene/</td>
<td>6.35</td>
<td>6.49</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1o</td>
<td>CH$_3$</td>
<td>6.31</td>
<td>6.40</td>
<td>-0.09</td>
</tr>
<tr>
<td>3.2o</td>
<td>t-Bu</td>
<td>6.36</td>
<td>6.39</td>
<td>-0.03</td>
</tr>
<tr>
<td>3.3o</td>
<td>F</td>
<td>6.44</td>
<td>6.38</td>
<td>+0.06</td>
</tr>
</tbody>
</table>

For compounds 3.3, 3.1 and 2.17 the difference in chemical shift $\Delta\delta$ for Hc can be correlated with the half life in the dark of the ring–closed isomers (Figure 3.23). The larger the $\Delta\delta$ the more unstable the ring-closed isomer is in the dark. On the other hand, compounds 3.2 and 3.4 do not fit in this trend.
Figure 3.23. Relationship between the difference in chemical shifts for Hc $\Delta \delta$ (ppm) and the respective half lives, at 60 °C for compound 2.17, 3.1, 3.2, 3.3 and 3.4.

Concluding Remarks for the $\pi-\pi$ Stacking Regarding the Compounds Studied in This Thesis in the Context of Thermal Stability of the Ring−Closed Isomers in the Dark

In conclusion for all ring−open isomers, the chemical shift of Hc (bold values in Table 3.3) should be upfield for all compounds compared to 2.17o if they will possess the same extent of $\pi-\pi$ stacking:

Compound 3.4o has the same amount of $\pi-\pi$ stacking as 2.17o, as expected as they have the same internal group, unsubstituted thiophene ring. They have similar chemical shifts for Hc (both isomers) and also a similar $\Delta \delta$. But compound 3.4c cycloreverts in the dark faster than parent compound 2.17c. This is due probably to the better stabilization of the diradical (transition state) in the case of the tetrathiophene derivative. Also compound 3.4 does not fit into the proposed trend of chemical shifts and half lives (Figure 3.23) because it is the only compound in the series that has different internal and external groups.
Compound \textbf{3.1o} has a slight upfield chemical shift for Hc (6.31 ppm) as compared to the compound used as standard, \textbf{2.17o} (6.35 ppm). As a reminder, this is to be expected for this type of substituent (Figure 3.18). The value for \( \Delta\delta \) of -0.09 ppm it is almost half that of the parent compound of -0.17 ppm. This shows that the CH\(_3\) groups in the \( \alpha \) positions of the inner and outer thiophene cycles do disrupt the \( \pi-\pi \) stacking to a certain extent. And because \textbf{3.1c} is 1.5 times more stable than \textbf{2.17c} at 60 °C, there is a correlation between the \( \Delta\delta \) for Hc and the stability in the dark. Also the DFT calculations showed that the distance between the reactive carbon atoms is smaller in the case of of \textbf{3.1o}, and this smalleer distance was correlated with a better stability in the dark of the ring–closed isomer.

Compound \textbf{3.2o} has a chemical shift for the same proton Hc of 6.36 ppm which is almost identical to that of compound \textbf{2.17o} of 6.35 ppm but the \( \Delta\delta \) is the smallest in the series of -0.03 ppm. Using the same type of reasoning as for compound \textbf{3.1}: smaller \( \Delta\delta \) value is indicative of a lower extent of \( \pi-\pi \) stacking, which will have as a result an increase in the stability of the ring–closed form, but this is not the case. This means that the stacking is not a decisive factor in the cycloreversion in the dark for this compound, as its influence upon this reaction is negligible. Because the stacking was eliminated as a decisive factor in the cycloreversion one remains only with the steric factor, the \textit{steric attraction} (Scheme 3-7) and the largest calculated difference between the reactive carbon atoms in the ring open isomer to explain why this compound is the most unstable in the dark.

Compound \textbf{3.3o} (tetrafluorinated derivative) is the only one that has a positive \( \Delta\delta \) value of +0.06 ppm which was correlated with the better stability of the ring–closed in the dark. This result (poor \( \pi-\pi \) stacking) was somewhat counter intuitive as fluorine have modest sizes, see Table 3.2 for the Charton values, so it will not disrupt the \( \pi-\pi \) stacking unlike the methyl and t-Bu groups. Furthermore one would have expected that the \( \pi-\pi \) stacking will be enhanced by the fluorine substituent as the arms of the molecule cycles will rotate in order to accommodate for an overlap of the positive zones with the negatives zones of the molecule. One has to mention that according to DFT calculations (Table 3.19) this compound has the smallest distance between the proton Hc and top shielding thiophene ring. In Figure 3.24 are aligned on top of each other two conformers
of 5,5''-difluoro-2,2':5',2''-terthiophene that will allow for the above mentioned overlap. The choice of presenting only the potential surfaces for terthiophene arms of the DTE molecule instead of the entire molecule is just for the sake of simplicity. But compound 3.3o has the smallest calculated distance between the reactive carbon atoms and this might be the decisive factor in dictating the better stability of the ring-closed isomer in the dark.

Figure 3.24. The calculated AM1 electrostatic potential surfaces for the fluorine α disubstituted terthiophene for the two conformers that will allow for a better stacking. The calculation was performed on Spartan. The bar on the right is the legend that indicates that the red are negative potential zones and with blue are the positive potential zones.

3.5. Photochemical Characterization

The photochemical characterization of DTEs presented in this work include the UV-absorption spectra and assessment of the photostationary states. Normally the solvent of choice for both photochemical and electrochemical studies of DTEs is CH₃CN due to its stability under UV-light irradiation and to its wider electrochemical window. On the other hand, CH₂Cl₂ can give small amounts of hydrogen chloride, carbon monoxide and phosgene under prolonged exposure to UV light (similar behaviour to chloroform) and has a narrower electrochemical window when compared to CH₃CN. For photochemical studies (UV-Vis spectroscopy) usually a concentration of 10⁻⁶ M will suffice. For electrochemical studies (CV) a concentration of 10⁻³ M is appropriate. For
the sake of consistency and for the ease of comparison, one needs to compare the results in the same solvent. Table 3.21 lists the compounds that are soluble in acetonitrile or dichloromethane at the given concentrations. All the compounds are soluble in CH$_2$Cl$_2$, compound 3.2 is insoluble in CH$_3$CN and compound 3.4 is soluble only at the lowest concentration. Both isomers have identical solubilities or the difference is minimal at best.

**Table 3.21.** Tabulated solubilities of compounds 2.17, 3.1, 3.2, 3.3 and 3.4 in CH$_3$CN and CH$_2$Cl$_2$ at the desired concentrations.

<table>
<thead>
<tr>
<th>compound</th>
<th>solvent</th>
<th>CH$_3$CN</th>
<th>10$^{-3}$ M</th>
<th>10$^{-6}$ M</th>
<th>CH$_2$Cl$_2$</th>
<th>10$^{-3}$ M</th>
<th>10$^{-6}$ M</th>
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<tr>
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<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<td>√</td>
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<tr>
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<td>x</td>
<td>x</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<tr>
<td>3.3</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<tr>
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<td>x</td>
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<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>

3.5.1. **Comparative UV Absorption Data for the Terthiophenes Derivatives Pertinent to This work and the Synthesized DTEs**

The electronic absorption spectra of short oligothiophenes (terthiophenes and quaterthiophenes) show two absorption maxima. The first one, which is a less intense band, is due to the n-$\pi^*$ local excitation of the heteronucleus (around 250 nm) and is not affected by the length of the chain or substituents. The second wavelength is more intense and is due to the $\pi$-$\pi^*$ electron transfer of the entire chromophore. This absorption band is strongly influenced by the number of thiophene units (shifts to the red as the number of thiophene units is increased). For example, for compound 3T and 4T (Table 3.22) the red shift is $\Delta \lambda = 35$ nm.$^{82}$ The influence of the substituents is minor. Alkyl groups (CH$_3$ and t-Bu) can induce a small bathochromic shift which is due to inductive effects $\Delta \lambda = 10$ nm.$^{83}$ Bromine substituted terthiophene 2Br-3T also shows a
small red shift due to inductive effects. Table 3.22 depicts the comparison between the related thiophene oligomers and DTEs. Table 3.22 also contains a complete tabulated list of photophysical data for DTEs presented in this work.

**Table 3.22.** Comparative absorption spectra for oligothiophenes and DTE(s).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>355</td>
<td>2.17α</td>
<td>323</td>
</tr>
<tr>
<td>2Me-3T</td>
<td>365</td>
<td>3.1α</td>
<td>337</td>
</tr>
<tr>
<td>2Bu-3T</td>
<td>365</td>
<td>3.2α</td>
<td>336</td>
</tr>
<tr>
<td>2Br-3T</td>
<td>365</td>
<td>3.3α</td>
<td>333</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.4α</td>
<td>373</td>
</tr>
<tr>
<td>4T</td>
<td>390</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.5.2. Comparative Absorption Studies for the DTE Compounds: 2.17, 3.1, 3.2, 3.3, 3.4 and 3.7

The absorption spectra for the ring–open isomers 2.17o, 3.1o, 3.2o, 3.3o, 3.4o and 3.7o are very related to their oligothiophene derivatives. On the other hand the ring–closed forms 2.17c, 3.1c, 3.2c, 3.3c, 3.4c and 3.7c present extended conjugation that run along the rigid backbones of the DTEs. The result of this change in structure accompanied by the appearance of a new band, which is bathochromic shifted by $\Delta \lambda \approx 300$ nm. The following discussion is divided into two parts: (1) a comparison of UV-Vis absorption of ring–open isomers, and (2) a comparison of differences between the ring–closed forms.

Comparative UV Absorption Studies for the Ring–Open Isomers

In the ring–open form, the two thiophene moieties can freely rotate and their electron systems are separated in a cross conjugated manner. For the ring–open isomers, the first absorption band remains unchanged around 250-255 nm, the second absorption band is influenced mainly by the EWG properties of the hexafluorocyclopentene (blue shift by a $\Delta \lambda = 20 - 30$ nm) when compared with the related oligothiophenes ($3T$, $2CH_3T$, $2tBu3T$, $2Br3T$ and $4T$). Figure 3.25 displays the overlapped normalized absorption spectra for compounds: 2.17o, 3.1o, 3.2o, 3.3o, 3.4o and 3.7o. There is a red shift of almost 50 nm between compounds 2.17o and 3.4o due to the extended conjugation provided by the addition of another thiophene ring. On the other hand, the positive inductive effect can be accounted for a more modest red shift of $\Delta \lambda = 10$ nm between compound 2.17o and 3.1o. Compound 3.2o presents the same modest red shift of 10 nm when compared to compound 2.17o, due to the same reasons. Compound 3.3o has very similar absorption spectra to compound 2.17o (slightly hypsochromic). Regarding the fluorine substituted DTEs depending upon its position on backbone of the molecule, it can provide a slight blue (internal position) or red shift (external position).85 The substituent effect of the fluorine atom can be the same as for the EW substituents or can be exactly the reverse: due to the contribution of the lone pair of electrons of the fluorine atom a conjugative ED group. It is possible similarly as the above mentioned situations to act both in equal parts such as the overall absorption spectra of compound 3.3o resembles that of compound 2.17o.
Comparative UV-Vis Absorption Studies for the Ring–Closed Isomers

Upon irradiation with UV light (from a low pressure mercury vapour lamp typically used for visualizing the TLC plates), the absorption bands corresponding to the ring–open isomers decrease in intensity and new bands corresponding to the ring–closed forms appear with absorption maxima at 632, 640, and 645, 626, 673 nm (Figure 3.26). These new absorption bands increase in intensity with the irradiation time until the photostationary state (PSS) is achieved. This process can be inspected visually as there is a significant colour change from yellow to blue-green, which accompanies the conversion to the ring–closed form. The colour change is due to geometry of the ring–closed form that has a nearly planar structure and the conjugation extends throughout the whole molecule. Furthermore, by irradiating the solutions containing the PSS with visible light $> 400$ nm the ring–open isomers were regenerated with no visible degradation seen after 10 cycles of toggling between the two isomers. In Figure 3.26 are the UV-Vis absorption studies for compounds 3.1, 3.2, 3.3, 3.4, and 3.7 in two solvents wherever solubility permits. It is clear that the conversion from one form to another occurs without degradation in each case as the isosbestic points are present. An isosbestic point is defined as the wavelength at which the absorption spectra for both isomers are intersecting and where the sum of the absorbance for the two species
remains constant. Although the presence of the isobestic point implies that the conversion from one species to another is “clean”, one has to keep in mind that this is true if there are not some other species formed in the photochemical step that might absorb at that particular wavelength. Usually the absence of the isobestic point is due to photodegradation products whereas the presence of the isobestic point is the first step in deciding if the conversion is without degradation. Multiple cycles of toggling between the two isomers and monitoring the reaction / isomerisation by $^1$H NMR spectroscopy was very helpful in deciding if the conversion does not render photodegradation compounds. Nevertheless the photoconversion in each case was deemed to be only the desired one and the absorption does not differ significantly in the two solvents (CH$_3$CN and CH$_2$Cl$_2$).
Figure 3.26. UV-Vis absorption spectra of the photoinduced isomerization between the two isomers with a wavelength of irradiation of 365 nm. (a) spectral changes for compound 3.1 in CH$_3$CN (b) spectral changes for compound 3.1 in CH$_2$Cl$_2$ (c) spectral changes for compound 3.2 in CH$_2$Cl$_2$ (d) spectral changes for compound 3.3 in CH$_3$CN, (e) spectral changes for compound 3.3 in CH$_2$Cl$_2$, (f) spectral changes for compound 3.4 in CH$_2$Cl$_2$ and (g) spectral changes for compound 3.4 in CH$_2$Cl$_2$. 
In Figure 3.27 is presented the normalized overlaid data for the PSS solutions (photochemically generated mixture of both isomers) containing the desired compounds in CH$_2$Cl$_2$ solutions and the numerical values are summarized in Table 3.23.

**Figure 3.27.** (a) Normalized UV-Vis absorption spectra of the PSS solutions for compounds 2.17, 3.1, 3.2, 3.3, 3.4 and 3.4 obtained by irradiation the solutions containing only the ring–open isomers in CH$_2$Cl$_2$ with a hand held UV-lamp at 365 nm (b) expansion in the 500–850 nm.

Compounds 3.1c and 3.2c are slightly red-shifted ($\Delta \lambda = 8$ and 13 nm, respectively) indicating that the alkyl substituents influence to a very small extent the absorbance of the coloured isomers. When compared to the ring–closed isomers, the difference in absorbance between the ring–open forms 2.17o and 3.1o (or 3.2o) the red-shift noticed for the ring–open isomers ($\Delta \lambda = 14$ and 12 nm, respectively) is also very modest and follows the same trend. The absorption band of compound 3.3c is only slightly blue-shifted when compared to compound 2.17c ($\Delta \lambda = 6$ nm). The only notable difference is when comparing compounds 2.17c and 3.4c ($\Delta \lambda = 41$ nm), which follows the same trend as for the ring–open isomers 2.17o and 3.4o ($\Delta \lambda = 49$ nm).
Table 3.23. Selected photophysical data in CH₃CN and CH₂Cl₂ of compounds 2.17, 3.1, 3.2, 3.3 and 3.4.

<table>
<thead>
<tr>
<th>entry</th>
<th>PSS (%)</th>
<th>CH₃CN</th>
<th>CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RO</td>
<td>RC</td>
<td>RO</td>
</tr>
<tr>
<td></td>
<td>λₘₐₓ / nm</td>
<td>λₘₐₓ / nm</td>
<td>λₘₐₓ / nm</td>
</tr>
<tr>
<td>2.17</td>
<td>80</td>
<td>255, 322</td>
<td>255, 325</td>
</tr>
<tr>
<td>3.1</td>
<td>73</td>
<td>256, 336</td>
<td>402, 647</td>
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<tr>
<td>3.2</td>
<td>85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.3</td>
<td>70</td>
<td>253, 320</td>
<td>393, 624</td>
</tr>
<tr>
<td>3.4</td>
<td>62</td>
<td>254, 371</td>
<td>670</td>
</tr>
</tbody>
</table>

As conclusion to the optical studies the photochemical toggling between isomers is occurring without degradation in every case. The absorption maxima for the ring–open forms are as expected in function of the R substituent and are following the general trends of the terthiophenes. The same trend is observed for the ring–closed isomers.

3.6. Electrochemical Characterization

3.6.1. Introduction

Cyclic voltammetry has commonly been employed:

1. to measure changes in the redox properties of DTE derivatives as a function of their molecular structures (for both isomers),
2. to characterize electrocatalytic isomerization reactions of the ring–closed isomers to their respective ring–open forms (catalytic oxidative ring–opening), and
3. to measure the extent of undesired electropolymerization during oxidation.

Electrochemical Characterization of Compound 3.1

In Figure 3.28 are illustrated three cyclic voltammograms (CVs). The top CV is for the ring–open isomer 3.1o and the central and bottom ones are for the PSS solution, generated by irradiation with 365 nm source light. The ring–open isomer 3.1o has two
oxidation peaks both reversible at 1.14 V and 1.28 V and a third irreversible one which overlaps with the background oxidation of solvent and electrolyte (> 1.6 V). The two oxidation waves can be attributed to the oxidation of the two terthiophene units of compound 3.1o thus forming 3.1o** and the fully cation (3.1o†). It is important to note that both oxidation processes are more reversible and no visible electropolymerization is noticed.

Regarding the reduction of the two isomers, the ring–opened isomer presents one reduction peak that overlaps with the reduction of the solvent. On the other hand the ring–closed isomer has two well resolved reduction peaks. In the same Figure 3.28 the middle and bottom CVs are for the PSS solution (that contain at least 80 % ring–closed isomer, as measured by ¹H NMR spectroscopy) but with different scan rates, 100 mV / s and 1000 mV / s. Our group previously reported the relatively small oxidation peaks that are barely noticeable above the capacitive current in the CVs of the PSS solutions. This particular oxidation is characteristic of electrocatalytic ring–opening reactions and is typical for DTE derivatives bearing aromatic rings on the "internal" positions. The reactions attributed to this ECE* type mechanism are presented in Scheme 3-9.
The ring-closed isomer is oxidized at the electrode thus forming the transient radical cation $3.1c^{+*}$ (Electrochemical step), which is unstable and goes ring-opening forming the radical cation $3.1o^{+*}$ (Chemical step). Once the radical cation is formed ($3.1o^{+*}$), it is followed by electron transfer ($e^-_T$ step) with another equivalent of $3.1c$ that is faster than the electron-transfer at the solution electrode interface. The

\textbf{Figure 3.28.} CVs of CH$_2$Cl$_2$ solutions ($1 \times 10^{-3}$ M) of compound 3.1 (a) the ring–open isomer with a scan rate of 100 mV / s (b) PSS scan with a scan rate of 100 mV / s (c) PSS solution (photochemically generated) with a scan rate 1000 mV / s. Black arrows show the direction of the scan, the red arrows are used to point out important features of the CV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
reader has to be aware that the notation ECE$_T$ is not a standard abbreviation in the field. In a regular ECE mechanism, to the best of my knowledge the second electrochemical step (ECE) implies that the electron transfer takes place at the electrode. However in the case of 3.1 and similar compounds (DTEs that are undergoing catalytic oxidative ring-opening) the electron transfer can also take place in solution. The notation e$_T$ accounts for the fact that electron transfer can be either at done at the electrode surface or in solution with another analyte molecule.

Scheme 3.9. Schematic representation of the ECE$_T$ mechanism that compound 3.1c is undergoing when is oxidized.

This fading can be monitored visually (Figure 3.29) and also by $^1$H NMR spectroscopy before electrolysis and after electrolysis.
Figure 3.29. Visualization of the electrochemical induced cycloreversion for compound 3.1c. The bulk electrolysis was performed using a platinum mesh working electrode, a silver wire counter electrode and 0.1 M Bu₄NPF₆ as the electrolyte in acetonitrile.

The electrochemical behaviour of compound 3.1 was also studied in CH₃CN. The CVs of both isomers are presented in Figure 3.30. Compound 3.1o presents two – one electron oxidations ($\Delta E = 140$ mV) in CH₂Cl₂. The two oxidations waves, both reversible, are attributed to the independent oxidation of the terthiophene subunits of the molecule. On the other hand, compound 3.1o presents a single reversible oxidation (most likely attributed to a two electron oxidation in CH₃CN). By increasing the scan rate from 100 mV to 800 mV, no increase in resolution was noticed. It is known that $\Delta E$ increases with the decreasing donor strength of the solvent. Hence in CH₂Cl₂, which has a lower donor strength, the second oxidation is shifted towards more anodic values. On the other hand, regarding the reduction of the ring-closed form in the two solvents the difference between the two reductions waves (electrochemical data tabulated in Table 3.24) in the two solvents is not affected by solvent ($\Delta E = 280$ mV in CH₂Cl₂ and $\Delta E = 290$ mV in CH₃CN).
Figure 3.30. CVs of \( \text{CH}_2\text{CN} \) solutions (1 \( \times \) 10\(^{-3}\) M) of compound 3.1 (a) the ring–open isomer with a scan rate of 100 mV / s (b) PSS scan with a scan rate of 100 mV / s (c) PSS solution (photochemically generated) with a scan rate 300 mV / s. Black arrows show the direction of the scan, the red arrows are used to point out important features of the CV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
Table 3.24. Electrochemical data for both isomers of compound 3.1 in CH$_2$Cl$_2$ and CH$_3$CN.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox1}$/V</th>
<th>$E_{ox2}$/V</th>
<th>$\Delta E$/mV</th>
<th>$E_{red1}$/V</th>
<th>$E_{red2}$/V</th>
<th>$\Delta E$/mV</th>
</tr>
</thead>
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<td>1.14</td>
<td>1.28</td>
<td>140</td>
<td>-1.70</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
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<td>CH$_2$Cl$_2$</td>
<td>CH$_3$CN</td>
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<tr>
<td><strong>3.1c</strong></td>
<td>0.72</td>
<td>—</td>
<td>—</td>
<td>-1.08</td>
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<td>CH$_2$Cl$_2$</td>
<td>CH$_3$CN</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Electrochemical Characterization for Compound 3.2

The CVs for compound 3.2 were run only in CH$_2$Cl$_2$ due to its poor solubility in CH$_3$CN. Its behaviour is similar to compound 3.1. The ring–open isomer has two monoelectronic oxidations (1.13 V and 1.33 V) that are reversible and no electropolymerization is noticed (Figure 3.31). The ring–opened isomer has one reduction peak that overlaps with the reduction of the solvent. The data is summarized in Table 3.25.

The ring–closed form during oxidation (0.75 V) forms the transient radical cation that undergoes the rearrangement to the ring–open form radical cation ($3.2c^- \rightarrow 3.2c^{+\ast} \rightarrow 3.2o^{+\ast}$). The last step is the fast electron transfer with another molecule of 3.2c. The process was monitored by $^1$H NMR spectroscopy.

Table 3.25. Summarized electrochemical data for compound 3.2 in CH$_3$CN and CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox1}$/V</th>
<th>$E_{ox2}$/V</th>
<th>$\Delta E$/mV</th>
<th>$E_{red1}$/V</th>
<th>$E_{red2}$/V</th>
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<tr>
<td><strong>3.2o</strong></td>
<td>1.13</td>
<td>1.33</td>
<td>200</td>
<td>-1.75</td>
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<td>—</td>
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<td></td>
<td>CH$_2$Cl$_2$</td>
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<tr>
<td><strong>3.2c</strong></td>
<td>0.75</td>
<td>—</td>
<td>—</td>
<td>-1.01</td>
<td>-1.40</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>CH$_3$CN</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Figure 3.31. CV(s) of CH$_2$Cl$_2$ solutions (1 X 10$^{-3}$ M) of (a) the ring–open isomer 3.2o and with a scan rate of 300 mV / s in anodic direction (b) the ring–open isomer with a scan rate of 300 mV / s in cathodic direction (c) PSS solution (photochemically generated) with a scan rate 300 mV / s. (c') a magnification in the highlighted area to show the oxidation wave for the ring–closed isomer (d) PSS solution (photochemically generated) with a scan rate 300 mV. Black arrows show the direction of the scan, the red arrows are used to point out important features of the CV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
Electrochemical Characterization of Compound 3.3

Due to its solubility compound 3.3 was characterized in two solvents (CH$_2$Cl$_2$ and CH$_3$CN). In Figure 3.32 on the left are the CVs in CH$_2$Cl$_2$ and on the right are the CVs in CH$_3$CN. Unlike the compounds presented before (3.1 and 3.2), the oxidation for the ring-open isomer is less reversible (Figure 3.32(a), Figure 3.32(d) therefore blocking the $\alpha$ positions with fluorine is not as helpful compared to alkyl groups (methyl and t-Bu) in mitigating the electopolymerization.

Regarding the ring-closed isomer (3.3c) the CVs in both solvents are very similar and the electrochemically induced cycloreversion is maintained and it was monitored with $^1$H NMR spectroscopy. The electrochemical data is summarized in Table 3.26.
CVs of compound 3.3 of (a) a CH₂Cl₂ solutions the ring-open isomer with a scan rate of 100 mV / s in cathodic direction (b) a PSS solution (photochemically generated) in CH₂Cl₂ with a scan rate of 100 mV / s in cathodic direction (c) PSS solution in CH₂Cl₂ with a scan rate of 500 mV / s in anodic direction (d) a CH₃CN solutions of the ring-open isomer with a scan rate of 100 mV / s in anodic direction (e) a PSS solution (photochemically generated) in CH₃CN with a scan rate 100 mV / s. Black arrows show the direction of the scan, the red arrows are used to point out important features of the CV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
Table 3.26. Summarized electrochemical data for compound 3.3.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$E_{\text{ox1}} / \text{V}$</th>
<th>$E_{\text{ox2}} / \text{V}$</th>
<th>$\Delta E / \text{mV}$</th>
<th>$E_{\text{red1}} / \text{V}$</th>
<th>$E_{\text{red2}} / \text{V}$</th>
<th>$\Delta E / \text{mV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3o</td>
<td>CH$_2$Cl$_2$</td>
<td>1.60 irr</td>
<td>—</td>
<td>-1.70 irr</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>1.44 irr</td>
<td>—</td>
<td>-1.73 irr</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3.3c</td>
<td>CH$_2$Cl$_2$</td>
<td>0.72 irr</td>
<td>—</td>
<td>-0.89 irr</td>
<td>-1.19 irr</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>0.93 irr</td>
<td>—</td>
<td>-0.79 irr</td>
<td>-1.11 irr</td>
<td>320</td>
</tr>
</tbody>
</table>

**Electrochemical Characterization for Compound 3.4**

The electrochemical behaviour of compound 3.4 was studied in CH$_2$Cl$_2$. The ring–open isomer presents one quasireversible oxidation wave at a potential of 1.28 V on the forward scan Figure 3.33(a). On the return scan there are two reduction waves that suggest that the oxidation was bielectronic. The ring–open isomer presents one reduction wave at a potential of -1.7 V that overlaps with the reduction of the solvent. The ring–closed isomer presents one irreversible oxidation wave at 0.68 V and two reduction waves at -0.92 and 1.18 V. The electrochemical induced cycloreversion was monitored by $^1$H NMR spectroscopy. Given the fact that at a scan rate of 200 mV/s the oxidation of the ring–closed isomer barely seen, it is tempting to assume that the cycloreversion is faster for compound 3.4c than for compounds 2.17c, 3.1.c, 3.2c and 3.4c. Even at a scan rate of 600 mV/s the oxidation of ring–closed isomer is barely observed above the capacitive current (Figure 3.33(e)).
Figure 3.33. CVs of CH$_2$Cl$_2$ solutions (1 X 10$^{-3}$ M) of (a) the ring-open isomer 3.4o with a scan rate of 200 mV / s in anodic direction (b) the ring-open isomer with a scan rate of 200 mV / s in cathodic direction (c) PSS solution scan with a scan rate of 200 mV / s in anodic direction (d) PSS solution (photochemically generated) with a scan rate 200 mV / s (e) PSS solution (photochemically generated) with a scan rate 200 mV (f) a magnification in the highlighted area to show the oxidation wave for the RC isomer scan rate 600 mV / s. Black arrows show the direction of the scan, the red arrows are used to point out important features of the CV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
3.6.2. **Comparative Electrochemical Studies for Compounds 2.17, 3.1, 3.2, 3.3 and 3.4**

Unlike organic compounds that are used for molecular electronics and photovoltaic applications where the HOMO-LUMO levels and gaps are of extreme importance as they have to match certain requirements, the HOMO-LUMO gap for the DTEs presented in this work is not crucial but the analysis might provide insights into the series.

The onset of the oxidation waves for both isomers are given in Table 3.27 and it can be seen that the oxidation processes for the ring–opened isomers 3.1o, 3.2o, 3.3o and 3.4o occur at higher potentials than for the corresponding ring–closed isomers. This is because the longer conjugation length of the closed-ring isomers generally leads to less positive potentials for oxidation. Furthermore, because the oxidation process involves the removal of an electron from HOMO (the highest occupied molecular orbital) and the reduction corresponds to the addition of an electron into LUMO (the lowest unoccupied molecular orbital), one can calculate the electrochemical gap using the information from the CV. Equations 3-7 and 3-8 relate the HOMO and LUMO energy values to the onset oxidation and reduction values. As it can be seen, the onset oxidation and reduction values are slightly different (lower) than the reported oxidation $E_p^a$ and $E_p^c$ due to the fact that they are estimated from the CV by taking the intersection point between the baseline (capacitive current) and the tangent line drawn to the rising current (Table 3.27). When comparing the values for the ring–open isomers, it is known that the EDG (CH$_3$ and t-Bu) decrease the HOMO-LUMO gap but they increase both the energy for HOMO and LUMO, the EWG (F) increase the HOMO-LUMO gap and they decreases both $E_{HOMO}$ and $E_{LUMO}$. When comparing the two isomers, the HOMO-LUMO gap decreases and $E_{HOMO}$ increases and $E_{LUMO}$ decreases.

If a substituent has an electron donating character (CH$_3$ and t-Bu), more electrons are available in the DTE system, which results in an increase in the energy level ($E_{HOMO}$). That means that less energy is required to remove an electron (during electrochemical oxidation) from the HOMO. The effect of the EDG on LUMO is the same but to a smaller extent. The $E_{LUMO}$ increases slower, because $E_{HOMO}$ increases more sharply than $E_{LUMO}$ that overall effect is a decrease in the energy HOMO-LUMO gap.
If a substituent has electron withdrawing character such as fluorine it should pull electron density from the framework of the DTE and decrease the $\pi$ electron density, hence making it more difficult to electrochemically oxidize the molecule, meaning a lower $E_{\text{HOMO}}$. Also in this case $E_{\text{LUMO}}$ decreases but the energy gap HOMO-LUMO increases.

Compound 3.4 has increased number of $\pi$ electrons, meaning that there are more electrons available for oxidation, hence it has a higher $E_{\text{HOMO}}$ when compared to compounds 2.17, 3.1, 3.2 and 3.3. The same as in the case of ED groups, the extended conjugation also affects slightly the $E_{\text{LUMO}}$ by lowering it, nevertheless the values are more pronounced as in the case of ED as the extended conjugation presents another factor stabilization through delocalization.

$$E_{\text{HOMO}} = -e \left( E_{\text{on}}^{\text{ox}} + 4.4 \right) \text{ (eV)}$$  \hspace{1cm} \text{eq 3-7}

$$E_{\text{LUMO}} = -e \left( E_{\text{on}}^{\text{red}} + 4.4 \right) \text{ (eV)}$$  \hspace{1cm} \text{eq 3-8}
Table 3.27. Selective electrochemical data for CH$_2$Cl$_2$ solutions of compounds 2.17, 3.1, 3.2, 3.3 and 3.4.

<table>
<thead>
<tr>
<th></th>
<th>Ep$_a$ / V</th>
<th>Ep$_c$ / V</th>
<th>$\Delta$E / V</th>
<th>$E_{ox}^{onset}$ / V</th>
<th>HOMO / eV</th>
<th>$E_{red}^{onset}$ / V</th>
<th>LUMO / eV</th>
<th>$E_g$ / eV</th>
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</thead>
<tbody>
<tr>
<td>2.17o</td>
<td>1.37 irr</td>
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<td>3.24</td>
<td>1.27</td>
<td>-5.67</td>
<td>-1.39</td>
<td>-3.01</td>
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<tr>
<td>2.17c</td>
<td>0.88 irr</td>
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<td>0.80</td>
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<td>-0.82</td>
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<td>1.62</td>
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<td>3.1o</td>
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<td>-1.71 irr</td>
<td>2.85</td>
<td>1.06</td>
<td>-5.46</td>
<td>-1.46</td>
<td>-2.94</td>
<td>2.51</td>
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<tr>
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<td>-0.96</td>
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<tr>
<td>3.3o</td>
<td>1.60 irr</td>
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<tr>
<td>3.3c</td>
<td>0.95 irr</td>
<td>-0.88 irr</td>
<td>1.86</td>
<td>0.93</td>
<td>-5.33</td>
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<td>-2.94</td>
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<tr>
<td>3.4c</td>
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<td>1.60</td>
<td>0.68</td>
<td>-5.08</td>
<td>-0.85</td>
<td>-3.55</td>
<td>1.53</td>
</tr>
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</table>

3.6.3. Electrochemical Stability, Multiple Electrochemical Cycles in Solution

Figure 3.34 presents multiple voltammetric cycles for compounds 2.17, 3.1, 3.2, 3.3 and 3.4. All the cycles are performed in CH$_2$Cl$_2$ and the concentrations for all compounds are similar.
Figure 3.34. Multiple cycles (CV) of compounds 2.17, 3.1, 3.2, 3.3 and 3.4 in CH$_2$Cl$_2$; the compound number is given on the top right corner of each voltammetric experiment. The single headed arrow shows the increase or decrease of the current. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.

Usually any increase in the peak currents for every cyclic voltammetric scan indicates the formation and growth of a polymeric material on the working electrode. For compound 2.17 the current for irreversible oxidation is increasing during all voltammetric cycles. This is suggestive of formation of a polymer on the electrode, hence compound
2.17 cannot be used in a device that requires multiple electrochemical cycling. Both compounds 3.1 and 3.2 show no increase in current during the voltammetric cycles indicating that the electropolymerization is minimal. The 20 cycles and respective 10 cycles for compound 3.1 and 3.2 do not suffice to assume that these compounds are fit for different devices and application but rather shows that by blocking the α positions with alkyl groups is a good approach in mitigating electrodegradation. Furthermore, the solvent and the electrolyte can have an important role in electropolymerization and most likely CH₂Cl₂ will not be used as a medium in various application. Hence caution should be taken when testing for the electrochemical properties of DTE if they are going to be used in various applications.

Compound 3.3 does not show the increase in current due to electropolymerization as does compound 2.17, and it does not show the oxidative reversibility shown by compounds 3.1 and 3.3. Usually the radical cation formed at the electrode can have three paths.⁸⁸

1. it will stay on the electrode and the polymer will grow (and the current should increase),
2. it will diffuse away from the electrode and react in solution (a decrease of current is noticed), or
3. it will polymerize to some extent on the electrode and if the oligomer is soluble, it will dissolve in solution hence, no polymer will be deposited on the electrode.

Given the fact that compound 3.3 has only α positions blocked with a relatively modest size atom (F) the β sites are left to electropolymerize. One can speculate that the β position (which are not sterically blocked) might electropolymerize. Also it is known that the polymerization of the fluorothiophene derivatives are harder to control and polymeric films are quite difficult to obtain as the oligomer diffuse in solution due to their solubility.⁸⁹ It is safe to assume that compound 3.3 undergoes electropolymerization at the β positions and the oligomers formed is soluble and is migrating in solution, hence no increase in current is seen. Compound 3.4 as expected undergoes the electropolymerization to almost same extent as compound 2.17.
3.7. Summary of Studies Done on DTE Series

In this work, four new compounds were prepared: 3.1, 3.2, 3.3 and 3.4. From the synthetic point of view it was shown that they can be prepared by relative facile methods. The compounds synthesized, 3.1, 3.2 and 3.3 do not electropolymerize. The alkyl groups in the α positions of terthiophene arms are great candidates in mitigating the electrodegradation. The photochemical properties (UV-Vis absorption and PSSs) of all the compounds are excellent and are comparable with the ones of parent compound 2.17.

Regarding the thermal stability of the ring–closed isomer in the dark: not all the substituents (3.1c, 3.2c and 3.3c), regardless of their size or electronic influence will decrease the stability of the ring–closed isomer (when compared with 2.17c) as believed previously. The reason for this particular behaviour is still not known but it can be speculated that the π–π stacking might play a role and that there is a correlation between the calculated distance between the reactive carbon atoms and the stability of the ring–closed form.

By extending the conjugation (3.4c) there was a relative high decrease in stability of the ring-closed form in the dark, most probably due to the better stabilization of the biradical intermediate.

The DFT calculations are useful to a certain point, as only will predict the stability of the ring closed isomers in the dark only as a bigger picture. Finer predictions such as stability of one particular ring closed isomer of $t_{1/2} = \text{one day}$, versus the stability of another ring closed isomer with similar molecular structure of $t_{1/2} = \text{week}$ cannot be determined by calculating $\Delta E(C-O)$.

As an overview for the DFT calculations:

1. the length of the calculated σ bond photochemically generated places the terthiophene DTE(s) in the same category as compound 2.8c (i-Pr as internal group), and
2. is almost equal for all the compounds, hence it is not useful as a comparison tool within the series of compounds presented in this work.
The calculated $\Delta E(E_{RC}-E_{RO})$:

1. cannot be placed in the frame of previous results, and
2. shows no major difference and it cannot be used to explain the difference in stability within the series.

Although the achievements are modest they represent the beginning of logical design of DTE(s) that can undergo catalytic oxidative ring-opening.

### 3.8. Experimental

#### 3.8.1. Materials

All solvents used for synthesis were dried and degassed by passing them through steel columns containing activated alumina under nitrogen using an MBraun solvent purification system or were prepared by distillation using sodium benzophenone still. Solvents for PSS analysis were purchased from Cambridge Isotope Laboratories and used as received, but kept on freshly activated molecular sieves. Column chromatography was performed using silica gel 60 (230-400 mesh) purchased from Silicycle Inc. and solvents purchased from Aldrich, Caledon and Anachemia. $\text{Bu}_4\text{NPF}_6$, was recrystallized three times from ethanol and dried in vacuo at 110 °C for 3 days and kept in a desiccator until used. 2,3,5-Tribromothiophene and 2-bromo-5-methylthiophene were purchased from Matrix Scientific. $\text{Pd(dppf)Cl}_2\cdot\text{CH}_2\text{Cl}_2$ was purchased from Strem Chemicals. Acetonitrile used in CV experiments was packed under nitrogen in a sure seal container from EMD Chemicals. Octafluorocyclopentene was purchased from SynQuest laboratories. All the other reagents were purchased from Aldrich. All the final compounds (DTEs) were dried before the electrochemical experiments using Abderhalden's drying pistol and $\text{P}_2\text{O}_5$ as drying reagent (Figure 3.35). The procedures for synthesizing compound 3.5, 3.6, and 3.1o were reported previously.¹
3.8.2. Instrumentation

$^1$H NMR and $^{13}$C NMR characterisations were performed on AVANCE III 400 MHz instrument operating at 400.13 MHz for $^1$H NMR and 100.61 MHz for $^{13}$C NMR. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in Hertz. UV-vis absorption spectroscopy measurements were performed using a Varian Cary 300 Bio spectrometer.

High resolution mass spectrometry measurements were performed at Simon University by Mr. Hongwen Chen on a Agilent 6210 TOF LC/MS instrument. Melting point apparatus used are Gallenkamp and Fisher-Johns and are not corrected. FT-IR measurements were performed using a Nicolet Nexus 670 instrument.

3.8.3. Photochemistry

All ring-closing reactions were carried out using the light source from a lamp used for visualising TLC plates at 312 nm (Spectroline E series, 470 W / cm²). The
ring–opening reactions were carried out using the light of a 300-W halogen photo-optic source passed through a 434 nm cut-off filter to eliminate higher energy light. All ring–closing and ring–opening reactions (photochemical) were carried out in dry and deoxygenated solvents. The solvents were deoxygenated by purging the respective solutions with nitrogen or argon for 10 minutes. The PSS studies were accomplished by $^1$H NMR spectroscopy and were performed in standard pyrex NMR tubes.

3.8.4. **Thermal Studies for Kinetic Evaluation**

Stock solutions of ring–open isomers were prepared in deoxygenated decane. From the stock solution, triplicate samples were prepared in quartz cuvettes (1 cm path). The quartz cuvettes were irradiated with UV light (365 nm) until the PSS was reached. The cuvettes were inserted into a Peltier temperature regulated multi-cell chamber and were allowed to equilibrate for 3 minutes at the desired temperature. Thermal ring–opening was monitored by the decrease in absorbance of the maximum visible absorbance wavelength of the ring–closed form as function of time.

3.8.5. **Electrochemical Studies**

**Cyclic Voltammetry**

Cyclic voltammetry was performed using a Pine AFCBP1 bipotentiostat. The electrochemical setup consisted of a four neck flame dried round bottom flask equipped with a Pt (3 mm) working electrode, a silver wire reference electrode (RE) and a coiled Pt wire counterelectrode (CE). The CE was separated from the bulk solution using a fritted glass tube. At the beginning of each experiment, the Pt coil was torched with a propane flame. The working electrode (WE) electrode was polished sequentially with 5 mm, 3 mm and 1 mm diamond paste followed by sonication in deionised water (10 minutes) and ethanol (10 minutes). In between the polishing with different sizes of diamond paste, the WE was washed thoroughly with distilled water. Stock solutions were prepared containing the desired compounds ($10^{-3}$ M) and the electrolyte Bu$_4$NPF$_6$ ($10^{-1}$ M). The solution in the electrochemical cell was changed frequently to ensure its freshness and the WE was cleaned with a Kimwipe tissue in between each scan. All samples were dissolved in deoxygenated solvent and maintained under a positive pressure of nitrogen for the duration of the experiment. All the peak potentials were
referenced using ferrocene as an internal standard at the end of each experiment
\( (E_{\text{ferrocene}} / \text{ferrocenium} = 475 \text{ mV vs SCE}) \). Because two solvents were used each one has its
one formal potential ferrocene couple vs SCE : \( E_{\text{acetonitrile}} = 0.40 \text{ V} \) and \( E_{\text{dichloromethane}} = 0.46 \text{ V} \).  

Electrolysis

**General procedure for the electrochemical triggered ring–opening reaction.**
A flame dried round-bottom flask containing a solution of the analyte at PSS (10\(^{-3}\) M) and
Bu\(_4\)NPF\(_6\) (10\(^{-1}\) M) was subjected to a fixed potential (as determined by CV, 100 mV more
anodic then the oxidation potential of the ring–closed isomer) using a Pt mesh working
electrode for 10 minutes. As a counter electrode Pt wire was used and as a reference
electrode a silver wire was used. The solution was stirred with a magnetic bar and
nitrogen or argon bubbled through the entire time of the experiment. The process was
monitored by \(^1\)H NMR spectroscopy.

### 3.8.6. **Synthesis and Characterization Data**

**Synthesis of compound 3.1o: 1,2-bis(2,5-bis(5-methyl-2-thienyl)3-thienyl)hexafluorocyclopent-1-ene.**
A flame dried 100 mL round bottom flask was charged with a yellow solution of 3-bromo-5,5’-dimethyl-2,2’,5,2”-terthiophene, (1.409 g, 3.98 mmol) (compound 3.6) in anhydrous ether (100 mL) and cooled to -40°C using a dry ice/acetone bath. The reaction mixture was treated with \( n \)-Butyllithium (\( n \)-BuLi) (1.7 mL of a 2.5 M solution in pentane, 4.25 mmol) dropwise under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 30 min and a yellow precipitate formed. Octafluorocyclopentene (0.42 g, 0.26 mL, 2 mmol) was added in one portion using a gas tight syringe previously cooled on a block of dry ice for 5 min. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction mixture was
allowed to warm to room temperature and stirred for 1 h. The reaction was quenched by pouring the contents of the round bottom flask into a solution of 5% HCl (20 mL). The organic layer was separated and set aside. The aqueous layer was extracted with diethyl ether (2 x 20 mL). The organic layers were combined and washed with water (50 mL), brine (50 mL), dried over MgSO$_4$ and filtered. The solvent was evaporated under reduced pressure and the crude brown oil was purified using column chromatography silica / 100% hexanes yielding 589 mg of pure product as yellow crystalline product.

Yield: 41%.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.84 (d, J = 3.5 Hz, 1H), 6.66 – 6.60 (m, 1H), 6.46 (d, J = 3.5 Hz, 1H), 6.44 (dd, J = 1.1 , 3.5 Hz, 1H), 6.31 (s, 1H), 2.47 (d, J = 0.8 Hz, 3H), 2.18 (d, J = 0.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.2, 139.7, 137.2, 135.7, 134.0, 130.7, 126.2, 126.0, 125.9, 124.2, 123.8, 122.8, 15.4, 15.1 (14 signals found out of 17).

**Synthesis of ring-closed isomer 3.1c.** The ring-open isomer was dried on a drying pistol having as drying reagent P$_2$O$_5$ and as heating solvent CH$_3$CN for 15 h. Photochemical ring-closed of (3.1c): A standard pyrex NMR tube was charged with 1 mL CDCl$_3$ solution containing the dried ring-opened isomer (1.6 mg) 3.1o. The solution was purged with argon for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 1 min intervals and the photoconversion was periodically monitored by $^1$H NMR spectroscopy. At this concentration approximately 20 minutes of irradiation were required to reach the photostationary state, which consisted of 73 % ring-closed isomer. The ring-closed isomer was not separated from the ring-opened isomer. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, J = 3.7 Hz, 1H), 7.01 (d, J = 3.7 Hz, 1H), 6.67 (dd, J = 1.1, 3.7 Hz, 1H), 6.53 – 6.47 (m, 1H), 6.40 (s, 1H), 2.47 (br. s, 3H), 2.36 (d, J = 0.9 Hz, 3H).
Synthesis of compound 3.2o: 1,2-bis(2,5-bis(5-tert-butyl-2-thienyl)3-thienyl)hexafluorocyclopent-1-ene. Compound 2.7o (0.0902 g, 0.013 mmol) was dissolved in CH₂Cl₂ 30 mL (SPS) in a round bottom flask equipped with a magnetic stirrer (the glassware was oven dried). The reaction mixture was kept under inert atmosphere and cooled down to 0 ºC with an ice and water mixture. Aluminium chloride (AlCl₃) (0.072 g, 0.052 mmol) was added to the reaction mixture. tert-Butyl chloride (0.0498 g, 0.052 mmol) was dissolved in 10 ml CH₂Cl₂ (SPS) and added to the reaction mixture with the aid of a gas tight syringe over 10 min. The reaction mixture changed the color from yellow to purple, as the time progressed the reaction mixture turned to brown. The reaction mixture was kept at 0 ºC for 30 min. The reaction mixture was quenched by pouring the contents of reaction mixture into a mixture of water and ice. The organic layer was extracted and set aside. The aqueous layer was washed 2 X 50 mL CH₂Cl₂. The organic layers were combined and washed with water (100 mL), followed by brine 100 mL. The organic layer was dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by flash-column chromatography (silica/100% hexanes Rf = 0.6) the desired compound with a purity of 90% (estimated by ¹H NMR spectroscopy) as a bright yellow powder. A second purification and a third purification were performed by flash column chromatography (mixture of 98% hexanes, 2 % CH₂Cl₂ / silica) yielding 0.0270 g of pure desired starting material. Yield 24 %.

M.p. 234 – 236 ºC; ¹H NMR (500 MHz, CDCl₃) δ 6.83 (d, J = 3.6 Hz, 1H), 6.68 (d, J = 3.6 Hz, 1H), 6.43 (d, J = 3.5 Hz, 2H), 6.36 (s, 1H), 1.38 (d, J = 12.9 Hz, 9H), 1.18 (s, 9H).¹³C NMR (101 MHz, CDCl₃) δ 159.2, 157.4, 137.3, 133.1, 129.9, 125.6, 124.0, 123.4, 122.8, 122.2, 122.0, 109.8, 34.7, 34.6, 32.4, 32.1 (16 signals found out of 19); FT-IR 3101, 2961, 2865, 1460, 1025, 518 cm⁻¹; HRMS (ESI) Calcd for C₄₅H₄₆F₆S₆ (M⁺) (892.1829) found (M+H)⁺ 893.1892.
Synthesis of ring-closed isomer 3.2c. The ring-open isomer was dried on a drying pistol having as drying reagent phosphorus pentoxide (P₂O₅) and as solvent CHCl₃ for 3 days. A standard glass NMR tube was charged with 1 mL C₆D₆ solution containing the dried ring-open isomer (2.2 mg) 3.2o. The solution was purged with argon for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 1 min intervals and the photoconversion was periodically monitored by ¹H NMR spectroscopy. At this concentration approximately 20 min of irradiation were required to reach the photostationary state, which consisted of 85 % ring-closed isomer. The ring-closed isomer was not separated from the ring-open isomer.

¹H NMR (500 MHz, C₆D₆) δ 7.69 (d, J = 3.9 Hz, 1H), 6.68 (s, 1H), 6.65 (d, J = 3.8 Hz, 1H), 6.47 (d, J = 3.8 Hz, 1H), 6.21 (d, J = 3.8 Hz, 1H), 1.08 (s, 9H), 1.03 (s, 9H).

Synthesis of compound 3.3o: 1,2-bis(2,5-bis(5-fluoro-2-thienyl)3-thienyl)hexafluorocyclopent-1-ene. A flame dried round bottom flask and magnetic stirrer was charged with compound 3.7o (0.252 g, 0.26 mmol) dissolved in tetrahydrofuran (75 mL) from freshly distilled sodium/bezophenone still. The reaction mixture was kept under nitrogen atmosphere and cooled down to −78 °C (dry ice and acetone). n-Butyllithium (nBu-Li) (0.5 mL, 2.5 M solution in hexanes, 1.17 mmol) was
added to this mixture over a period of 7 min with a gas tight syringe. The reaction was allowed to mix at this temperature for 15 min. A solution of N-fluoro-N-(phenylsulfonyl) benzenesulfonylamide (0.380 g, 0.117 mmol) dissolved in dry THF (5 mL) was added at once with the aid with an air tight syringe. The reaction was mixed at this temperature for 1 h and then allowed to warm up to room temperature and mixed for 14 h. The reaction was quenched by pouring the reaction mixture into ammonium chloride (NH₄Cl) saturated solution (50 mL). The organic layer was extracted and put aside. The aqueous layer was washed with diethyl ether (50 mL). The organic layers were combined and washed with brine (50 mL) and dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by flash-column chromatography (silica/100% hexanes Rf = 0.7) afforded 16 mg of the desired compound as a yellow powder (2 purifications by flash chromatography were necessary in order to get the pure compound). Yield 9 %.

1H NMR (1H–19F coupled), 1H NMR (500 MHz, CDCl₃) δ 6.69 (t, J = 3.8 Hz, 1H), 6.44 (s, 1H), 6.42 (dd, J = 1.8, 4.0 Hz, 1H), 6.28 (t, J = 3.8 Hz, 1H), 6.22 (dd, J = 1.8, 4.0 Hz, 1H); 1H NMR 1H–19F decoupled (400 MHz, CDCl₃) δ 6.69 (d, J = 4.1 Hz, 1H), 6.44 (d, J = 4.9 Hz, 1H), 6.42 (d, J = 4.1 Hz, 1H), 6.31 – 6.26 (m, 1H), 6.22 (d, J = 4.0, Hz 1H). 19F NMR (470 MHz, CDCl₃) δ -110.73, -124.81, -124.82, -126.75, -130.41. 13C NMR (125 MHz, CDCl₃) δ 165.2, 163.9, 137.7, 135.2, 125.0, 124.0, 123.2, 122.9, 121.1, 121.0, 120.9, 108.3, 108.3, 108.2, 108.2 (15 signals). FT-IR 2999, 2987, 1423, 512 cm⁻¹; HRMS (ESI) Calcd for C₂₉H₁₀F₁₀S₆ (M)⁺ (739.8947) found (M+H)⁺ 793.8943.

Synthesis of ring–closed isomer 3.3c. A standard glass NMR tube was charged with 0.9 mL CH₂Cl₂ solution containing 2.5 mg of ring–open isomer 3.3o. The solution was purged with argon for few minutes (just enough not to evaporate the
solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 2 min intervals and the photoconversion was periodically monitored by $^1$H NMR spectroscopy. At this concentration approximately 17 min of irradiation were required to reach the photostationary state, which consisted of 70% ring-closed isomer. The ring-closed isomer was not separated from the ring-opened isomer. $^1$H NMR ($^1$H–$^{19}$F coupled) (400 MHz, CD$_2$Cl$_2$) δ 7.01 (t, J = 4.1 Hz, 1H), 6.96 (t, J = 4.0 Hz, 1H), 6.54 (dd, J = 1.7, 4.3 Hz, 1H), 6.46 (s, 1H), 6.31 (dd, J = 1.9, 4.3 Hz, 1H).

### Synthesis of compound 3.7o: 1,2-bis(2,5-bis(5-bromo-2-thienyl)3-thienyl)hexafluorocyclopent-1-ene.

A round bottom flask with magnetic stirrer was charged with compound 3.1o (1.726 g, 2.58 mmol) dissolved in a mixture of dichloromethane (50 mL) and acetic acid (400 mL). Br$_2$ (1.652 g, 10.3 mmol) was dissolved in 50 mL of acetic acid and transferred to the reaction mixture with the aid of a dropping funnel over a period of 1 h. The reaction was allowed to mix at room temperature for 15 h. At the end of this period the contents of the reaction flask was poured over a mixture of dichloromethane (50 mL) and water (200 mL). The organic layer was extracted and put aside. The aqueous layer was washed with dichloromethane (50 mL). The organic layers were combined and washed successively with water (4 X 200 mL), Na$_2$CO$_3$ solution (200 mL), brine (100 mL) and dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation yielding a yellow-greenish powder. Purification by flash-column chromatography (silica/mixture of hexanes 98% and CH$_2$Cl$_2$ 2%, R$_f$ = 0.7) afforded 1.549 g of the desired compound as a yellow-greenish powder (two purifications by flash chromatography were necessary in order to get the pure compound). Yield: 61%.

M.p. 235–237 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.98 (d, J = 3.9 Hz, 1H), 6.87 (d, J = 3.9 Hz, 1H), 6.76 (d, J = 3.8 Hz, 1H), 6.45 – 6.38 (m, 2H). $^{13}$C NMR (100 MHz,
CDCl₃ δ 137.4, 136.9, 134.7, 134.0, 130.8, 130.7, 126.7, 125.0, 124.8, 123.4, 114.3, 112.5 (12 C atoms found out of 14 C atoms). HRMS (ESI) Calcd for C₂₉H₁₀Br₄F₆S₆ (M)⁺ (979.5744) found (M+H)⁺ 983.5709 {2 X [⁷⁹ Br] and 2 X [⁸¹ Br]}

**Synthesis of ring–closed isomer 3.7c.** A standard pyrex NMR tube was charged with 1 mL CHCl₃ solution containing 4 mg of ring–open isomer 3.7o. The solution was purged with nitrogen for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 2 min intervals and the photoconversion was periodically monitored by ¹H NMR spectroscopy. At this concentration approximately 17 min of irradiation were required to reach the photostationary state, which consisted of 30 % ring–closed isomer. The ring-closed isomer was not separated from the ring–open isomer. ¹H NMR (500 MHz, CDCl₃) δ 7.06 (d, J = 4.0 Hz, 1H), 7.01 (d, J = 4.0 Hz, 1H), 6.83 (d, J = 4.1 Hz, 1H), 6.45 (d, J = 5.2 Hz, 1H). One doublet with the integration of 1 was not observed due to its overlap with a signal from the ring–open isomer at 6.98 ppm, but is consistent for a mixture of 30 % ring–closed isomer and 70 % ring–opened isomer.

![Image of molecule 3.8o with labels](image)

**Synthesis of compound 3.8o: 1,2-bis(5-(5-bromo-2-thienyl)-2-(2-thienyl)-3-thienyl)hexafluorocyclopent-1-ene.** A round bottom flask with magnetic stirrer was charged with compound 3.1o (2.010 g, 3.09 mmol) dissolved in a mixture of dichloromethane (75 mL) and acetic acid (300 mL). Br₂ (1.13 g, 7.02 mmol) was dissolved in 50 mL of acetic acid and transferred to the reaction mixture with the aid of a dropping funnel over a period of 1 h. The reaction was allowed to mix at room temperature for 15 h. At the end of this period the reaction mixture was poured over a mixture of dichloromethane (50 mL) and water (200 mL). The organic layer was
extracted and put aside. The aqueous layer was washed with dichloromethane (50 mL). The organic layers were combined and washed successively with water (4 X 200 mL), Na₂CO₃ solution (200 mL), brine (100 mL) and dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation yielding a yellow-greenish powder. Purification by flash-column chromatography (silica/mixture of hexanes 99% and dichloromethane 1%, Rf = 0.6) afforded 0.937 g of the desired compound as a yellow-greenish powder (two purifications by flash chromatography were necessary in order to get the pure compound). Yield: 38 %

M.p. 196–200 °C; ¹H NMR (500 MHz, CDCl₃) ¹H NMR (500 MHz, CDCl₃) δ 7.22 (dd, J = 1.0, 5.1 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.87 (dt, J = 4.6, 9.3 Hz, 1H), 6.83 (d, J = 3.8 Hz, 1H), 6.72 (dd, J = 1.0, 3.6 Hz, 1H), 6.32 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 137.4, 136.3, 136.2, 132.6, 127.9, 127.6, 126.6, 124.8, 124.45, 123.7, 112.0. Calcd for C₂₉H₁₂Br₂F₆S₆ (M)⁺ (823.7534) found (M+H)⁺ 826.7599 {1 X [⁷⁹Br] and 1 X [⁸¹Br]} intensity 100%, 2 X [⁷⁹Br] intensity ~ 60 % 824.7614, 2 X [⁸¹Br] intensity ~ 75% 828.7575.

**Synthesis of compound 3.9o.** Compound 3.9o was obtained along with compound 3.8o as a byproduct in the bromination reaction, being the last to elute form the column chromatography (silica/mixture of hexanes 99% and dichloromethane 1 %, Rf = 0.5).

¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, J = 1.4, 4.7 Hz, 1H), 7.20 (ddd, J = 1.1, 5.1, 16.1 Hz, 2H), 7.09 (dd, J = 1.0, 3.6 Hz, 1H), 7.04 (dd, J = 3.6, 5.1 Hz, 1H), 7.00 (d, J = 3.8 Hz, 1H), 6.87 (dt, J = 4.6, 9.1 Hz, 1H), 6.84 (dd, J = 3.7, 5.2 Hz, 2H), 6.76 – 6.70 (m, 2H), 6.39 (s, 1H), 6.33 (s, 1H).
Synthesis of compound 3.4o: 1,2-bis(5-(5-(2-thienyl)-2-thienyl))-2-(2-thienyl)-3-thienyl)hexafluorocyclopent-1-ene. 2-Bromothiophene (0.307 g, 1.90 mmol) was dissolved in anhydrous Et₂O (50 mL), treated with magnesium ribbon, freshly polished (0.25 g, 10 mmol). The reaction mixture refluxed on its own for 30 min. When the reflux stopped the reaction was heated to reflux for another 30 min under a nitrogen atmosphere. The heat source was removed and the reaction was allowed to cool down to room temperature for 30 min. The reaction mixture was cooled to 0°C (bath of ice and water) for 15 minutes when the catalyst Pd(dppf)Cl₂⋅CH₂Cl₂ (20 mg, 0.021 mmol) was added. Compound 3.8o (0.6026 g, 0.75 mmol) was dissolved in 25 mL of anhydrous Et₂O and added to the reaction mixture with a cannula over 5 min. The reaction was stirred at this temperature for 1 h, when the cooling bath was removed and allowed to stir at room temperature for 14 h. The reaction was quenched by pouring the contents of the round bottom flask over 20 mL of HCl solution (5 %). The aqueous layer was separated and extracted with Et₂O (2 X 50 mL). Organic layers were combined and washed with brine (50 mL), dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure and the crude was purified using column chromatography through silica / 80% hexanes and 20% CH₂Cl₂ yielding 0.2873 g of product as a yellow solid. Yield: 46 %

$^{1}$H NMR (600 MHz, CDCl₃)  δ 7.29 (dd, J = 4.5, 1.1 Hz, 1H, overlap with CHCl₃), 7.23 (ddd, J = 1.1, 4.3, 6.3 Hz, 2H), 7.11 (d, J = 3.7 Hz, 1H), 7.08 (dd, J = 3.6, 5.1 Hz, 1H), 7.00 (t, J = 3.5 Hz, 1H), 6.88 (dd, J = 3.5, 5.1 Hz, 1H), 6.75 (dd, J = 1.2, 3.5 Hz, 1H), 6.39 (s, 1H); $^{13}$C NMR (150 MHz, CDCl₃)  δ 137.01, 136.9, 135.7, 134.6, 134.6, 132.7, 128.0, 127.9, 127.6, 126.5, 124.9, 124.3, 124.0, 123.3 (13 out 17 signals); FT-IR 3074, 2942, 1423, 683, 466 cm⁻¹; HRMS (ESI) Calcd for C₃₇H₁₈Br₂F₆S₈ (M)$^+$ (831.9078) found (M+H)$^+$ 832.9167.
4. Benzothiophene DTE Derivatives as Candidates for Catalytic Oxidative Ring-Opening

4.1. Research objectives

Some of the compounds studied in Chapter 3, are not prone to electrodegradation (depending upon the substitution pattern) and have quite good photochemical properties (high photostationary states (PSS). On the other hand, they undergo moderate to fast thermal cycloreversion in the dark. The goal of the work presented in this chapter is to find the best electrochromic DTEs candidates that have the next ideal properties:

1. minimal cycloreversion in the dark,
2. minimal photodegradation, and if possible
3. different absorption spectra (as compared to compounds presented in Chapter 3).

Among the DTE derivatives, the benzothiophene compounds have three key properties:

1. they show almost no photochemical fatigue (Figure 2.3). (The reason for this stability is due to the absence of the hydrogen in the C-3 position of the central thiophene ring.) Therefore, the photochemical decomposition paths for the ring open isomer cannot take place (Scheme 2.4),
2. the ring-closed isomer 2.2c has an excellent stability in the dark. (It shows almost no thermal ring-opening upon storage in the dark for 6 months at 80 °C,) and
3. compound 2.2o has an absorption maxima of $\lambda_{\text{max}} = 258 \text{ nm}$ and its ring-closed form 2.2c has an $\lambda_{\text{max}} = 526 \text{ nm}$ (benzene). The internal substituents effect the
absorption spectrum of the ring–closed isomer minimally, due to the fact they are not part of conjugation (they are above and below the plane). On the other hand the substituents on the external positions dictate the absorption spectrum of the ring–closed form (Scheme 4.1). This is important in the context of the catalytic oxidative cycloreversion, where only the DTEs with internal aromatic substituents are electrochromic in the desired direction.

Benzothiophene DTE derivatives have the above mentioned benefits but they are known to electropolymerize. In Scheme 4.1 one of the positions susceptible to anodic polymerization is circled.\textsuperscript{92}

In the next sections are discussed the synthesis, the optical and electrochemical properties and the thermal stability of the ring–closed isomers in the dark of two compounds synthesized.
Scheme 4.1. Photochemical reaction of compound 2.2 and the general structure of a benzothiophene derivative DTE that is undergoing catalytic oxidative ring opening and the structures of the compounds synthesized 4.1 and 4.2.

4.2. Synthesis of compounds 4.1 and 4.2

The synthesis of compound 4.1 (Scheme 4.2) started by dibrominating the commercially available benzothiophene by a known procedure, thus compound 4.3 was obtained. By performing a Kumada coupling with a single equivalent of (5-methylthiophen-2-yl)magnesium bromide, compound 4.4 was obtained. Next a metal-halogen exchange with n-BuLi was employed, followed by treatment with octafluorocyclopentene.
Compound 4.1o was obtained as a pale yellow powder. Unlike previous cases presented in this work (Scheme 3-7) where the formation of the monosubstituted compound was the main reason for the lower yield, the synthesis of the benzothiophene derivatives present another factor in lowering the yield. In Scheme 4.3 is presented the path that the lithiated species is undergoing. Because copious amounts of “protonated” material were recovered, the first thought was that the reaction conditions are not anhydrous as required by the general procedure of lithiation (path i). Nevertheless, path ii is the most likely situation where there is a ring-opening reactions in situ followed by a cyclization upon workup yielding the “protonated” material. The best conditions for performing these type of reactions is a fast addition of n-BuLi as opposed to the precise titration of the starting material (bromide) with the organolithium reagent as required so far for the general DTE synthesis. The very precise monitoring of the temperature of the reaction is also important.
Compound 4.2 was synthesized in a similar fashion as compound 4.1 (Scheme 4.4). Suzuki coupling of the dibromide 4.3 with one equivalent of boronic acid afforded compound 4.5. Compound 4.5 was treated with n-BuLi and subsequently with octafluorocyclopentene and afforded compound 4.2 as a white powder.

**Scheme 4.3.** Proposed pathway of decomposition for the lithiated species.

**Scheme 4.4.** Synthesis of compound 4.2.

### 4.3. Photochemical Properties of Compounds 4.1 and 4.2

#### 4.3.1. Comparative Photostationary State Values for Compounds 4.1 and 4.2

Two important photochemical properties of compounds 4.1 and 4.2 are the PSS and the absorption spectra. Unlike the compounds presented in Chapter 3 that have good to excellent PSS, the benzothiophene derivatives present very modest values. Compound 4.1 has a PSS of 17% and compound 4.2 has a PSS slightly lower than 30%, according to $^1$H NMR spectra. Irradiation of solution of the colourless isomer with
UV light generates the corresponding coloured isomer (ring−closed form). The reason for this lower PSS is not yet know but some speculations can be made. The general mechanism of orbital correlation was presented in Chapter 2. Overall if a ground state molecule is irradiated with UV-light, it forms the excited state. In general the preferred path of excited ring−open isomer is to undergo cyclization, but this is not the only path of relaxation, for example fluorescence can a be a way of relaxation. Nevertheless the extent to which the ring−closed isomer is formed is important, as only the compounds with high PSS might be useful in different applications.

In this thesis the PSS of the photochemically induced ring−closing isomerisation reactions of DTEs are determined by comparing peak integrals of select proton resonances for both isomers. The ratio of peak integrals is directly proportional to the relative concentrations of each isomeric structure in that particular solvent. Given the fact that at room temperature the DTEs reported in this work do not undergo extensive thermal cycloreversion and given the short time scale of the experiment 30 minutes it is safe to assume that the results are only a function of the irradiation wavelength and of the competing ring−opening and ring−closing yields at the irradiation wavelength.

The substitution pattern can affect the path of a photoexcited photochromic compound, thus by synthesizing compound 4.2 (phenyl internal group) I was probing to see if another benzothiophene DTE with an aromatic group will have the same low photostationary state (as 4.1). Albeit compound 4.2 has a higher PSS (29%) it is still lower by DTEs standards. Further synthetic modifications are required in order to get a useful benzothiophene DTE. In Figure 4.1 are stacked the $^1$H NMR spectra of ring−opened isomers and their respective PSS solutions. The latter were obtained by irradiating the NMR pyrex tubes containing ring−open solutions with 313 nm hand held UV-lamp source. One can see that the peaks belonging to the ring−closed isomer (highlighted with red cycle) are barely visible when compared to the peaks from the ring open isomer.
Figure 4.1. Selected $^1$H NMR spectra (500 MHz) of a CDCl$_3$ solution from bottom to top: 4.1o (1.7 x 10$^{-3}$ M) before irradiation, after irradiation with 313 nm light for 25 minutes to produce the PSS (17 %). A CDCl$_3$ solution (2.0 x 10$^{-3}$ M) of 4.2o before irradiation, after irradiation with 313 nm light for 30 minutes to produce the PSS (29 %). Red arrows are signalling the appearance of the new peaks.

4.3.2. Comparative UV-Vis Studies for Compounds 4.1 and 4.2

Upon irradiation of the colourless solutions of ring–open isomers 4.1o and 4.2o with 313 nm light, the ring–closing reaction takes place and red solutions are formed that contain a mixture of the two isomers. In Figure 4.2(a) are the overlapped absorption spectra of the ring–open isomers 4.1o and 4.2o and in Figure 4.2(b) are the overlapped spectra for the PSS solutions.
Figure 4.2. UV-Vis absorption spectra of CH$_3$CN solutions of (a) ring open–isomers 4.1o and 4.2o (b) PSS solutions obtained by irradiation of the pure ring–open solutions with 313 nm light source.

The electronic absorption spectra of the colourless forms show one strong absorption band around 300 nm that is due to the $\pi$-$\pi^*$ electronic transition. Upon photochemical cyclization, the conjugation becomes longer and the absorption is shifted into the visible region. Selective photochemical data is given in Table 4.1.

Table 4.1. Selective photochemical data in CH$_3$CN.

<table>
<thead>
<tr>
<th>entry</th>
<th>CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>RC</td>
</tr>
<tr>
<td>$\lambda_{max}$ / nm</td>
<td>$\lambda_{max}$ / nm</td>
</tr>
<tr>
<td>4.1</td>
<td>&lt;250, 303, 360(s), 556</td>
</tr>
<tr>
<td>4.2</td>
<td>&lt;250, 274, 368, 460,530</td>
</tr>
</tbody>
</table>

4.4. Comparative Electrochemical Data for Compounds 4.1 and 4.2

Figure 4.3 presents the cyclic voltammograms (CV) for the ring–open isomer 4.1o and the PSS solution of compound 4.1 (obtained by irradiation with 313 nm light). The colourless form (4.1o) has one irreversible oxidation wave due to the anodic electropolymerization as expected for the unprotected “benzothiophenes” and one
irreversible reduction. One would have expected that the two CVs to be different. Due to the fact that the photochemical ring–closing yields only a small amount of the ring–closed isomer the oxidation and the reduction peaks are not visible regardless of the scan rate. Furthermore, it is expected that the oxidation wave of the ring–closed isomer to be very small, which is characteristic for the electrocatalytic ring–opening reactions, and typical for DTE derivatives bearing aromatic rings on the "internal" positions. The potential that triggers the catalytic oxidative ring–opening reaction was found by trial and error to be 1.0 V. The ring opening reaction was monitored by $^1$H NMR spectroscopy, which revealed that the electrochemical cycloreversion is taking place. In Figure 4.5(a) are displayed the different stages of electrochemically driven reaction.

![Figure 4.3](image)

**Figure 4.3.** CVs of CH$_3$CN solutions (1.1 X 10$^{-3}$ M) of (a) compound 4.1o (b) PSS obtained by irradiating ring–open solution with 313 nm source light (both CVs) are done with a sweep rate of 100 mV / s). A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.

As in the case for compound 4.1, compound 4.2 showed some degree of electropolymerization. The oxidation wave is not reversible, (Figure 4.4). Furthermore, the oxidation wave of the ring–closed isomer was not distinguishable above the capacitive current in the CV due to the low concentration of this isomer formed.
photochemically and to the fact that in general this peak is hardly visible at best of times. Nevertheless, this compound undergoes catalytic oxidative ring-opening if a potential greater than 1.1 V is applied. The electrochemically induced cycloreversion was monitored by $^1$H NMR spectroscopy. Figure 4.5(b) are displays the different stages of electrochemically driven reaction for compound 4.2c.

**Figure 4.4.** CVs of CH$_3$CN solutions (1 x $10^{-3}$ M) (a) of compound 4.2o with a sweep rate of 100 mV / s (b) PSS (obtained by irradiation with 313 nm light for 30 minutes) solution with a sweep rate of 200 mV/s. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
4.5. Thermal Stabilities of Compounds 4.1c and 4.2c in the Dark

Compounds 4.1c and 4.2c show remarkable stability in the dark. For example, if deuterated toluene solutions are incubated at 80°C for three days no thermal dark back reaction is observed by NMR spectroscopy. If the NMR tubes are incubated at 100°C, the ring-opening is minimal. Compound 4.1c has a 3% ring-opening and compound
4.2c shows a 7% ring-opening upon heating at 100 °C for two days, as determined by ¹H NMR spectroscopy. The reason for this much better thermal stability in the dark might be due to lower capability of stabilization of the diradical like character of the intermediate of the benzothiophene DTE derivatives when compared to the compounds presented in Chapter 3. Further measurements at other temperatures were not attempted. Therefore, values of the half live and activation energy cannot be reported.

4.6. Summary

In this chapter the synthesis of the first benzothiophene DTEs that undergo catalytic oxidative ring-opening reaction was presented. Benzothiophenes DTE derivatives have a great potential to be used in various devices because of their great photochemical inertness and thermal stability of the colored form in the dark. However, due to their very low PSS and to the electrodegradation, the project needs further investigation. Below, the key features of the compounds presented in this work are tabulated and together with standard compound 2.2 and with compound 2.17 in order to place the results into context of the previous work.
<table>
<thead>
<tr>
<th>compound</th>
<th>photochemical properties / PSS (^a)</th>
<th>observations regarding PSS</th>
<th>compound</th>
<th>thermal dark reaction (^b)</th>
<th>observations regarding thermal cycloreversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>17 %</td>
<td>benzothiophene DTEs have lower PSS than their terthiophene counterparts</td>
<td>2.17c</td>
<td>(t_{1/2} = 17) minutes at 100 °C</td>
<td>the dark reaction in the case of benzothiophene DTEs is much slower than in their terthiophene counterparts</td>
</tr>
<tr>
<td>4.2</td>
<td>30 %</td>
<td>substitution at C-2 of benzothiophenes with aromatic groups decreases the PSS further</td>
<td>4.2c</td>
<td>7 % cycloreversion after 2 days at 100 °C</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>45 %</td>
<td></td>
<td>4.1c</td>
<td>3 % cycloreversion after 2 days at 100 °C</td>
<td></td>
</tr>
<tr>
<td>2.17</td>
<td>80 %</td>
<td></td>
<td>2.2c</td>
<td>no cycloreversion observed after 6 months at 80 °C</td>
<td></td>
</tr>
</tbody>
</table>

Notes: a) PSS experiments were performed in different solvents, b) same is true for cycloreversion reactions
4.6.1. Future Directions Regarding Benzothiophene DTEs

Better versions of benzothiophene derivatives can be designed that might have higher PSS and one way is to synthesize asymmetrical compounds of the type presented in Figure 4.6. The structure on the left (A) will have the advantage of being even more stable in the dark regarding the cycloreversion, but on the other hand not much it is known about the efficiency of the electrocatalytic ring-opening in such asymmetric systems. The structure on the right (B) also incorporates a terthiophene moiety might have the advantage of increasing the PSS, but it will decrease the stability in the dark of the ring-closed form, although to what extent is harder to predict. Nevertheless, it is quite difficult to speculate to what extend the PSS will be increased and caution needs to be taken before the design of such type of molecules. It might be useful looking into the intermediates of the photochemical ring-closing, the necessary energy from the ground state to the excited state and the possible path (paths) of the excited species with the help of TD-DFT (time-dependent DFT). Furthermore, no research was attempted into looking what influence might have the blocking the electropolymerizable positions.

Figure 4.6. Proposed molecular architecture for asymmetric benzothiophene DTE derivatives that might posses better PSS.
4.7. Experimental

4.7.1. Materials

All solvents used for synthesis were dried and degassed by using the Na/benzophenone drying still. Solvents for PSS analysis were purchased from Cambridge Isotope Laboratories and used as received, but kept on freshly activated molecular sieves. Column chromatography was performed using silica gel 60 (230-400 mesh) purchased from Silicycle Inc. and solvents purchased from Aldrich. Bu₄NPF₆ was purchased form Fluka Analytical and recrystalized three times from ethanol and dried in vacuo at 110 °C for three days and kept in a desiccator until used. 2-Bromo-5-methylthiophene was purchased from Matrix Scientific. Pd(PPh₃)₄ and Pd(dppf)Cl₂·CH₂Cl₂ were purchased from Strem Chemicals. Acetonitrile used in the CV experiments was packed under nitrogen in a sure seal container from EMD Chemicals. Octafluorocyclopentene was purchased form SynQuest laboratories. All the other reagents were purchased from Aldrich.

4.7.2. Instrumentation

¹H NMR and ¹³C NMR characterisations were performed on AVANCE III 400 MHz instrument operating at 400.13 MHz for ¹H NMR and 100.61 MHz for ¹³C NMR. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in Hertz. UV-vis absorption spectroscopy measurements were performed using a Varian Cary 300 Bio spectrometer instrument.

Microanalysis (C, H, N) were performed at Simon Fraser University by Mr. Mulyk Paul on a Carlo Erba EA 1110 CHN Elemental Analyser. Low resolution mass spectrometry measurements were performed at Simon University by Mr. Hongwen Chen on a Agilent 6210 TOF LC/MS instrument. Melting point apparatuses used are Gallenkamp and Fisher-Johns.
4.7.3. **Photochemistry**

All ring-closing reactions were carried out using the light source from a lamp used for visualising TLC plates at 312 nm (Spectroline E series, 470 W/cm²). The ring-opening reactions were carried out using the light of a 300-W halogen photo-optic source passed through a 434 nm cut-off filter to eliminate higher energy light. All ring-closing and ring-opening reactions (photochemical) were carried in dry and deoxygenated solvents. The solvents were deoxygenated by purging the respective solutions with nitrogen or argon for 20 minutes. The PSS studies were accomplished by ¹H NMR spectroscopy and were performed in standard pyrex NMR tubes.

4.7.4. **Electrochemical Studies**

**Cyclic Voltammetry**

Cyclic voltammetry was performed using a Pine AFCBP1 bipotentiostat. The electrochemical cell consisted of a four neck flame dried round bottom flask. The electrodes used are: Pt (3 mm) working electrode, RE silver wire and as a CE a coiled Pt wire. The counter electrode was separated from the bulk solution with the aid of a glass tube with a fritted bottom. At the beginning of each experiment the electrodes were thoroughly cleaned as explained in section 3.9.5.1. Stock solutions were prepared containing the desired compounds with a concentration of 10⁻³ M and the electrolyte Bu₄NPF₆ with a concentration of 10⁻¹ M. The solution in the electrochemical cell was changed frequently to assure its freshness and the WE was cleaned with a Kimwipe tissue in between each scan. All samples were dissolved in deoxygenated solvent and maintained under a positive pressure of nitrogen for the entire time of the experiment. All the peak potentials were referenced using ferrocene as an internal standard at the end of each experiment (E₆₇₅ / ferrocenium = 475 mV vs SCE).

**Electrolysis**

General procedure for the electrochemical triggered ring-opening reaction. A flame dried round bottom flask containing a solution of the compound at PSS, (10⁻³ M) and Bu₄NPF₆ (10⁻¹ M) was subjected to a fixed potential, using a Pt mesh working electrode for 10 minutes. The fixed potential was not determined form the CV as the concentration of the RC isomer as to low and it was a trial and error until the right
potential was found. As a counter electrode Pt wire was used and as a reference electrode a silver wire was used. The solution was stirred with a magnetic bar and nitrogen or argon bubbled through the entire time of the experiment. The ring–opening was monitored by $^1$H NMR spectroscopy.

### 4.7.5. Experimental Data

![Chemical Structure](image)

#### Synthesis of compound 4.4: 3-bromo-2-(5-methyl-2-thiophenyl)benzo[b]thiophene.

A solution of 2-bromo-5-methylthiophene (4.1839 g, 23.7 mmol) was dissolved in anhydrous Et$_2$O (100 mL), treated with magnesium ribbon freshly polished (2.410 g, 100 mmol) the reaction mixture refluxed on its own for 20 min. When reflux stopped the reaction was heated to reflux for 30 min under a nitrogen atmosphere. The heat source was removed and the reaction was allowed to cool down to room temperature for 30 min. The reaction mixture was cooled to 0 °C for 15 min when the catalyst Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (18 mg, 0.02mmol) was added. 2,3-Dibromobenzo[b]thiophene (6.930g, 23.7 mmol) was dissolved in 25 mL of anhydrous Et$_2$O and added to the reaction mixture with a cannula over 10 minutes. The reaction was stirred at this temperature for 1 h, when the cooling bath was removed and allowed to stir at room temperature for 14 h. The reaction was quenched by pouring the contents of the round bottom flask over 200 mL of HCl solution (5 %). The aqueous layer was separated and extracted with Et$_2$O (2 X 100 mL). Organic layers were combined and washed with brine (50 mL), dried over MgSO$_4$ and filtered. The solvent was evaporated under reduced pressure and the crude was purified using column chromatography through silica gel and hexanes (100%) yielding 4.8210 g of product as a white solid.

Yield: 67 %

M. p. 87 - 92 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.31 (m, 2H), 6.80 – 6.75 (m, 1H), 2.53 (d, J = 0.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.3, 139.4, 136.5, 132.6, 132.3, 128.1,
125.6, 125.5, 125.3, 121.9, 103.9, 15.4 (13 carbon atoms found out of 13); FT-IR
3061, 2916, 2853, 1509, 1222, 480 cm\(^{-1}\); HRMS (APCI) Calcd for C\(_{13}\)H\(_9\)BrS\(_2\) M\(^+\)
(307.9329) found 306.9256 \([^{79}\text{Br}]\) and 307.9322 \([^{81}\text{Br}]\); Anal. Calcd for C\(_{13}\)H\(_9\)BrS\(_2\): C = 50.49, H = 2.93, S = 20.74. Found C = 50.69, H= 3.03, S = 20.58.

**Synthesis of compound 4.1o: 1,2-bis(2-(5-methyl-2-thiophenyl)-3-benzo[b]thiophenyl)-hexafluorocyclopent-1-ene.** A flame dried 100 mL round bottom flask was charged with a colourless solution of 3-bromo-2-(5-methylthiophen-2-yl)benzo[b]thiophene (0.989 g, 3.21 mmol) (compound 4.4) in anhydrous tetrahydrofuran (100 mL) and cooled to -78 °C using a saturated dry ice / acetone bath. The solution was treated with n-Butyllithium (n-BuLi) (1.5 mL of 2.5 M solution 3.75 mmol) over the course of 5 min. The resulting dark red solution was stirred at -78 °C for another 2 min. Octafluorocyclopentene (0.340 g, 0.22 mL, 1.6 mmol) was rapidly added using a single use syringe and single use needle, previously cooled (in their own package) on a block of dry ice. The resulting dark solution was left stirring at -78 °C for 1 h, at which point was removed from cooling bath and left to stir at room temperature for 2 h. The reaction was quenched with saturated NH\(_4\)Cl (25 mL) and the layers were separated. The aqueous layer was extracted with Et\(_2\)O (2 x 50 mL). The organic layers were combined, washed with water (100 mL) and then brine (50 mL), dried over MgSO\(_4\) and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by flash-column chromatography afforded 271 mg of the desired compound as a yellow powder (recrystallized at room temperature from equal parts of hexanes / dichloromethane).

Yield: 27 %.

M. p. 221 – 224 °C (with slight decomposition); \(^1\)H NMR; (400 MHz, CDCl\(_3\)) \(\delta\)
7.58 (d, J = 8.0 Hz, 1H), 7.21 (ddd, J = 1.6, 6.7, 8.1 Hz, 1H), 7.12 – 7.01 (m, 2H), 6.53
(d, \( J = 3.5 \) Hz, 1H), 6.36 – 6.30 (m, 1H), 2.19 (d, \( J = 0.8 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 142.9, 138.7, 138.6, 138.3, 131.0, 127.4, 126.3, 124.3, 123.8, 123.3, 123.2, 121.1, 118.5, 118.4, 15.1 (14 out of 16 signals found); FT-IR 3061, 2925, 2859, 1431, 1279, 797, 582 cm\(^{-1}\); LRMS (ESI) Calcd for [M]** 632 found [M+1]** 633; Anal. Calcd. for C\(_{31}\)H\(_{18}\)F\(_6\)S\(_4\): C = 58.85, H = 2.87, S = 20.27. Found C = 58.71, H = 2.91, S = 20.62

Photochemical ring–closed 4.1c. The ring–open isomer was dried on a drying pistol having as drying reagent Phosphorus pentoxide (P\(_2\)O\(_5\)) and as solvent CHCl\(_3\) for 2 days. A standard glass NMR tube was charged with 1 mL CDCl\(_3\) solution containing the freshly dried ring–opened isomer (1.5 mg) 4.1o. The solution was purged with Ar for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 313 nm light from a handheld TLC visualization lamp for 2 min intervals and the photoconversion was periodically monitored by \(^1\)H NMR spectroscopy. At this concentration approximately 20 min of irradiation were required to reach the photostationary state, which consisted of 17 % ring-closed isomer 4.1c. The ring-closed isomer was not purified.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.93 (d, \( J = 8.3 \) Hz, 1H), 7.17 (s, 1H), 7.12 (d, \( J = 2.9 \) Hz, 1H), 6.42 (dd, \( J = 1.1, 3.7 \) Hz, 1H), 2.28 (d, \( J = 1.0 \) Hz, 3H) (only 7 protons observed out of 9, the other two are overlapped with the signal from the ring–open isomer).
Synthesis of compound 4.5: 3-bromo-2-phenylbenzo[b]thiophene. In a 3-neck round bottom flask equipped with a jacketed condenser and a magnetic stirrer were added together: phenylboronic acid (5.3 g, 4.3 mmol), 2,3-dibromobenzo[b]thiophene (9.200 g, 4.3 mmol), Na$_2$CO$_3$ (5.9 g, 4.3 mmol), EtOH (5 mL), toluene (200 mL), water (75 mL). The reaction mixture was refluxed for an hour while purged with nitrogen. After one hour the catalyst Pd(PPh$_3$)$_4$ (0.428 g, 0.37 mmol) was added to the reaction mixture. The reaction mixture was refluxed under nitrogen for 20 h. The heat source was removed and the reaction mixture was allowed to cool down at room temperature for an hour, the layers were separated and aqueous layer was extracted with Et$_2$O (3 x 100 mL). The combined organic layers were washed with water (200 mL), brine (200 mL), dried over MgSO$_4$ and filtered. The solvent was removed under reduced pressure and the crude (dark brown oil) was purified using column chromatography (silica/hexanes) yielding a white powder as the desired compound (Rf = 0.4) 5.3 g. Yield: 42 %.

M.p. 57–58 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.84 – 7.73 (m, 3H), 7.50 -7.38 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.2, 138.26, 137.7, 133.1, 129.7, 128.8, 128.6, 125.5, 125.3, 123.7, 122.2, 105.0. (12 carbon atoms out of 14 found, 2C atoms magnetically equivalent)

Synthesis of compound 4.2o: 1,2-bis(2-phenyl-3-benzo[b]thiophenyl)hexafluorocyclopent-1-ene. A flame dried 100 mL round bottom flask was charged with a colourless solution of 3-bromo-2-phenylbenzo[b]thiophene (1.2309 g, 4.24 mmol) (compound 4.2o) in anhydrous tetrahydrofuran (100 mL) cooled to -78 °C using a dry ice / acetone bath. The solution was treated with n-Butyllithium (n-BuLi) (1.7 mL of 2.5 M solutin in pentane 4.3 mmol) over the course of 5 min. The resulting dark red solution was stirred at – 78 °C for another 5 minutes until the majority of the material reacted as monitored by TLC (silica/hexanes). Octafluorocyclopentene (0.44 g, 0.28 mL, 2.10 mmol) was rapidly added using a single use syringe and single
use needle, previously cooled (in their own package) on a block of dry ice. The resulting dark solution was left stirring at -78 °C for 1 h, at which point was removed from cooling bath and left to stir at room temperature for 4 h. The reaction was quenched with saturated NH₄Cl (25 mL) and the layers were separated. The aqueous layer was extracted with Et₂O (2 x 50 mL). The organic layers were combined, washed with water (100 mL) and then brine (50 mL), dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by flash-column chromatography afforded 422 mg of the desired compound as a yellow powder (recrystallized at room temperature from of hexanes. Yield: 34%.

M. p 221 – 224 °C (with slight decomposition); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.0 Hz, 1H), 7.19 – 7.10 (m, 1H), 6.99 (ddd, J = 1.7, 4.1, 7.1 Hz, 1H), 6.94 (ddd, J = 1.1, 7.2, 8.2 Hz, 1H), 6.89 – 6.76 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 138.5, 138.2, 132.4, 129.2, 128.3, 128.2, 125.0, 123.9, 123.2, 123.1, 121.1, 118.60; FT-IR 3074, 3036, 2919, 1453, 1103, 736, 492 cm⁻¹; HRMS (APCI) calcd for C₃₃H₁₈F₆S₂ (592.0754) found 592.0751 (M)⁺;

![4.2c](image)

**Synthesis of ring-closed isomer 4.2c.** The ring-open isomer was dried on a drying pistol having as drying reagent P₂O₅ and as a heating solvent CHCl₃ for 16 h. A standard glass NMR tube was charged with 1 mL CDCl₃ solution containing 1.0 mg of ring-opened isomer 4.2o. The solution was purged with Ar for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 313 nm light from a handheld TLC visualization lamp for 2 min intervals and the photoconversion was periodically monitored by ¹H NMR spectroscopy. At this concentration approximately 25 minutes of irradiation were required to reach the photostationary state, which consisted of 29% ring-closed isomer. The ring-closed isomer was not separated from the ring-opened isomer. Only two signals belonging to the ring-closed isomer were not
overlapping with the ring-opened isomer $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 8.2$ Hz, 1H), 7.79 – 7.74 (m, 1H)
5. Fully Electrochromic and Photochromic DTEs

The development of a bidirectional electrochromic and photochromic DTE is very useful as this type of hybrid molecule will be readily used in applications such as optical filtering and display technologies. The appeal is due to the multiple factors described in Chapter 1. Just to review few of them: large spectral difference between the two forms (ring–open isomer is usually colourless and the ring–closed isomer is coloured), facile synthesis and processability.

In Chapters 3 and 4 the issues associated with the bidirectional photochromic and unidirectional electrochromic (catalytic oxidative ring–opening) for two particular classes of DTEs (terthiophenes and benzothiophenes derivatives) were addressed. The work presented in this chapter was aimed to incorporate the knowledge acquired previously regarding the electropolymerization and thermal dark reaction in the context of a fully electrochromic and photochromic DTE. In this chapter, a compound is referred to as fully photo-electrochromic when its isomerisation, regardless of direction and can be achieved either by light or by applying an electrical potential.

The two molecular structural requirements for a DTE to show electrochromic and photochromic behaviour are: external pyridinium groups for the reductive triggered cyclization and aromatic groups as internal groups for the oxidative ring–opening reactions (Figure 5.1).
Figure 5.1. Structures of unidirectional \((2.18o^{2+} \text{ and } 2.17)\)^50.9 and bidirectional \((1.4o^{2+})\)^29 electrochromic DTEs. Structural requirements are circled in each case and the counteranions are omitted for clarity (\(PF_6^{-}\)).

Although DTEs present great advantages as outlined previously (Chapter 2, the work of Gorodetsky et al.),^29 they are still limited by two major factors:

1. The electrochromic reactions are unidirectional and only one of the two reactions, ring–closing or ring–opening can be triggered using electron transfer as a stimulus for the majority of compounds.

2. There are only two examples of fully bidirectional (electrochromic and photochromic) DTEs compounds \((2.18^{2+} \text{ and } 1.4^{2+})\) but they have shortcomings, thus deeming them unusable in a useful marketable device:
   - The ring–closed form is thermally unstable,
   - Both isomers are prone to electrodegradation,^36 and
   - Photodegradation of compound \(1.4^{2+}\) is quite pronounced as it decomposes upon irradiation with 365 nm in about 24 h.\(^{35}\)
The compounds synthesized and their properties analyzed are presented in Table 5.1. Unlike the compounds presented above (2.18\(^{2+}\) and 1.4\(^{2+}\)) all the compounds synthesized in this work have methyl groups in the \(\alpha\) positions of pyridinium moieties in order to mitigate the electrodegradation during reduction. The first three compounds, 5.1\(^{2+}\), 5.2\(^{+}\) and 5.3, differ only in the degree of alkylation of the external pyridine groups. These compounds were analyzed for two reasons:

1. To determine the extent to which the addition of pyridinium groups decreases the thermal stability of the ring–closed isomer in the dark, and
2. To probe the mechanism of the ring–closing reaction through reduction. This reaction was found to be monoelectronic as proven by chronocoulometry. Electrolysis of a solution of compound 2.18o\(^{2+}\) consumes one Faraday (one mole of electrons) for each mol of electrochromic compound 2.18o\(^{2+}\). An idea to be tested is if only one pyridinium group is necessary for the molecular architecture, such as compound 5.2\(^{+}\).

The electrochemical characterization of the monopyridinium compound 5.2\(^{+}\) was somewhat challenging due to the thermal instability of it is ring–closed form in the dark. Compound 5.4\(^{+}\) was synthesized because it was envisioned that the thermal stability of the ring–closed form in the dark will be much better than that of 5.2c\(^{+}\), and its manipulation at room temperature will be much easier for longer periods of time. Lastly compound 5.5\(^{2+}\) was synthesized to be used as a standard for compounds that are undergoing only reductive ring–closing.
Table 5.1. Compounds presented and analyzed in Chapter 5.

<table>
<thead>
<tr>
<th>entry</th>
<th>RO isomer</th>
<th>photochemistry</th>
<th>electrochemistry</th>
<th>t_{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1o^2+</td>
<td>![Compound 5.1o^2+]</td>
<td>20 % due to extensive thermal back cycloreversion in the dark at RT</td>
<td>✓</td>
<td>within minutes</td>
</tr>
<tr>
<td>5.2o^+</td>
<td>![Compound 5.2o^+]</td>
<td>65 % with thermal back cycloreversion in the dark at RT</td>
<td>✓</td>
<td>29 minutes</td>
</tr>
<tr>
<td>5.3o</td>
<td>![Compound 5.3o]</td>
<td>60 % with thermal back cycloreversion in the dark at RT</td>
<td>✓</td>
<td>4.8 h</td>
</tr>
<tr>
<td>5.4o^+</td>
<td>![Compound 5.4o^+]</td>
<td>65 % no thermal cycloreversion noticed at RT</td>
<td>✓</td>
<td>18 days</td>
</tr>
<tr>
<td>5.5o^2+</td>
<td>![Compound 5.5o^2+]</td>
<td>97 % no thermal cycloreversion noticed at RT</td>
<td>✓</td>
<td>-</td>
</tr>
</tbody>
</table>
5.1. Synthesis and Characterization of Compound 5.1o\textsuperscript{2+}, 5.2o\textsuperscript{+} and 5.3o

5.1.1. Synthesis of Compounds 5.1o\textsuperscript{2+}, 5.2o\textsuperscript{+} and 5.3o

The synthesis of compounds 5.1o\textsuperscript{2+}, 5.2o\textsuperscript{+} and 5.3o is presented in Scheme 5.1. Treating the commercially available 2,6-dimethyl-\(\gamma\)-pyrone (5.6) with ammonium hydroxide afforded compound 5.7, which upon treatment with PBr\(_5\) formed compound 4-bromo-2,6-dimethylpyridine (5.8).\textsuperscript{95} The DTE 5.12 was synthesized in just three steps starting with the commercially available 2,3-dibromothiophene, which was coupled using standard Suzuki conditions with another commercially available compound, phenylboronic acid. Thus compound 5.10 was obtained. By treatment of compound 5.10 with N-chlorosuccinimide, compound 5.11 (3-bromo-5-chloro-2-phenylthiophene) was formed. By temperature controlled metal halogen exchange with \(n\)-BuLi, only the bromine is exchanged with lithium, a step that is followed by the rapid addition of octafluorocyclopentene that afforded compound 5.12.

The main feature in the synthesis is the one pot palladium-catalyzed coupling (Suzuki coupling) synthesis of the DTE 5.12 with 4-bromo-2,6-dimethylpyridine, which yielded compound 5.3o. The alkylation of compound 5.3o is achieved using dimethyl sulfate. Depending upon the number of equivalents of dimethyl sulfate used, one can obtain either the dialkylated compound 5.1o\textsuperscript{2+} or the monalkylated compound 5.2o\textsuperscript{+}. The last step in the synthesis is the counter anion exchange. Initially in the reaction the sulfate ion is formed, which upon purifying by column chromatography turns into the nitrate. The final ion exchange affords the desired and the more organic soluble hexafluorophosphate salt 5.2o\textsuperscript{+}. 

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Scheme 5.1. Synthesis of compounds 5.1o²+, 5.2o⁺ and 5.3o.

Compounds 5.1o²+, 5.2o⁺ and 5.3o were characterized with the aid of NMR spectroscopy, mass spectrometry and UV-Vis spectroscopy. Figure 5.2 presents overlapping ¹H NMR spectra of bispyridinium 5.1o²+, monopyridinium 5.2o⁺ and
bispyridine derivative 5.3o with the proton assignments. Compounds 5.1o2+ and 5.3o are symmetric, therefore their 1H NMR spectra looks relatively uncomplicated both in the aromatic and aliphatic regions. Nevertheless, the chemical shift of the hydrogen atoms of the methyl group (starred) attached to the nitrogen atom of pyridine at 4 ppm is a useful tool in determining which one is the alkylated product. The middle of Figure 5.2 displays the 1H NMR spectrum of the asymmetric compound (monoalkylated pyridine), 5.2o+. As expected, in the aliphatic region there are three signals, the two most upfield ones are the signals belonging to the protons of the CH3 groups on the α positions of the pyridine and pyridinium. The third signal in the aliphatic region (marked with an star) has the characteristic chemical shift of a CH3 group bound to the nitrogen atom of the pyridinium.
Figure 5.2. Stacked $^1$H NMR spectra of compounds: (bottom) $5.3o$, spectrum acquired in CDCl$_3$ on a 400 MHz instrument, (centre) $5.2o^*$, spectrum acquired in CD$_3$CN on a 500 MHz instrument, (top) $5.1o^{2+}$, spectrum was acquired in CD$_3$CN and on a 400 MHz instrument.

In the process of synthesizing compound $5.1o^{2+}$, initially the alkylation reaction proved to be somewhat difficult, as the first choice for a methylation reagent MeI (methyl iodide) was inefficient in this case. The methylation reaction required several trials in order to identify optimal conditions. During this time, it was noticed that the compound $5.2c^*$ is more thermally stable in the dark at room temperature on the TLC plate (Scheme 5.2). As determined by visual inspection, in half an hour there was no fading
reaction. This fact is to be expected as there is only one EWG (pyridinium group) that will pull away electron density from the $\sigma$ bond photochemically generated.

Scheme 5.2. Methylation reaction of compound 5.3o (top), (bottom) cartoon depiction of the TLC plate used to determine the extent of the alkylation reaction and also the cycloreversion reaction half life as estimated by visual inspection. The TLC conditions are: basic alumina plate CH$_3$CN : KNO$_3$ (saturated sol) 97 : 3. ($X^-$ = NO$_3^-$).

The next discussion is presenting the photochemical, electrochemical and thermal stability of compounds 5.1$^{2+}$, 5.2$^+$ and 5.3.
5.1.2. Photochemical properties of compounds 5.1\(^{2+}\), 5.2\(^{+}\) and 5.3

The photochemical interconversion between the ring-open (5.1\(^{2+}\) 5.2\(^{+}\) and 5.3\(^{o}\)) and the ring-closed (5.1\(^{c2+}\) 5.2\(^{c+}\) and 5.3\(^{c}\)) isomers can be achieved by using as an irradiation source a hand held TLC lamp. Exposure of the respective solutions of the ring-open isomer to UV light resulted in a colour change and subsequent differences in the UV-Vis absorption profiles of the two isomers, as illustrated in Figure 5.3.

Irradiation of a colourless CH\(_3\)CN solution (1.5 x 10\(^{-5}\) M) of 5.1\(^{2+}\) with 365 nm light resulted in the immediate development of a green colouration, that corresponds to the formation of the ring-closed isomer 5.1\(^{c2+}\), which faded back to the initial colourless state within minutes.

The other two compounds 5.2\(^{+}\) and 5.3\(^{o}\) presented a somewhat higher stability of the coloured form and their absorption spectra were easier to obtain. Their photochemical interconversions were monitored also by UV-vis absorption spectroscopy, and the appearance of a broad visible absorption band characterisitic to the ring-closed form was marked with a concomitant decrease in the UV absorption band of the ring-opened isomer. The UV-vis spectrum changes upon irradiation with 365 nm of compound 5.2\(^{+}\) and is presented in Figure 5.4 b. Upon photocyclization, an absorption band at \(\lambda_{\text{max}} = 650\) nm appeared belonging to the ring-closed form with a concomitant decrease in the absorption band of the ring-open isomer (\(\lambda_{\text{max}} = 358\) nm). The thermal back reaction of ring-opening in the dark was slower as in the case of compound 5.1\(^{c2+}\) and photostationary state was achieved in seconds. By allowing the cuvette to rest in the dark for 60 minutes, mainly the ring-open isomer was detected by UV-vis spectroscopy.

A solution of compound 5.3\(^{o}\) (1.1 x 10\(^{-5}\) M) was interconverted photochemically to its blue coloured isomer 5.3\(^{c}\) by irradiation with 365 nm (Figure 5.3 c). Due to its somewhat slower thermal back reaction the ring-open isomer can be obtained back photochemically by irradiating the PSS solution using filtered visible light state (> 400 nm) for 2 minutes.
Figure 5.3. Changes in the UV-Vis absorption spectra of a CH$_3$CN solution (a) (1.5 x 10$^{-5}$ M) of the ring-open form $5.1^2$ (b) 2.0 x 10$^{-5}$ M of the ring-open isomer $5.2^+$ (c) 1.1 x 10$^{-5}$ M of the ring-open isomer $5.3^+$ (upon irradiation with 365 nm light until no further increase in the absorption band in visible was observed at the PSS).

5.1.3. Electrochemical Characterization of Compounds $5.1^2$ and $5.2^+$

Once the photophysical properties were determined, the next step was to test the proposed plan: that a single pyridinium group is sufficient for the reductive ring closing. The next discussion presents the electrochemical characterization of compounds $5.1^2$ and $5.2^+$ by cyclovoltammetry.

Electrochemical Properties of Compound $5.1^2$

By scanning towards cathodic potentials, compound $5.1^2$ undergoes two irreversible reduction process (labelled I, II in Figure 5.4(a) at $E_{1/2}$ = -0.92 V vs SCE, $E_{1/2}$
= -1.40 V vs SCE). In Figure 5.4(b) is presented the results of scanning in the cathodic direction only until the first irreversible reduction wave (I) and one anodic peak is observed on the return scan at \( E_{1/2} = -0.15 \) V:

1. This irreversible reduction (I) is assigned to the reduction of one of the two somewhat independent pyridinium moieties. (Scheme 5.3).

\[
\text{Scheme 5.3. Proposed mechanistic path for the reductive triggered ring–closing reaction of compound 5.1o}^{2+}. \text{PF}_6^- \text{counteranions are omitted for clarity.}
\]

2. The new anodic peak formed after the irreversible reduction of the ring–open isomer \( 5.1\text{o}^{2+} \) represents the oxidation of the newly formed ring–closed isomer. The cyclization reaction is faster than the scan rate therefore making it possible to see the characteristic peaks of \( 5.1\text{c}^{2+} \).

3. Unfortunately, the CV of the ring–closed form could not be obtained, (it would have been useful for comparison reasons), due to the thermal back reaction being faster than the various scanning rates tried.
Figure 5.4. CVs of CH$_3$CN solutions (1 x 10$^{-3}$ M) of (a) the ring–open isomer 5.1o$^{2+}$ with a scan rate of 300 mV / s in cathodic direction (b) sweep in the cathodic region, but stopped at the first irreversible reduction wave the ring-open isomer with a scan rate of 300 mV / s in cathodic direction. With red is circled the wave pertinent to the ring closed form as formed through the reduction of the ring-open form 5.1o$^{2+}$. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.

Figure 5.5 shows the formation of green species around the working platinum mesh electrode, which was concluded to be the radical cation 5.1c$^{+}$, although spectroelectrochemistry was not employed to confirm the hypothesis. In conclusion, compound 5.1o$^{2+}$ undergoes reductive ring–closing and thermal ring–opening reaction at room temperature. As expected by blocking the $\alpha$ positions of the pyridinium moieties with methyl groups does not affect the electrochromic behaviour, as the CV of compound 5.1o$^{2+}$ is similar to that of compound 1.4o$^{2+}$.
Figure 5.5. Visual changes as seen on the Pt mesh electrode by applying a negative potential -1.1 V vs SCE on a CH$_3$CN solution containing compound 5.1o$^{2+}$.

Electrochemical characterization of compound 5.2o$^+$

Figure 5.6 presents the cyclic voltammograms of the open form 5.2o$^+$ and of the PSS solution. Although the PSS of compound 5.2$^+$ was found to contain around 60 % of the ring-closed isomer, the two CVs are very much alike. Circled with red are the only two minor peaks of the ring-closed form. The monopyridinium compound 5.2o$^+$ has four irreversible reductions waves labelled I ($E_{1/2} = -0.65$ V vs SCE), II ($E_{1/2} = -1.12$ V vs SCE) and III ($E_{1/2} = -1.41$ V vs SCE) and IV ($E_{1/2} = -1.90$ V vs SCE). And now the task was to find out which of the four irreversible reductions are triggering the ring-closing reaction. In the case of the bispyridinium compound 5.1o$^{2+}$ the first reduction (-0.92 V) which is assigned to the reduction of the pyridinium moiety, is the one that is triggering the cyclization. Therefore, the scanning in the cathodic direction was done sequentially and stopped at the desired potential. For example, the first scan was done carefully in order to include the first reduction wave (I), but stopped just before the potential where the second reduction peak starts (II) of -0.75 V. The return scan was monitored closely and carefully to see if new peaks appear which are characteristic to the formation of the ring-closed isomer.
Figure 5.6. CVs of CH$_3$CN solutions using a 3mm diameter Platinum working electrode of (a) the ring-open isomer 5.2o with a scan rate of 300 mV/s in cathodic direction (b) PSS solution obtained by irradiation with 365 nm light for 40 minutes at room temperature, with a scan rate of 300 mV/s.

Although this reduction is irreversible, no new peaks were noticed on the return scan the conclusion was that the cyclization does not take place at this potential. Therefore the next CV included the scanning of the first and second reduction waves (I and II) but it was stopped just before the third reduction wave started (III). The second reduction wave appears to be quasireversible but once again the return scan did not reveal new peaks. In Figure 5.7(d) is presented the scanning that includes the first three reductions and even in this case no cyclization is noticed. Unlike the previous case, where the presence of the even more thermally unstable ring-closed form (5.1c$^{2+}$) was detected by cyclic voltammetry on the return scan (Figure 5.4(b)) and visually observed by performing bulk electrolysis (Figure 5.5), this time no detectable trace of the ring-closed isomer was noticed. The first reduction (I) $E_{1/2} = -0.65$V is the only
irreversible one and the reductions II and III are quasireversible. In conclusion, the cyclic voltammograms of a solution of 5.2o+ did not show any electrochemically induced cyclization through reduction. On the other hand, by applying a positive potential to a PSS solution (obtained photochemically by irradiation with a 365 nm UV lamp), this compound underwent the oxidative triggered cycloreversion. Nevertheless, the proposal of having a single pyridinium group had to be tested in depth and compound 5.2+ will not be able to allow this type of investigation as it has several shortcomings, the most important being the thermal instability of the ring-closed form in the dark. The next discussion presents the design and synthesis of compound 5.4+, which will allow for an in depth characterization of the monopyridinium approach towards the reductively triggered ring-closing.
Figure 5.7. Sequential scanning of a CH$_3$CN solution of 5.20$^+$ using a 3mm diameter Platinum working electrode in order to include (a) the full electrochemical window, (b) only the first (I) reduction wave (c) only the first (I) and second (II) reduction waves and (d) only the first (I) second (II) and third (III) reduction waves. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
5.2. Synthesis and Characterization of Compound 5.4⁺

The idea behind this proposal is consistent with the previous results that the cyclization is triggered by the monoelectronic reduction (local reduction of the pyridinium moiety) of the ring–open isomer. In this way by synthesizing an asymmetric DTE molecule such as compound 5.4⁺ that contains (Figure 5.8):

1. a single external pyridinium group, which will allow the cyclization through reduction,
2. a single aromatic internal group, which will allow the oxidative ring–opening, and
3. the thermal stability of compound 5.4c⁺ was anticipated to be around one week at room temperature in the view of previous results: half life of compound 3.1c (determined in Chapter 3) and of compound 2.8o2⁺.

![Proposed structural requirements for a compound to undergo reductive ring-closing and oxidative ring-opening and to be thermally stable in the dark.](image)

**Figure 5.8.** Proposed structural requirements for a compound to undergo reductive ring-closing and oxidative ring-opening and to be thermally stable in the dark.

5.2.1. Synthesis of Compound 5.4⁺

The synthesis of desired compound is presented in Scheme 5.4. Compound 3.6 was prepared in one step using a Kumada coupling according to the procedure already published. Compound 3.10 was prepared by a lithium halogen exchange reaction and by subsequent treatment with a small excess of octafluorocyclopentene to make sure that
the monosubstituted compound is formed in the favour of the disubstituted compound 3.10, which was noticed only in traces under these conditions. By treating 3-bromo-5-chloro-2-methylthiophene with $n$-BuLi at lower temperature, a selective metal halogen exchange takes place (Li-Br) and the lithiated species was treated with the previously synthesized compound 3.10 to give 5.13 in good yield. Compound 5.14 was prepared by a lithiation of compound 5.13, followed by treatment with tri-$n$-butylborate. No workup was done in order to purify and isolate the intermediate borate ester. The next step of the synthesis was the palladium-catalyzed coupling (Suzuki coupling) synthesis of the intermediate borate ester with 4-bromo-2,6-dimethylpyridine. The synthesis of compound 5.40$^+$ was achieved by the alkylation reaction using dimethylsulfate. However the last step of synthesis is the counter anion exchange, initially in the reaction the sulfate was formed, upon purification conditions of the column chromatography the nitrate was formed and the final exchange afforded the desired the hexafluorophosphate salt 5.40$^+$. 
Scheme 5.4. Synthesis of compound 5.4o*.

In Figure 5.9 is presented the $^1$H NMR spectrum of compound 5.4o*, which is consistent with the proposed structure. All the protons are accounted for and their assignment is given in the aromatic (seven signals) and aliphatic (five signals) regions.
5.2.2. Optical Properties of Compound 5.4o⁺

The photochemical interconversion of compound 5.4o⁺ to 5.4c⁺ and the reverse reaction was monitored by UV-vis spectroscopy and by ¹H NMR spectroscopy. The UV-vis absorption spectra of both isomers were obtained by irradiating with a low pressure mercury vapour lamp, a quartz cuvette containing a CH₃CN solution of compound 5.4o⁺ and by monitoring by UV-vis absorption spectroscopy (Figure 5.10). Upon
photocyclization an absorption band $\lambda_{\text{max}} = 668$ nm appears belonging to the ring–closed form, with concomitant decrease in the absorption band of the ring–open isomer ($\lambda_{\text{max}} = 343$ nm). The thermal back reaction of ring–opening in the dark is completely absent at room temperature and on the time scale of the experiment thus the real photostationary state was achieved in 1423 sec.

![UV-Vis absorption spectra](image)

Figure 5.10. Changes in the UV-Vis absorption spectra of a CH$_3$CN solution (2.0 x 10$^{-5}$ M) of the ring-open form 5.4o$^+$ upon irradiation with 365 nm light until no further increase in the absorption band.

The photostationary state was monitored by $^1$H NMR spectroscopy and was found to be equal to 65 %. In the view of the previous results (see compound 5.2$^+$) where the cyclic voltammograms of the PSS state (almost equal parts of ring–opened ring–closed isomer) was deemed not to be useful, it was clear that there was a necessity to obtain the pure ring–closed isomer 5.4c$^+$. In the case of compound 5.2$^+$, the thermal instability of the ring–closed form was the major drawback, but also the overlap of the reductive peaks of the two isomers did not allow a clear interpretation of the results.

Attempts to purify the photochemically generated ring–closed form 5.4c$^+$ by recrystallization and column chromatography failed. A new short synthesis was envisioned (Scheme 5.5). Compounds 5.14o and 5.14c have different retention factors.
and they can be easily separated by column chromatography on a somewhat larger scale. Therefore, the first step of synthesis was the photochemical reaction of obtaining 5.14c that was purified by column chromatography with a modest yield of 41%, compared to the fact that the reaction mixture contained mainly ring-closed isomer. The alkylation reaction of 5.14c and the counteranion exchange were all done in the dark with a yield of 21%. In Figure 5.11 are overlapped three 1H NMR spectra: in the middle is the spectrum belonging to the ring-open isomer and top to the photochemically generated mixture of both forms. The bottom spectrum belongs to the compound 5.4c∗ synthesized by the procedure depicted in Scheme 5.5.

Scheme 5.5. Independent chemical synthesis of compound 5.4c∗.
5.2.3. **Electrochemical Characterization of Compound 5.4⁺**

In Figure 5.13 are presented three CVs. The top plot is the CV for the ring–open form 5.4o⁺. The one in the middle is the CV for the PSS mixture (mixture of both isomers photochemically obtained). The bottom one is the CV for the pure independently synthesized ring closed isomer 5.4c⁺.

The CV for the ring–open form 5.4o⁺ shows two irreversible reductions waves labelled $I_{\text{red}}$ ($E_{1/2} = -1.19\text{V vs SCE}$) and $II_{\text{red}}$ ($E_{1/2} = -1.58\text{V vs SCE}$) in the cathodic region.
and two reversible oxidation waves ($E_{1/2}^{\text{oxid}} = 1.23V$) and ($E_{1/2}^{\text{oxid}} = 1.45V$). The cyclic voltammogram for the PSS is very similar to that for the ring–open isomer, except it has two more reductive peaks, (circled in Figure 5.12) and one irreversible oxidation peak ($E_{1/2} = 1.08 V$ vs SCE) (the latter being associated with the catalytic oxidative ring-opening). The CV belonging to 4.5c⁺ is quite complicated in the cathodic region and has at least eight reduction waves. On the other hand, in the anodic region, it has the very clear peak associated with the oxidative ring–opening ($E_{1/2} = 1.1 V$ vs SCE). Once the cyclic voltammograms for both isomers were obtained, the next step was to identify which of the irreversible reductive waves of 5.4o⁺ are triggering the ring closing. Therefore, the scanning in the cathodic direction was done sequentially and stopped at the desired potential. In Figure 5.13 are presented the above mentioned cyclic voltammograms. The first scan was done carefully in order to include the first reduction wave (I) -1.2 V vs SCE, but stopped just before the potential where the second reduction peak starts (II) of -1.6 V vs SCE. Unfortunately, in none of the CV(s) was seen the formation of the ring–closed isomer.
Cyclic voltammograms of CH$_3$CN solution (1 x 10$^{-3}$ M) using a 3mm diameter Platinum working electrode (a) of 5.4o$^+$ with a scan rate of 300 mV /s (b) of a photochemically generated PSS solution (containing 65% RC form) with a scan rate of 300 mV /s and (c) of 5.4c$^+$ independently synthesized with a scan rate of 500 mV. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.

Bulk electrolysis at various negative potentials, using a Pt mesh working electrode did not yield any visible formation of at least a coloured species. Therefore, compound 5.4o$^+$ is not undergoing, the reductive ring closing at the specified conditions. On the other hand, by performing bulk electrolysis at the fixed potential of 1.2 V vs SCE, the PSS solution containing 65% coloured form undergoes the oxidative ring-opening reaction. The process was monitored with $^1$H NMR spectroscopy.
Figure 5.13. Sequential scanning of a CH₃CN solution (1 x 10⁻³ M) of compound 5.4o⁺ using a 3 mm diameter Platinum working electrode in the cathodic direction. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
5.3. Synthesis and Characterization of Compound 5.5o$^{2+}$

The reason for compound 5.4o$^+$ not undergoing the mono-electronic reductive triggered ring closing is still unknown. This somewhat disappointing result led to a more detailed investigation of the reductive ring-closing process on a relatively uncomplicated molecule. Therefore, compound 5.5o$^{2+}$ was synthesized, which is the analogue to compound 2.18o$^{2+}$, previously reported as the first DTE to undergo the ring-closing reaction triggered by electrochemical reduction (Figure 5.15).

![Structure of compounds 2.18o$^{2+}$ and 5.5o$^{2+}$](image)

Figure 5.14. Structure of compounds 2.18o$^{2+}$ and 5.5o$^{2+}$.

5.3.1. Synthesis of Compound 5.5o$^{2+}$

The synthesis of compound 5.5o$^{2+}$ is presented in Scheme 5.6. Compound 5.15 was prepared according to a procedure already published. Compound 5.16 was prepared by a one pot palladium catalyzed coupling: the first step is metal halogen exchange of compound 5.15 with n-BuLi, which is followed by treatment with tri-n-butylborate. The borate ester was further reacted with 4-bromo-2,6-dimethylpyridine in the typical conditions dictated by the Suzuki coupling. The final steps of the synthesis are the alkylation with dimethylsulfate and the counteranion exchange with a solution of NH$_4$PF$_6$. 

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5.3.2. Optical Properties of Compound 5.52+  

The photochemical toggling between the two isomers 5.5o2+ to 5.5c2+ was monitored by UV-Vis spectroscopy and by 1H NMR spectroscopy. The PSS was monitored by using 1H NMR spectroscopy and was found to be 97%. Due to this almost total photochemical interconversion, no purification of the ring-closed isomer was deemed necessary.

By irradiation with UV light (365 nm light source from the lamp used to visualise TLC plates) of the respective ring-open isomer solutions, a colour change is observed (colourless to blue) and subsequent differences in the UV-Vis absorption profiles of the two isomers, as illustrated in Figure 5.15. Upon irradiation of a colourless solution an absorption band $\lambda_{\text{max}} = 651$ nm appears, belonging to the ring-closed form with the concomitant decrease in the absorption band of the ring-open isomer ($\lambda_{\text{max}} = 348$ nm).
**Figure 5.15.** Changes in the UV-Vis absorption spectra of a CH$_3$CN solution (1.2 x 10$^{-5}$ M) of the ring-open form 5.5o$^{2+}$ upon irradiation with 365 nm light until no further increase in the absorption band at 651 nm was observed at the PSS.

### 5.3.3. Electrochemical Properties of Compound 5.5$^{2+}$

By scanning towards cathodic potentials, compound 5.5o$^{2+}$ undergoes three irreversible reduction process (labelled I, II and III in figure 5.16 (a) at $E_{1/2} = -1.25$V vs SCE, $E_{1/2} = -1.50$V vs SCE and the third at around -1.9V, which overlaps with the reduction of the solvent. By scanning in the cathodic direction only to include the first irreversible reduction wave (I), two anodic peaks are observed on the return scan at $E_{1/2} = -0.15$V. These two reduction waves might be assigned to the reduction of the two independent pyridinium moieties. The two new anodic peaks formed after the reduction of the ring-opened isomer 5.5o$^{2+}$ represent the oxidation of the newly formed ring-closed isomer. The cyclization reaction is faster than the scan rate, hence it is possible to see the characteristic peaks of 5.5c$^{2+}$. In Figure 5.16(c) is given the full cyclic voltammogram of the ring-closed isomer (synthesized photochemically by irradiation with 365 nm light source of a solution containing the 5.5o$^{2+}$). The ring-closed isomer presents two reductions each one being probably monoelectronic, although further electrochemical studies are necessary.
Figure 5.16.  
Cv(s) of CH₂Cl₂ solution (1.3 x 10⁻³ M) (a) of 5.5o²⁺ using a 3 mm diameter Platinum WE with a scan rate of 300 mV/s (b) scanning in the cathodic direction, to include only the first reduction wave, with a scan rate of 300 mV s⁻¹ (c) of 5.5c²⁺ photochemically synthesized (97 % ring-closed form) with a scan rate of 300 mV /s. A 3 mm Pt and Ag wire were employed as WE and RE, respectively. The results were corrected to calomel values.
Although it is very tempting to assume that the electrochemical ring-closing reaction for compound 5.5o^{2+} is bielectronic and the diradical formed by the reduction of each pyridinium group is the only species that undergoes the desired cyclization some important notes have to mentioned:

1. Even though two anodic peaks are seen on the return scan of the reduction of the ring–open form, another scenario can be envisioned and is depicted by path a) in Scheme 5.7. First, the monoelectronic reduction of the ring–open isomer takes place followed by the cyclization reaction; once formed the monoradical cation 5.5c^{+} is further reduced to the diradical form 5.5c^{2+}, hence the two anodic peaks on the return scan.

2. The first monoelectronic reduction of the ring–open isomer takes place and this particular event does not trigger the electrochemical driven cyclization path b) in Scheme 5.7. It is necessary a second monoelectronic reduction of the other pyridinium group in order to form the diradical that is the sole intermediate that undergoes the cyclization through a reduction process, path c) in Scheme 5.7. This scenario is somewhat consistent with the previous results of compound 5.4^{+}, that has a single pyridinium group, hence a single monoelectronic reduction and no cyclization is observed.

3. The last scenario allows for the cyclization to take place both from the monoradical and biradical intermediates with probably different efficiencies.
Scheme 5.7. Possible three pathways of the cyclization triggered by the reduction of 5.5o2+.

5.4. Comparative Photochemical Studies

Because compound 5.4+, which is an asymmetric molecule can be regarded as a combination of compound 3.1 and 5.52+, UV-Vis comparison can be done between these compounds. The changes upon irradiation with UV light are discussed below. Table 5.2 summarizes the most important photophysical values.
Table 5-2. Selective photophysical data for CH$_3$CN solutions of DTEs: 3.1o, 5.5o$^{2+}$ and 5.4o$^+$ and their ring-closed isomers 3.1c, 5.5c$^{2+}$ and 5.4c$^+$ and the corresponding PSS values.

<table>
<thead>
<tr>
<th>entry</th>
<th>PSS</th>
<th>RO</th>
<th>RC</th>
<th>λ$^{\text{max}}$</th>
<th>λ$^{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>75  %</td>
<td>256</td>
<td>336</td>
<td>402, 647</td>
<td></td>
</tr>
<tr>
<td>5.4o$^+$</td>
<td>65  %</td>
<td>345</td>
<td></td>
<td>413, 670</td>
<td></td>
</tr>
<tr>
<td>5.5o$^{2+}$</td>
<td>97  %</td>
<td>280</td>
<td>347</td>
<td>418, 648</td>
<td></td>
</tr>
</tbody>
</table>

First is presented a short discussion of the PSS as determined by $^1$H NMR spectroscopy. Compound 5.4$^+$ has a lower PSS state (65 %) than both of the related compounds. As determined by $^1$H NMR spectroscopy, compound 3.1 has a PSS of 75 % and compound 5.5$^{2+}$ possess a conversion from ring-open to ring-closed isomer quantitative (> 97 % transformation) by irradiation with 365 nm. The high PSS of the dicationic species, 5.5$^{2+}$ usually is regarded as a result of the of the preference of the open–ring isomer to be in the reactive antiparallel conformation due to the Coulombic repulsions of the two pyridinium moieties.$^96$ It is possible for compound 5.4$^+$ to have a lower PSS due to a preferred stacking between the pyridinium and the thiophene ring in the open form. Also it is interesting to note that the PSS is achieved in much longer time (at the same concentration), 2 hours for 5.4$^+$ as opposed to almost 30 to 40 minutes for compounds 3.1 and 5.5$^{2+}$.

Regarding the ring-open isomers (Figure 5.17 a), all three derivatives 3.1o, 5.5o$^{2+}$ and 5.4o$^+$ have a somewhat different UV-vis absorption spectra. This is expected due to the differences in their overall molecular structures. As mentioned in Chapter 3, the UV absorptions of ring-closed DTEs shift to longer wavelengths (bathochromic shift) when compared to the open form due to the increase in the extent of π-conjugation. Because the closed isomer presents an increase in the π-conjugation, the HOMO–LUMO energy gap of the molecule decrease and having as a result lower energy excitations.
Comparative Thermal Studies for Compounds 5.1c\(^{2+}\), 5.2c\(^{+}\) and 5.4c\(^{+}\)

The dark thermal cycloreversion can be evaluated by monitoring the decrease in absorbance of the ring–closed isomer as function of time and temperature (Figure 5.18). As presented in the case of the terthiophene derivatives (Chapter 3), all the thermal cycloreversions follow first order reaction kinetics. Although two of the compounds are asymmetrical (5.2c\(^{+}\) and 5.4c\(^{+}\)), the bond breaking is assumed to be homolytic and to follow the same mechanism. The results are presented in Figure 5.18 and the points

**Figure 5.17.** (a) Overlapped absorption spectra of CH\(_3\)CN solutions (1.0 x 10\(^{-5}\) M) of 3.1o, 5.4o\(^+\) and 5.5o\(^{2+}\) (b) Overlapped UV-Vis absorption spectra of the PSS solutions for compounds 3.1, 5.4\(^+\) and 5.5\(^{2+}\) obtained by irradiation the solutions containing the ring–open isomers in CH\(_3\)CN with a hand held UV-lamp at 365 nm.
were fitted to a straight line: \( \ln[A] \) vs. time (s) with a slope of \(-k\), which is the first order rate constant.

![Graph of compound 5.1c](image)

![Graph of compound 5.2c](image)

![Graph of compound 5.4](image)

**Figure 5.18.** Normalized ring–opening reactions for compounds 5.1c\(^{2+}\), 5.2c\(^+\) and 5.4c\(^+\) in CH\(_3\)CN as monitored by UV-Vis spectroscopy, using fixed wavelengths corresponding to the decrease of the maximum visible absorption intensity of each compound (667, 650, 612 and 670 nm) at four different temperatures as mentioned in the graph.

It is clear that for compound 5.1c\(^{2+}\), the lines are curved and not straight, nevertheless they were fitted to a straight line model in order to obtain the approximate half life values. The results from the kinetic analysis in the case of this compound
suggest that the dark thermal ring–opening reaction is not a first order reaction, or at least not a pure first order reaction. The reason for this behaviour is not known, and they do not fit second or third order reaction kinetics. In Table 5.3 are given the equations of the straight lines for each compound at monitored temperature and the $R^2$ values.

**Table 5.3.** The equations of the straight lines, that were fitted to the monitored ring–opening reactions for 5.2c$^+$ and 5.4c$^+$ in CH$_3$CN and in the dark at four temperatures and the $R^2$ values, (software used Excel).

<table>
<thead>
<tr>
<th>compound</th>
<th>temperature</th>
<th>equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2c$^+$</td>
<td>20 °C</td>
<td>$y = -6E-05x - 0.0007$</td>
<td>0.99987</td>
</tr>
<tr>
<td></td>
<td>30 °C</td>
<td>$y = -0.0002x - 0.0149$</td>
<td>0.99913</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>$y = -0.0005x - 0.2678$</td>
<td>0.98845</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>$y = -0.0005x - 0.2678$</td>
<td>0.9728</td>
</tr>
<tr>
<td>5.4c$^+$</td>
<td>40 °C</td>
<td>$y = -4E-07x - 0.002$</td>
<td>0.95496</td>
</tr>
<tr>
<td></td>
<td>50 °C</td>
<td>$y = -1E-06x - 0.0028$</td>
<td>0.99897</td>
</tr>
<tr>
<td></td>
<td>60 °C</td>
<td>$y = -1E-05x - 0.0359$</td>
<td>0.99939</td>
</tr>
<tr>
<td></td>
<td>80 °C</td>
<td>$y = -0.0001x - 0.0136$</td>
<td>0.99826</td>
</tr>
</tbody>
</table>

As expected, the biscation derivative 5.1c$^{2+}$ is the most unstable compound in the dark due to the two electron withdrawing groups (pyridinium) that are weakening the $\sigma$ bond photochemically generated (Table 5.4). The half lives for compound 5.1c$^{2+}$ were calculated from initial from initial concentration values and the results are presented in Table 5.4. Compound 5.4c$^+$ has a half life of almost 20 days which is superior to both compounds 3.1c (11 days at 40 °C in decane) and 2.18c$^{2+}$ (2.75 days at 40 °C in acetonitrile). Caution has to be taken when comparing the half lives of ring–closed isomers that were determined in different solvents as there is a report regarding the dark thermal cycloreversion being slower in acetonitrile than in hexane.\(^{97}\)
Table 5.4. The half lives at four temperatures for compounds 5.1c\textsuperscript{2+}, 5.2c\textsuperscript{+} and 5.4c\textsuperscript{+} in CH\textsubscript{3}CN and in the dark.

<table>
<thead>
<tr>
<th>compound</th>
<th>t\textsubscript{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 °C</td>
</tr>
<tr>
<td>5.1c\textsuperscript{2+}</td>
<td>58.0 min</td>
</tr>
<tr>
<td>5.2c\textsuperscript{+}</td>
<td>20 °C</td>
</tr>
<tr>
<td></td>
<td>3.8 ± 0.3 hours</td>
</tr>
<tr>
<td>5.4c\textsuperscript{+}</td>
<td>40 °C</td>
</tr>
<tr>
<td></td>
<td>18 ± 2 days</td>
</tr>
</tbody>
</table>

Note: There was a certain variation in the half lives of the 3 cuvettes (experiment done in triplicates) hence the average is reported ± the standard deviation. Some cuvettes do not present any deviation hence the ± 0.

5.6. Comparative Electrochemical Data

The reduction of the ring–closed isomers occur at more anodic potentials that the ring–open isomers. The reason for this is that the ring–closed isomers are better electron acceptor than the ring–open forms. In the ring–closed form, the two external groups (electron deficient pyridinium and thiophene) are linearly conjugated through the DTE backbone. Furthermore, due to the extended electronic conjugation the ring–closed isomer will stabilize better the radical cation resulted from the reduction process. The reduction of the ring–closed isomer appear reversible.

On the other hand, the reduction of ring–open isomer occurs at more negative potentials than ring–closed form and it is irreversible. These irreversible reductions are associated with:

1. an ECE type mechanism in the case of 5.1o\textsuperscript{2+} and 5.5o\textsuperscript{2+}
   - reduction of the ring–open isomer to form the radical cation form, which is unstable (E step),
   - cyclization to the radical cation of the ring closed form (C step),
   - oxidation of the radical cation of the ring–closed form (E step),
2. probably just degradation (electropolymerization) as in the case of $5.2o^+$ and $5.4o^+$.

5.7. Prospective and Future Direction of Research

The goal of this project was to investigate the role of the pyridinium groups in the reductive ring-closing reaction. Although it was suggested that the ring-closing is monoelectronic and thus a single pyridinium group will suffice for the desired cyclization, so far my results suggest a bielectronic reduction. It is not clear yet if compounds $2.18o^{2+}$ and $5.5o^{2+}$ have the same mechanism for the electrochemically induced ring-closing. Although structurally they are quite similar, one has to take into account that by incorporating the four methyl groups that are inductively ED groups in the $\alpha$ positions of the pyridine the mechanism might be changed.

As future work, chronocoulometry is a necessary experiment to determine if the cyclization takes place from the monoelectronic or bielectronic species (for both cases $2.18o^{2+}$ and $5.5o^{2+}$). Although this task might be quite difficult as both of the species: mono and bireduced ring-open might undergo the desired cyclization when subjected to the respective reducing conditions. If the process of ring closure triggered by reduction is bielectronic, the task of finding a DTE that is full electrochromic and that has good thermal stability in the dark (ring-closed isomer) will become quite hard to achieve. Although this might not be the end of the road, to the best of my knowledge there are no studies done on the thermal stabilities of the oxidized DTEs. So far, all the thermal studies (including the ones in this work) are done on “neutral species”. It will be interesting to see if the oxidized species have lower half lives in the dark when compared to the “neutral species”. This can be relatively easily tested on a compound similar to compound $5.17c^{2+}$ (Figure 5.19). When oxidized this DTE might undergo the catalytic oxidative ring-opening reaction. The sterically demanding isopropyl group might speed up the cycloreversion faster in the oxidized state.
Figure 5.19. Proposed structure of a DTE that will undergo cyclization triggered by reduction and thermal cycloreversion triggered by oxidation.

5.8. Experimental

5.8.1. Materials

All solvents used for synthesis were dried and degassed by passing them through steel columns containing activated alumina under nitrogen using an MBraun solvent purification system or by using the freshly distilled from the sodium / benzophenone still. Deuterated solvents for PSS analysis were purchased from Cambridge Isotope Laboratories and used as received, and kept on freshly activated molecular sieves. Column chromatography was performed using silica gel 60 (230-400 mesh) purchased from Silicycle Inc. and alumina Basic Brockman activity 1. All the solvents were purchased from Aldrich. Bu₄NPF₆ was purchased from Fluka Analytical and recrystallized three times from ethanol and dried in vacuo at 110 °C for 3 days and kept in a desicador until used. 2,3,5-tribromothiophene and 2-bromo-5-methylthiophene were purchased from Matrix Scientific. Pd(PPh₃)₄ and Pd(ddpf)Cl₂·CH₂Cl₂ were purchased from Strem. 2,6-Dimethyl-γ-pyrone was purchased from Acros. All the other reagents were purchased from Aldrich.

5.8.2. Instrumentation

¹H NMR and ¹³C NMR characterisations were performed on AVANCE III 400 MHz instrument operating at 400.13 MHz for ¹H NMR and 100.61 MHz for ¹³C NMR. Chemical shifts (ppm) are reported in ppm relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in Hertz. UV-vis absorption spectroscopy measurements were performed using a Varian Cary 300 Bio spectrometer.
High resolution mass spectrometry measurements were performed at Simon University by Mr. Hongwen Chen on an Agilent 6210 TOF LC/MS instrument. Melting point apparatus used are Gallenkamp and Fisher-Johns and are not corrected. FT-IR measurements were performed using a Nicolet Nexus 670 instrument.

5.8.3.  **Photochemistry**

All ring-closing reactions were carried out using the light source from a lamp used for visualising TLC plates at 365 nm (Spectroline E series, 470 W/cm²). The ring-opening reactions were carried out using the light of a 300-W halogen photo-optic source passed through a 434 nm cut-off filter to eliminate higher energy light. All ring closing and ring-opening reactions (photochemical) were carried in dry and deoxygenated solvents. The solvents were deoxygenated by purging the respective solutions with nitrogen or argon for 20 minutes. The PSS studies were accomplished by ¹H NMR spectroscopy and were performed in standard pyrex NMR tubes.

5.8.4.  **Electrochemical studies**

**Cyclic voltammetry**

Cyclic voltammetry was performed using a Pine AFCBP1 bipotentiostat. The electrochemical cell consisted of a four neck flame dried round bottom flask. The electrodes used are: as a working electrode (WE) a Pt (3 mm) working electrode, as a reference electrode (RE) a silver wire and as a counter electrode (CE) a coiled Pt wire (the later being separated by a fritted tube glass form the bulk of reaction). At the beginning of each experiment the electrodes as thoroughly cleaned as explained in section 3.9.5.1. All the peak potentials were referenced using ferrocene as an internal standard at the end of each experiment ($E_{\text{ferrocene / ferrocenium}} = 475$ mV vs SCE).

**Electrolysis**

A flame dried round bottom flask containing a solution of the PSS, containing the compound to be analyzed ($10^{-3}$ M) and Bu₄NPF₆ ($10^{-1}$ M) was subjected to a fixed potential, using a Pt mesh working electrode for 10 min. As a counter electrode Pt wire was used and as a reference electrode a silver wire was used. The solution was stirred
with a magnetic bar and nitrogen or argon bubbled through the entire time of the experiment. The ring–opening process was monitored by $^1$H NMR spectroscopy.

5.8.5. Synthesis and Characterization

Synthesis of compound 5.7: 4-Hydroxy-2,6-Dimethylpyridine. 2,6-dimethyl-4H-pyran-4-one, compound 5.6 (10.01g, 80.5 mmol) was dissolved in 28% ammonium hydroxide (50 mL) and the reaction was heated at 50 °C for 15 h. The solution was cooled to room temperature and the reaction flask was left at the same temperature in the fumehood until crystals were formed (1 day); at which point the crystals were filtered, crushed, dried on high vacuum pump (1 day) and identified as the desired compound (3.82 g) which was taken into next step without further purification. Yield 36%.

M.p 221–222 °C; $^1$H NMR (400 MHz, D$_2$O) δ 6.27 (s, 2H), 2.33 (s, 6H), OH not seen; $^{13}$C NMR (100 MHz, D$_2$O) δ 180.2, 149.8, 113.7, 18.1; HRMS (ESI) calcd for C$_7$H$_9$NO 123.0684 found (M+H)$^+$ 124.0769.

Synthesis of compound 5.8: 4-bromo-2,6-dimethylpyridine. 1L round bottom flask was charged with compound 5.7 (5.031 g, 36.7 mol) was dissolved in CHCl$_3$ (100 mL) and to this solution was added Phosphorus pentabromide (PBr$_5$) (15.21 g, 33.7 mmol) in 10 portions. The reaction was heated at 60 °C for 1 h until the solvent was evaporated. The resulting orange residue was heated at 120-140 °C for 4 h until a black tar was formed. After cooling for 1 h, the reaction mixture – the black tar was broken into pieces with a spatula and added over a solution of NaOH (4 g) in water (250 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were dried over sodium sulfate and concentrated. Flash column chromatography (0% to 50% EtOAc in
hexanes) gave the desired product as a transparent pungent oil (2.54 g) that solidifies upon standing in the fridge. Yield (38 %)

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.16 (s, 2H), 2.69 – 2.25 (br s, 6H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 159.4, 133.1, 123.2, 24.0; FT-IR 3064, 2922, 1561, 1448, 1108, 715 cm\(^{-1}\); HRMS (ESI) calcd for C\(_7\)H\(_8\)BrN 184.9840 found (M+H\(^+\)) 185.9938.

**Synthesis of compound 5.9: 3-bromo-2-phenylthiophene.** In a 3 neck round bottom flask equipped with a jacketed condenser and a magnetic stirrer were added together: phenylboronic acid (4.308 g, 35.3 mmol), 2,3-dibromothiophene (8.548 g, 35.3 mmol), Na\(_2\)CO\(_3\) (3.00 g, 35.3 mmol), toluene (100 mL) and water (75 mL). The reaction mixture was refluxed for 1 h while purged with nitrogen. After one h the catalyst Pd(PPh\(_3\))\(_4\) (0.268 g, 0.23 mmol) was added to the reaction mixture. The reaction mixture was refluxed under nitrogen for 15 h. The heat source was removed and the reaction mixture was allowed to cool down at room temperature for 1 h, the layers were separated and aqueous layer was extracted with Et\(_2\)O (3 x 100 mL). The combined organic layers were washed with water (200 mL), brine (200 mL), dried over MgSO\(_4\) and filtered. The solvent was removed under reduced pressure and the crude, a dark brown oil, was purified using column chromatography (silica/hexanes) yielding colorless oil as the desired compound (R\(_f\) = 0.8) 5.41 g. Yield: 64 %.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 – 7.68 (m, 2H), 7.51 – 7.44 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 5.5 Hz, 1H), 7.09 (d, J = 5.4 Hz, 1H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 138.3, 132.9, 131.8, 129.2, 128.6, 128.4, 125.2, 107.7. LRMS (CI) calcd for C\(_{10}\)H\(_7\)BrS (M\(^+\)) 237.9 found (M+H\(^+\)) 239.1.
Synthesis of compound 5.11: 3-bromo-5-chloro-2-phenylthiophene. 3-Bromo-2-phenylthiophene (5.9) (9.00 g, 3.67 mmol) was dissolved in benzene (250 mL) and glacial acetic acid (100 mL). N-Chlorosuccinimide (5.020 g, 3.67 mmol) was added and the solution was refluxed for 16 h with the aid of a sand bath. The heat source was removed and the reaction mixture was allowed to cool down at room temperature and neutralized by pouring slowly the content of the round bottom flask over a saturated solution of Na$_2$CO$_3$. The layers were separated and the aqueous layer was extracted Et$_2$O (2 X 100 mL). The combined organic extracts were washed with brine (100 mL) and dried over MgSO$_4$ and filtered. The solvent was removed under reduced pressure. The crude (light brown oil) was purified by column chromatography through silica gel and hexanes yielding 8.10 g (29.6 mmol) of pure colorless oil that solidifies on high vacuum pump. Yield: 78%.

M.p = 39–40 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.59 (dd, J = 1.2, 8.3 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.41 – 7.37 (m, 1H), 6.92 – 6.90 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.1, 132.0, 130.2, 129.5, 128.9, 128.7, 128.6, 106.0; HRMS (APCI) Calcd for C$_{10}$H$_6$BrClS (M)$^+$ (271.9062) found (M)$^+$·271.9063, 273.9040, 274.9071.

![Image of molecule](image)

5.12

Synthesis of compound 5.12: 1,2-bis(5-chloro-2-phenyl-3-thienyl)hexafluorocyclopent-1-ene. A flame dried 100 mL round bottom flask was charged with a solution of 3-bromo-5-chloro-2-phenylthiophene (5.11) (5.00 g, 18.2 mmol) in anhydrous ether (100 mL) from a Na / benzophenone still and cooled to -78 °C using a dry ice / acetone bath. The reaction mixture was treated with n-Butyllithium (n-BuLi) (7.30 mL of a 2.5 M solution in hexanes) dropwise under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 30 min and a yellow precipitate formed. Octafluorocyclopentane (1.22 mL, 9.10 mmol) was added at once using a gas tight syringe previously cooled on a block of dry ice. After stirring at this temperature for an h, the cooling bath was removed and the reaction mixture was allowed to warm at room temperature and stirred for 1 h. The reaction was quenched by pouring the content
of the round bottom flask over a solution of 5% HCl (25 mL). The organic layer was
separated and set aside. The aqueous layer was extracted with diethyl ether (2 X 100
mL). The organic layers were combined and washed with water (100 mL), brine (100
mL), dried over MgSO4 and filtered. The solvent was evaporated under reduced
pressure and the crude brown solid was purified using column chromatography
silica/hexanes yielding (three successive purifications) 2.83 mg of pure product as white
crystalline product. Yield: 56%.

M.p = 157-161 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.27 (tt, \(J = 6.0, 12.0\) Hz, 1H),
7.21 (br t, \(J = 7.5\) Hz, 2H), 6.86 – 6.83 (m, 2H), 5.79 (s, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\))
\(\delta\) 143.72, 135.84 (broad triplet), 131.3, 131.3, 129.8, 129.1, 129.0, 128.2, 128.7, 127.8,
127.76, 125.80, 125.80, 122.74, (tt, \(J = 25.5, 229.5\) Hz,116.03,), (tt \(J = 22.5, 274.5\) Hz,
110.89,). The coupling \(^{13}\)C-\(^{19}\)F constants are consistent with reported values for
perfluorinated alkanes. FT-IR 3064, 2985, 2909, 1491, 1272, 701, 578; HRMS (APCI)
calcd C\(_{25}\)H\(_{12}\)Cl\(_2\)F\(_6\)S\(_2\) 559.9662 found (M)\(^+\) 559.9648.

Synthesis of compound 5.3o: 1,2-bis(2-phenyl-5(2,6-dimethylpyridin-4-yl-3-thienyl)hexafluorocyclopent-1-ene. A flame dried two neck round bottom flask
equipped with a stirrer was charged with compound 5.12. With the aid of a canula diethyl
er ether (from Na / benzophenone still) was added to the round bottom flask appreciatively
150 mL. The reaction mixture was mixed at room temperature, under inert atmosphere
in order to completely dissolve the switch in the solvent. The reaction mixture was
cooled down to 0 °C (ice and water bath). With the aid of a air tight syringe n-Butyllithium
(n-BuLi), 2.5M in hexanes, (5.6 mL, 14 mmol) over a period of 5 min. Once the lithiation
was deemed completed tributyl borate (B(OBu)\(_3\)) (3.22 g, 14 mmol) was added at once
with the aid of an air tight syringe. The cooling bath was removed and the reaction
mixture was allowed mix at room temperature for an h. The reaction was monitored by
TLC (silica, hexanes 100%) and was deemed complete when the majority of the material
did not move from the baseline. The solvent was removed in vacuo and the resulted brown sticky material was suspended in a mixture of THF (50 mL) and water (25 mL). A mixture of 4-bromo-2,6-dimethylpyridine (2.52 g, 13.6 mmol), K$_2$CO$_3$, 6.91 g, 50.0 mmol) was added and the reaction mixture was deoxygenated by purging with N$_2$ for an h. Catalytic Pd(PPh$_3$)$_4$ (45 mg, 0.04 mmol) was quickly added and the mixture heated to reflux under positive N$_2$ for 14 h. The heating source was removed and the reaction mixture was allowed to cool down to room temperature for one h. The layers were separated and the aqueous layer was further extracted with Et$_2$O (2 X 100 mL). The combined organic layers were washed with water (2 X 100 mL) and then with brine (100 mL), dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by combi-flash chromatography using gradient hexanes/ethyl acetate (50-100%) yielded the product as off white solid (1.386 g). Yield: 29%.

M.p 216–219 °C; $^1$H NMR (400 MHz, CD$_3$CN) δ 7.16 – 7.09 (m, 3H), 7.06 – 6.98 (m, 4H), 6.53 (s, 1H), 2.49 (s, 6H); $^{13}$C NMR (100 MHz, CD$_3$CN) δ 158.2, 146.0, 141.0, 139.9, 131.3, 128.8, 128.4, 127.2, 124.4, 123.8, 117.0, 115.7, 22.3 (13 signals observed out of 14); FT-IR 2987, 2902, 1600, 1067, 565 cm$^{-1}$; HRMS (ESI) calcd for C$_{39}$H$_{28}$F$_6$N$_2$S$_2$ 702.1598 found (M+H)$^+$ 703.1672.

![Synthesis of compound 5.2o](image)

**Synthesis of compound 5.2o:** 1-(2-phenyl-5-(1,2,6-trimethylpyridinium-4-yl)-3-thienyl)-2-(2-phenyl-5-(2,6-dimethylpyridin-4-yl)-3-thienyl)-hexafluorocyclopenten-1-ene hexafluorophosphate. A solution of compound 5.3o (0.203 g, 0.23 mmol) and dimethyl sulfate (0.03 g, 0.23 mmol) in anhydrous CH$_2$Cl$_2$ (25 mL) was refluxed for 15 hours. The reaction was monitored by TLC (silica, CH$_3$CN:H$_2$O:KNO$_3$ (sat), 10:1.0:0.1). Purification of the desired compound from a mixture containing the unreacted started material and the double methylated product was achieved by column chromatography: basic alumina reactivity 1 and CH$_3$CN:KNO$_3$(sat) 89 : 2. The obtained pure product was dissolved in minimal DMF (1 mL) and added
dropwise to as stirred aqueous solution NH₄PF₆ (1.5 g) in water (10 mL). The off white precipitate was collected by centrifugation. Excess ammonium salts were removed by centrifugation by re-suspending the precipitate in deionized water. The process was repeated for 6 times with copious amounts of water, at which point the solid pellet was dissolved in CH₃CN, transferred to a tared vial and concentrated by rotary evaporation yielding 158 mg of the product as an off white solid. Yield 80 %.

M.p 225–230 °C; ¹H NMR (400 MHz, CD₃CN) δ 7.57 (s, 2H), 7.31 (s, 2H), 7.12 – 7.04 (m, 6H), 7.00 – 6.94 (m, 4H), 6.77 (s, 1H), 6.66 (s, 1H), 3.88 (s, 3H), 2.68 (s, 6H), 2.56 (s, 6H); ¹³C NMR (100 MHz, CD₃CN) δ 155.7, 154.7, 151.1, 149.6, 145.9, 145.6, 138.5, 136.6, 130.6, 130.4, 129.8, 129.7 129.2, 129.2, 129.2,128.9, 128.0 (3 signals very close at 128.0, probably ¹⁹F-¹³C coupling), 127.2, 127.1, 124.8, 124.4, 121.3, 118.2, 39.3, 20.7, 19.9 (27 signals found out of 30); FT-IR 2995, 2922, 2859, 1572, 831, 492 cm⁻¹; HRMS (ESI) calculated for C₄₀H₃₁F₁₂N₂PS₂ 862.1475 found 717.1832 [ (M)⁺ - (PF₆)].

Synthesis of compound 5.1o²⁺: 1,2-bis(2-phenyl-5-(1,2,6-trimethylpyridinium-4-yl)-3-thienyl)hexafluorocyclopenten-1-ene bis(hexafluorophosphate). A solution of compound 5.3o (0.174 g, 0.247 mmol) and dimethyl sulfate (0.224 g, 1.77 mmol) in anhydrous CH₃CN (10 mL) was refluxed for 15 hs. The reaction was monitored by TLC (silica, CH₃CN : H₂O : KNO₃ (sat), 10:1.0:0.1). Purification of the desired compound from a mixture containing the unreacted started material and the single methylated product was achieved by column chromatography: basic alumina reactivity 1 and CH₃CN : KNO₃(sat) 95:5. The obtained pure product was dissolved in minimal DMF (1 mL) and added dropwise to as stirred aqueous solution NH₄PF₆ (1 g) in water (10 mL). The off white precipitate was collected by centrifugation. Excess ammonium salts were removed by centrifugation by re-suspending the precipitate in deionized water. The process was repeated for six times with copious
amounts of water, at which point the solid pellet was dissolved in CH$_3$CN, transferred to a tared vial and concentrated by rotary evaporation yielding 0.1918g of the product as an off white solid. Yield: 76 %.

M.p > 275 °C; $^1$H NMR (400 MHz, CD$_3$CN) δ 7.68 (s, 2H), 7.25 – 7.13 (m, 3H), 7.08 (dd, J = 6.5, 3.0, 2H), 6.88 (s, 1H), 3.99 (s, 3H), 2.80 (s, 6H); $^{13}$C NMR (100 MHz, CD$_3$CN) δ 156.1, 151.4, 146.1, 137.0, 130.7, 130.0, 129.6, 129.5, 127.5, 125.0, 121.6, 39.6, 21.0. (13 signals found out of 15); FT-IR 2989, 2976, 2903, 1643, 1398, 556 cm$^{-1}$; HRMS (ESI) cald for C$_{41}$H$_{34}$N$_2$S$_2$F$_6$ (1022.1351) found 366.1032 { [ M - (2 X PF$_6$) ] / 2}.  

3.10

Synthesis of compound 3.10: 1-(2,5-bis(5-methyl-2-thienyl)-3-thienyl)heptafluorocyclopent-1-ene. A 100 mL round bottom flask was charged with a solution of compound 3.6 (1.318 g, 3.70 mmol) in anhydrous ether (100 mL) from freshly distilled and cooled to -78 °C using a dry ice / acetone bath. The reaction mixture was treated with n-BuLi (1.48 mL of a 2.5 M solution in pentane) dropwise under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 30 minutes and a yellow precipitate formed. Octafluorocyclopentane (1.00 mL, 7.40 mmol) was added at once using a gas tight syringe previously cooled on a block of dry ice. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction mixture was allowed to warm at room temperature and stirred for 1 h. The reaction was quenched by pouring the content of the round bottom flask over a solution of 5% HCl (25 mL). The organic layer was separated and set aside. The aqueous layer was extracted with diethyl ether (3 X 100 mL). The organic layers were combined and washed with water (100 mL), brine (100 mL), dried over MgSO$_4$ and filtered. The solvent was evaporated under reduced pressure and the crude brown solid was purified using column chromatography silica/hexanes yielding (three successive purifications) 0.964 g of pure product as a bright yellow powder. Yield: 56 %.
Synthesis of compound 5.13: 1-(2,5-bis(5-methyl-2-thienyl)-3-thienyl)-2-(5-chloro-2-methyl-3-thienyl)hexafluorocyclopent-1-ene. A flame dried 100 mL round bottom flask was charged with a solution of 3-bromo-5-chloro-2-methylthiophene (0.3611 g, 1.71 mmol) in anhydrous ether (100 mL) freshly distilled and cooled to -78 °C using a dry ice / acetone bath. The reaction mixture was treated with n-Butyllithium (n-BuLi) (0.7 mL of a 2.5 M solution in pentane) dropwise under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 30 min and a yellow precipitate formed. Compound 3.10 was dissolved in a 15 mL of anhydrous ether freshly distilled and added at once to the reaction mixture with the aid of a glass tight syringe. The reaction was allowed to warm up to -40 °C and allowed to react at this temperature for 4 h. The cooling bath was removed and the reaction mixture was allowed to react for 15 h. The reaction mixture was quenched by slowly pouring the content of the round bottom flask to a 5 % HCl solution (100 mL). The organic layer was separated and set aside, the aqueous layer was washed 2 X 50 mL diethyl ether. The combined organic layers were washed with brine (100 mL) and dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by flash-column chromatography (silica / hexanes Rf = 0.8) afforded 226 mg of the desired compound as an off white powder. Yield: 23 %.

M.p 148–150 °C; 'H NMR (400 MHz, CDCl₃) δ 7.18 (s, 1H), 7.02 (d, J = 3.5 Hz, 1H), 6.75 – 6.69 (m, 1H), 6.62 (dd, J = 1.1, 3.5 Hz, 1H), 6.52 (d, J = 3.5 Hz, 1H), 6.13 (s, 1H), 2.53 (d, J = 0.6 Hz, 3H), 2.49 (d, J = 0.7 Hz, 3H), 1.83 (s, 3H); ¹³C NMR (100 MHz,
CDC\textsubscript{3}) \(\delta\) 142.8, 140.5, 139.4, 138.5, 133.3, 130.4, 126.8, 126.7, 126.2, 126.0, 125.6, 124.5, 124.3, 123.9, 122.4, 15.4, 15.3, 13.9 (found 18 signals out of 21); HRMS (APCI) calcd for C\textsubscript{24}H\textsubscript{15}ClF\textsubscript{6}S\textsubscript{4} 579.9649 found 579.9672 (M)\textsuperscript{+}.  

\[ \text{Synthesis of compound 5.140: } 1-(2,5-bis(5-methyl-2-thienyl)-3-thienyl)-2-(2-methyl-5-(2,6-dimethylpyridin-4-yl)-3-thienyl)hexafluorocyclopent-1-ene. \]

A flame dried two neck round bottom flask equipped with a stirrer was charged with: compound 5.13 (1.876 g, 3.24 mmol). With the aid of a canula diethyl ether (freshly distilled) was added to the round bottom flask approximately 250 mL. The reaction mixture was cooled down to 0 °C (ice and water bath). With the aid of a air tight syringe n-Butyllithium (n-BuLi), 2.5M in hexanes, (1.3 mL, 3.3 mmol) over a period of 5 minutes. Once the lithiation was deemed completed by TLC monitorization, B(OBu)\textsubscript{3} (0.7558 g, 3.5 mmol) was added at once with the aid of an air tight syringe. The cooling bath was removed and the reaction mixture was allowed mix at room temperature for an h. The reaction was monitored by TLC (silica, hexanes 100%) and was deemed complete when the majority of the material did not move from the baseline. The solvent was removed in vacuo and the resulted brown sticky material was suspended in a mixture of THF (50 mL) and water (30 mL). A mixture of 4-bromo-2,6-dimethylpyridine (0.62 g, 3.3 mmol), K\textsubscript{2}CO\textsubscript{3}, (0.45 g, 3.5 mmol) was added and the reaction mixture was deoxygenated by purging with N\textsubscript{2} for an h. Catalytic Pd(PPh\textsubscript{3})\textsubscript{4} (26 mg, 0.022 mmol) was quickly added and the mixture heated to reflux under positive N\textsubscript{2} for 14 hs. The heating source was removed and the reaction mixture was allowed to cool down to room temperature for one h. The layers were separated and the aqueous layer was further extracted with Et\textsubscript{2}O (2 X 50 mL). The combined organic layers were washed with water (2 X 100 mL) and then with brine (100 mL), dried over MgSO\textsubscript{4} and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by comby-flash chromatography using
gradient hexanes/ethyl acetate (50-100%) yielded the product as a greenish oil that expanded on the high vacuum pump forming a solid greenish foam (0.5687 g), 26%.

M.p 175–178 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (s, 1H), 7.01 (d, $J = 3.5$, 1H), 6.95 (s, 2H), 6.71 (d, $J = 2.5$, 1H), 6.66 (s, 1H), 6.48 (dd, $J = 3.5$, 11.6, 2H), 2.56 (s, 6H), 2.51 (s, 3H), 2.21 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.35, 142.30, 142.17, 141.20, 140.53, 138.54, 138.52, 136.68, 133.27, 130.71, 126.60, 126.21, 125.98, 125.77, 124.65, 124.52, 124.31, 122.48, 116.04, 24.48, 15.39, 15.09, 14.19 (22 signals out of 25 expected). HRMS (ESI) calcd for C$_{31}$H$_{23}$F$_6$NS$_4$ 651.0618 found (M+H)$^+$ 652.0720.

Synthesis of ring–closed 5.14c. A standard pyrex round bottom flask was charged with 300 mL anhydrous CH$_3$CN (SPS) solution containing 0.1516g, 0.239 mmol of ring–open isomer 5.14o. The solution was purged with Argon for 30 min, upon the reaction flask was kept under inert atmosphere. The round bottom was irradiated with a 313 nm light from a handheld TLC visualization lamp for 4 h and a half and the photoconversion was periodically monitored by $^1$H NMR spectroscopy (every hour). Every hour small aliquots were taken out of the reaction mixture, the solvent evaporated in vacuo and dissolved in CD$_3$CN. All the steps were done in the dark. The reaction mixture contained approximately 92 % ring–closed isomer and 8 % ring–opened isomer. The purification was done by column chromatography (in the dark) silica/ EtOAC : Hexanes 70:30. Due to the very close Rf of the isomers only about half of the material was deemed pure ring–closed isomer the other half contained also the ring–opened isomer hence the yield 0.0650 g yield 43% as dark-blue powder. Yield: 43%.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (d, $J = 3.7$ Hz, 1H), 7.08 (d, $J = 3.7$ Hz, 1H), 7.01 (s, 2H), 6.74 (s, 1H), 6.72 (dd, $J = 1.0$, 3.7 Hz, 1H), 6.49 (dd, $J = 1.1$, 3.7 Hz, 1H),
6.43 (s, 1H), 2.53 (s, 6H), 2.50 (s, 3H), 2.35 (d, J = 0.9 Hz, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.6, 148.5, 147.8, 145.8, 141.6, 140.3, 133.9, 129.5, 128.8, 127.2, 124.0, 117.2, 116.4, 112.8, 24.4, 15.9, 15.2.

**Synthesis of compound 5.4o**: 1-(2,5-bis(5-methyl-2-thienyl)-3-thienyl)-2-(2-methyl-5-(1,2,6-trimethylpyridinium-4-yl)-3-thienyl)hexafluorocyclopent-1-ene hexafluorophosphate. A solution of compound 5.14o (403 mg, 0.62 mmol) and dimethyl sulfate 0.189 g, 1.50 mmol) in anhydrous CH$_3$CN (10 mL) was refluxed for 15 h. The reaction was monitored by TLC (silica, CH$_3$CN:H$_2$O:KNO$_3$ (sat), 10:1.0:0.1).

Purification of the desired compound from a mixture containing the unreacted started material and the single methylated product was achieved by column chromatography: basic alumina reactivity 1 and CH$_3$CN : KNO$_3$(sat) 95 : 5. The obtained pure product was dissolved in minimal DMF (1 mL) and added dropwise to as stirred aqueous solution NH$_4$PF$_6$ (1 g) in water (10 mL). The off white precipitate was collected by centrifugation. Excess ammonium salts were removed by centrifugation by re-suspending the precipitate in deionized water. The process was repeated for 6 times with copious amounts of water, at which point the solid pellet was dissolved in CH$_3$CN, transferred to a tared vial and concentrated by rotary evaporation yielding 405 mg of the desired product as an off white/yellowish solid. Yield: 81%.

M.p 164–167 °C, with decomposition from yellow solid to a dark brown solid; $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 7.69 (s, 2H), 7.36 (s, 1H), 7.18 (s, 1H), 7.15 (d, J = 3.6 Hz, 1H), 6.81 (dd, J = 3.6, 1.04 Hz, 1H), 6.50 (d, J = 3.56 Hz, 1H), 6.48 (dd, J = 3.4 Hz, 0.8), 3.94 (s, 3H), 2.74 (s, 5H), 2.52 (s, 3H), 2.25 (s, 3H), 2.02 (s, 3H); $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta$ 155.9, 148.8, 146.5, 142.9, 141.3, 138.7, 136.8, 134.6, 132.6, 130.3, 129.9, 127.2, 126.7, 126.7, 125.3, 123.7, 122.5, 121.2, 121.2, 39.5, 20.9, 14.4, 13.8. FT-IR 2988,
Photochemical route: synthesis of photochemical ring-closed isomer of compound 5.4c\(^+\). A standard pyrex NMR tube was charged with 1 mL CD\(_3\)CN solution containing 1.04 mg of ring-opened isomer 5.4o\(^+\). The solution was purged with nitrogen for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 5 min intervals and the photoconversion was periodically monitored by \(^1\)H NMR spectroscopy. PSS state achieved in 2 h of 64 %.

Synthesis of compound 5.4c\(^+\) (synthetic route). A solution of compound 5.14c (0.0650 mg, 0.099 mmol) and dimethyl sulfate (0.025 g, 0.19 mmol) in anhydrous CH\(_3\)CN (25 mL) was stirred at room temperature and in the dark for 3 days. The reaction was monitored by TLC (silica, CH\(_3\)CN : H\(_2\)O : KNO\(_3\) (sat), 9 : 1.0 : 0.1). Purification of the desired compound from a mixture containing also the unreacted starting material was achieved by column chromatography: basic alumina reactivity 1 and CH\(_3\)CN : KNO\(_3\) (sat) 95 : 5. The obtained pure product was dissolved in minimal DMF (1 mL) and added dropwise to as stirred aqueous solution NH\(_4\)PF\(_6\) (0.25 g) in water (5 mL). The off white precipitate was collected by centrifugation. Excess ammonium salts were removed by
centrifugation by re-suspending the precipitate in deionized water. The process was repeated for 6 times with copious amounts of water, at which point the solid pellet was dissolved in CH₃CN, transferred to a tared vial and concentrated by rotary evaporation yielding 12 mg (15 %) of the product as black blue long crystals. All the manipulation of the ring–closed isomer was done in the dark. ¹H NMR (500 MHz, CD₃CN) δ 7.75 (s, 2H), 7.34 (d, J = 3.8 Hz, 1H), 7.22 (s, 1H), 7.18 (d, J = 3.7 Hz, 1H), 6.90 (s, 1H), 6.66 (s, 1H), 6.60 (s, 1H), 3.93 (s, 3H), 2.72 (s, 7H), 2.53 (s, 3H), 2.36 (s, 3H). (the singlet at 2.36 overlaps with water traces).

Synthesis of compound 5.16: 1,2-bis(2-methyl-5-(2,6-dimethyl-4-pyridinyl)-3-thienyl)hexafluorocyclopent-1-ene. A flame dried two neck round bottom flask equipped with a stirrer was charged with compound 5.15 (2.00 g, 4.5 mmol). With the aid of a canula diethyl ether from the SPS was added to the round bottom flask approximately 150 mL. The reaction mixture was cooled down to -20 °C (some dry ice and acetone). With the aid of an airtight syringe n-Butyllithium (n-BuLi), 2.5M in hexanes, (4.1 mL, 10 mmol) over a period of 10 min. Once the lithiation was deemed completed by TLC minitorization, tributyl borate (B(OBu)₃) (2.31 g, 10 mmol) was added at once with the aid of an air tight syringe. The cooling bath was removed and the reaction mixture was allowed mix at room temperature for an h. The reaction was monitored by TLC (silica, hexanes 100%) and was deemed complete when the majority of the material did not move from the baseline. The solvent was removed in vacuo and the resulted brown sticky material was suspended in a mixture of THF (80 mL) and water (20 mL). A mixture of 4-bromo-2,6-dimethylpyridine (1.84 g, 10 mmol), K₂CO₃, (1.24 g, 10 mmol) was added and the reaction mixture was deoxygenated by purging with N₂ for 1 h. Catalytic Pd(PPh₃)₄ (50 mg, 0.32 mmol) was quickly added and the mixture heated to reflux under positive N₂ for 14 h. The heating source was removed and the reaction mixture was allowed to cool down to room temperature for 1 h. The layers were separated and the aqueous layer was further extracted with Et₂O (2 X 50 mL). The
combined organic layers were washed with water (2 X 100 mL) and then with brine (100 mL), dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation yielding a brown oil. Purification by comby-flash chromatography using gradient hexanes / ethyl acetate (50-80%) yielded the product as a greenish oil that solidifies on the high vacuum pump forming greenish powder 1.03 g. Yield: 38%.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, J = 19.1 Hz, 1H), 7.13 – 7.08 (m, 2H), 2.57 (s, 6H), 1.96 (d, J = 10.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.7, 143.3, 140.7, 139.9, 126.00, 124.3, 116.3, 24.5, 14.7. HRMS (ESI) calcd for C$_{29}$H$_{24}$F$_6$N$_2$S$_2$ 578.1285 found (M+H)$^+$ 579.1379.

**Synthesis of compound 5.5o$^{2+}$**: 1,2-bis(2-methyl-5-(1,2,6-trimethylpyridinium-4-yl)-3-thienyl)hexafluorocyclopent-1-ene bis(hexafluorophosphate). A solution of compound 5.15 (0.323 g, 0.56 mmol) and dimethyl sulfate 0.15 g, 1.2 mmol) in anhydrous CH$_3$CN (20 mL) was refluxed for 15 hs. The reaction was monitored by TLC (silica, CH$_3$CN:H$_2$O:KNO$_3$ (sat), 10:1.0:0.1). Purification of the desired compound from a mixture containing traces of: unreacted starting material and the single methylated product was achieved by column chromatography: basic alumina reactivity 1 and CH$_3$CN : KNO$_3$(sat) 95 : 5. The obtained pure product (as a nitrate salt) was dissolved in minimal DMF (1 mL) and added dropwise to as stirred aqueous solution NH$_4$PF$_6$ (0.7 g) in water (10 mL). The off white precipitate was collected by centrifugation. Excess ammonium salts were removed by centrifugation by re-suspending the precipitate in deionized water. The process was repeated for 5 times with copious amounts of water, at which point the solid pellet was dissolved in CH$_3$CN, transferred to a tared vial and concentrated by rotary evaporation yielding 0.279 mg of the product as an off white solid. Yield: 56%.

M.p 222–227 °C with decomposition from white solid to dark solid; $^1$H NMR (400 MHz, CD$_3$CN) δ 7.98 (s, 1H), 7.88 (s, 2H), 3.99 (s, 3H), 2.79 (s, 6H), 2.11 (s, 3H); $^{13}$C
NMR (100 MHz, CD3CN) δ 156.1, 149.5, 145.9, 135.3, 130.2, 126.5, 121.8, 116.9, 39.7, 20.2, 14.2; FT-IR 2987, 2972, 2906, 1643, 1414m 1066, 557 cm⁻¹; HRMS (ESI) calcd for C₃₁H₃₀N₂S₂F₆ (898.1038) found 304.0874 { [ M-(2 X (PF₆)] / 2};

**Synthesis of photochemical ring–closed isomer of compound 5.5c²⁺.** A standard pyrex NMR tube was charged with 2 mL CD₃CN solution containing 1.20 mg of ring–opened isomer 5.5o²⁺. The solution was purged with Nitrogen for few minutes (just enough not to evaporate the solvent). The entire tube was irradiated with a 365 nm light from a handheld TLC visualization lamp for 1 min intervals and the photoconversion was periodically monitored by 'H NMR spectroscopy. PSS state achieved in 15 minutes 97 %. 'H NMR (400 MHz, CD₃CN) δ 7.84 (s, 2H), 7.26 (s, 1H), 3.97 (s, 3H), 2.76 (s, 6H), 2.25 (s, 3H).
6. Conclusions and Future Direction

The dithienylethenes (DTEs) are well-suited to be used in light filtering technologies (Chapter 2). However, these devices require DTEs to have desirable properties: good photochemical behaviour, no electrodegradation and good thermal stability. The photochemistry of such compound is well documented in the literature. On the other hand, only a few electrochromic DTEs are reported and they degrade regardless of the stimulus (photo, electrochemical or thermal). The research presented in this thesis has focused not only in presenting a few more versatile compounds, but rather finding trends between the molecular architecture (appropriate functional groups) and key aspects of their complex behaviour.

There are two novel contributions to science:

One can make educated guesses, based on the trends and observations reported in Chapters 3 and 4, to design and synthesize a DTE molecule that undergoes catalytic oxidative ring−opening suitable for devices that require extended life operation.

From the photochemical point of view all the compounds presented in Chapter 3, have similar properties as the parent compound 2.17. The functional groups appended in $\alpha$ positions of the terthiophene backbone (compounds 3.1, 3.2 and 3.3) do not change significantly the photostationary states, the values ranging from 70 % to 85 % (Table 3.23). One idea tested within this work, was that the dynamic equilibrium between the photochemical ring−closing (desired) and ring−opening (undesired) can be shifted towards the wanted reaction, by increasing the conjugation of the external substituents. This approach might not be useful in the context of DTEs with an aromatic internal group, as even the second member of the family presented in Figure 5.1 (3.4c) shows significant instability in the dark.
The compounds presented in Chapter 4 (benzothiophene derivatives) have lower photostationary values, hence they cannot be used in photoelectrochromic devices without further structural modifications (Figure 4-6).

Within terthiophene series (Chapter 3) it was proven that the electrodegradation can be avoided by carefully choosing the appending groups, so far alkyl moieties showed to be great candidates (compounds 3.1 and 3.2). Compound 3.3 (α fluorine substituted) undergoes electropolymerization. A perfluorinated version, compound 6.1 (Figure 6-2) was not proposed as the π-π stacking might favour the thermal ring–opening in the dark. Compounds 4.1 and 4.2 exhibit extensive electropolymerization and further research is necessary to find the proper candidates from the benzothiophene series.

From the point of view of thermal stability in the dark it was speculated that π–π stacking might be a driving force to the thermal ring–opening in the dark. Furthermore one will know when and how to employ DFT calculations to predict the stability of the ring–closed form in the dark, for this type of compounds. For example, one cannot use the calculated difference in total energy to predict the half life values, but

Figure 6.1. Structures of compounds 2.17 and 3.4, the first two compounds in the “extended conjugation” series.

Figure 6.2. Proposed structure for a perfluorinated DTE from the terthiophene series.
one can examine different calculated parameters (such as the distance between a particular proton (Hc) and the top shielding thiophene ring (Figure 3.19) and the distance δ between the reactive carbon atoms (Figure 3.15)) to determine which one among the proposed candidates is the most stable in the dark.

The second relevant contribution is the research presented in Chapter 5, that shows the electrochemically driven reductive-ring–closing might be bielectronic. If this is the case synthesizing a fully photo- electrochromic DTE that is stable in the dark is not achievable. In the view of results presented within this work and in the literature,\textsuperscript{29} that the efficiencies of the oxidative catalytic ring–opening are enhanced in the case of the “neutral” ring–closed isomers that are thermally unstable in the dark (the more unstable the ring–closed isomer in the dark, the smaller the oxidation peak of this form) one can bypass the requirement of aromatic internal groups. One can use $i$-Pr as internal group (Figure 5.19) instead of α methylated thiophene (2.1±), to find the balance between the steric and electronic factors, both in “neutral” state and oxidized state.

The main objective of this study was to determine whether one can logically design DTE compounds that would integrate the three key properties, photochromic, electrochromic and thermal bistability in a predictable manner. The results presented thought this work are suggesting that this goal is achievable. One can use the research presented here as a tool in designing, synthesizing and handling (Figure 3.35) compounds with a predictable behaviour.
7. References


35. Gorodetsky, B. The Design of Dual-Mode Photochromic and Electrochromic 1,2-Dithienylcyclopentene Dyes. Simon Fraser University, Simon Fraser University Library Burnaby, BC, Canada, 2008.
   1988, 53, 6136-6138.


66. Wadford, C. C. A Dithienylethene that gates a spontaneous reaction and photolyzes with visible light and synthetic progress towards a corresponding hexatriene. Simon Fraser University Library Burnaby, BC, Canada, 2012.


74. Frisch, M. J. e. a., *Gaussian 09*, Gaussian, Inc.: Wallingford CT, 2009


