The Photochromism of a Diester Linked Bisanthracene

by
Russel Goldberg
B.Sc., Concordia University, 2013

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science

in the
Department of Chemistry
Faculty of Science

© Russel Goldberg 2016

SIMON FRASER UNIVERSITY
Spring 2016
Approval

Name: Russel Goldberg
Degree: Master of Science (Chemistry)
Title: The Photochromism of a Diester Linked Bisanthracene

Examining Committee:

Dr. Vance E. Williams
Senior Supervisor
Associate Professor

Dr. Jeffrey J. Warren
Supervisor
Assistant Professor

Dr. Andrew J. Bennet
Supervisor
Professor

Dr. Neil R. Branda
Internal Examiner
Professor

Chair: Dr. Michael H. Eikerling
Professor

Date Defended/Approved: April 15, 2016
Abstract

A bisanthracene diester was synthesized in an effort to increase the rate of the anthracene photochemical dimerization. Preliminary reactions of the bisanthracene resulted in the formation of an intramolecular product that cyclizes across the 9, 10, 1', 4'-position of the anthracenes. This results in an unsymmetrical dianthracene that possesses an isolated alkene group. The research in this thesis describes the photochromic properties of the bisanthracene, as well as studies into the reactivity of the isolated alkene.

Different photochromic properties of the bisanthracene were investigated. The optimized conditions were found using a dilute solution in benzene while selectively exciting the bisanthracene.

The addition of a peroxycarboxylic acid to the photoproduct resulted in the formation of an epoxide, which caused the intramolecular product to become more photochemically and thermally stable. This resulted in a locked state. Attempts to unlock this system by removal of the epoxide resulted in only low yields of the bisanthracene, but does represent a preliminary gated system for anthracene photochemical reaction.

**Keywords**: Bisanthracene; Unsymmetrical dianthracene; Gating; Photoswitch; Alkene; Epoxide
Dedication

To my friends and family.
Acknowledgements

I would like to thank my supervisor, Dr. Vance Williams, for letting me work in his lab as well as teaching me so many things in the time that I worked with him. I would also like to thank my committee members, Dr. Jeff Warren and Dr. Andrew Bennet for their advice throughout my time here. I also appreciate Dr. Neil Branda for agreeing to be my internal examiner.

I would like to thank the past and current members of the Williams group, especially Dr. Kevin Bozek, for their help in the lab even though we did not do research in the same field. I would also like to mention Kevin Nickel for his initial experiments in my area of research. Another thanks goes to the members of the Branda lab for their help and insights as well as to the Britton group for the use of some equipment. And I would like to thank the faculty and staff in the SFU chemistry department.

Finally I would like to thank my friends and family for their support.
Table of Contents

Approval .................................................................................................................. ii
Abstract .................................................................................................................. iii
Dedication .............................................................................................................. iv
Acknowledgements ............................................................................................... v
Table of Contents .................................................................................................. vi
List of Tables ......................................................................................................... viii
List of Schemes ...................................................................................................... viii
List of Figures ....................................................................................................... x
List of Acronyms ................................................................................................... xii

Chapter 1. General Introduction .............................................................................. 1
  1.1. Introduction .................................................................................................... 1
  1.2. Photochromism ............................................................................................. 1
  1.3. Anthracene .................................................................................................... 2
    1.3.1. Excitation Pathway ................................................................................ 3
    1.3.2. Anthracene Dimers ............................................................................... 4
    1.3.3. Applications .......................................................................................... 4
  1.4. Intramolecular Anthracene Reaction ............................................................. 6
  1.5. Unusual Dianthracenes ............................................................................... 9
    1.5.1. Unsymmetrical Dianthracenes ............................................................. 10
    1.5.2. Anthracene-Naphthalene Hybrids ....................................................... 16
  1.6. Gated Photochromism ................................................................................. 17
    1.6.1. Gated Anthracene ................................................................................. 20
  1.7. Research Described in this Thesis ................................................................. 21

Chapter 2. Photochromism of the Bisanthracene ..................................................... 22
  2.1. Introduction .................................................................................................... 22
  2.2. Previous Research ......................................................................................... 22
    2.2.1. Photochromism of Bisanthracene 2.1a .............................................. 23
    2.2.2. Photoswitching of 2.3a ..................................................................... 25
  2.3. Proposed Research ......................................................................................... 27
    2.3.1. Synthesis of the Bisanthracene ............................................................ 28
  2.4. Photochemical Reactions in the Rayonet® .................................................... 29
    2.4.1. Photooxidation .................................................................................... 29
    2.4.2. Effects of Solvent and Reaction Time ............................................... 29
    2.4.3. Concentration ...................................................................................... 33
    2.4.4. Effects of Different Length Linkers .................................................... 34
    2.4.5. Photoreversion Reaction .................................................................... 36
  2.5. Monochromatic Light ..................................................................................... 37
  2.6. LED Light Source ......................................................................................... 39
    2.6.1. Reaction Time ...................................................................................... 39
    2.6.2. Concentration ....................................................................................... 40
    2.6.3. Effects of Different Length Linkers .................................................... 41
  2.7. Conclusion ...................................................................................................... 42
  2.8. Future Work .................................................................................................. 42
Chapter 3. Functionalized Dianthracene and its Photochromic Properties ................................................................. 44
3.1. Introduction ............................................................................................................. 44
3.2. Substitution Reactions ........................................................................................ 46
3.3. Addition Reactions ................................................................................................ 48
   3.3.1. Bromination .................................................................................................... 48
   3.3.2. Epoxidation .................................................................................................... 49
      3.3.2.1. Stability of Epoxide ................................................................................ 49
         3.3.2.1.1. Thermal Stability ............................................................................. 49
         3.3.2.1.2. Photochemical Stability ................................................................. 50
3.4. Deoxygenation of Epoxide .................................................................................. 53
3.5. Reactions with Epoxide ....................................................................................... 54
3.6. Conclusion ............................................................................................................. 56
3.7. Future Work ........................................................................................................... 57

Chapter 4. Experimental ............................................................................................... 59
4.1. Chapter 2 .............................................................................................................. 59
   4.1.1. General Procedure of Synthesizing Bisanthracenes 2.1a, 2.1b, and 2.1c ..... 59
   4.1.2. Photochemical Experiments for 2.1a .......................................................... 60
   4.1.3. Photochemical Experiments for 2.1b and 2.1c ............................................ 61
   4.1.4. Rayonet® Irradiation .................................................................................... 61
   4.1.5. Fluorometer Irradiation ............................................................................... 61
   4.1.6. LED Irradiation ............................................................................................ 61
4.2. Chapter 3 .............................................................................................................. 62
   4.2.1. Wacker Reaction ......................................................................................... 62
   4.2.2. Typical procedure for Bromination of Alkene ............................................. 62
   4.2.3. Typical procedure for Epoxidation of Alkene .............................................. 63
   4.2.4. Deoxygenation of Epoxide ........................................................................... 63
   4.2.5. Typical procedure with Boron Trifluoride Etherate ..................................... 63

References ..................................................................................................................... 65
Appendix A. Emission of Devices .................................................................................. 68
Appendix B. Beer-Lambert plots .................................................................................. 70
Appendix C. 1H-NMR spectra of Reactions Resulting in Complex Mixtures ............ 72
Appendix D. 2D-NMR spectra of 2.3a .......................................................................... 73
Appendix E. Crystal Structure Data of 2.3a ............................................................... 75
List of Tables

Table 1.1. Quantum yield of unimolecular photodimerization of linked bisanthracene 1.1 .................................................................................................................. 8
Table 2.1. The distribution of products from 2.1a, 2.1b, and 2.1c ........................................ 35
Table 2.2. The distribution of products from 2.1a, 2.1b, and 2.1c ........................................ 41

List of Schemes

Scheme 1.1. a) Azobenzene and b) Diarylethene photoreaction ........................................ 2
Scheme 1.2. The photodimerization reaction of anthracene to dianthracene ................. 2
Scheme 1.3. The mechanistic conversion of anthracene to dianthracene i) fluorescence, ii) non-radiative decay, iii) concentration quenching, iv) intersystem crossing, v) dissociation, vi) dimerization ........................................ 3
Scheme 1.4. Formation of the different isomers of a 9-mono-substituted photoreaction .................................................................................................................. 4
Scheme 1.5. The representative photoreaction of a bisanthracene with various Z (linker) from table 1 .................................................................................................. 7
Scheme 1.6. The intramolecular reaction of bisanthracene to form [4+2]- and [4+4]-photocycloaddition products ................................................................. 9
Scheme 1.7. The intramolecular reaction of bisanthracene to form solely the [4+2]-photocycloaddition product ........................................................................... 9
Scheme 1.8. Anthracene dimerization occurring as [6+6] and [2+2] photocycloadditions ........................................................................................................... 10
Scheme 1.9. The different products formed in the photoreactions of 1.6, 1.8, and 1.10 .................................................................................................................. 11
Scheme 1.10. The photoreaction of the bis(anthracene)-crown ether with and without metal ions ................................................................................................. 12
Scheme 1.11. The unsymmetrical dianthracene produced from the dimerization of the I_{2,6} didecyloxyanthracene derivatives .............................................. 13
Scheme 1.12. The photoreaction of anthracene containing the SiMe_{2}(CH_{2})_{2}SiMe_{2} linker ............................................................................................................ 14
Scheme 1.13. a) The formation of products from the photoreaction of 1-acetylanthracene and methyl 1-anthracencarboxylate. b) The formation of products of photoreacting 1-acetylanthracene with anthracene ............................................................................. 15
Scheme 1.14. a) The photoproducts of the cyclization of 9-methylanthroate and b) 9-butylanthroate with furan ............................................................................. 16
Scheme 1.15. The dimerization of anthracene and naphthalene to synthesize the unsymmetrical anthracene-naphthalene hybrids .......................................................... 17

Scheme 1.16. Representative scheme of the irradiation of linked anthracene-naphthalene systems .................................................................................................................. 17

Scheme 1.17. The equilibrium of the diarylethene to undergo ring-closing reaction ................................................................................................................................. 18

Scheme 1.18. Using a disulphide bridge to gate the ring-closing reaction of a diarylethene ..................................................................................................................... 19

Scheme 1.19. Changing the functional group to allow the ring-closing reaction to occur .......................................................................................................................... 20

Scheme 2.1. The optimized conditions for the formation of 2.1a ........................................ 28

Scheme 2.2. The photodimerization of the bisanthracene with various linker lengths ........................................................................................................................... 35

Scheme 3.1. The pathway to functionalize the 2- or 3- position of an anthracene by substitution of the unsymmetrical dianthracene .................................................................. 45

Scheme 3.2. The effect of an addition reaction on an alkene site to induce gated photochromism ............................................................................................................. 46

Scheme 3.3. Proposed pathway to functionalize the bisanthracene via the Wacker synthesis .................................................................................................................. 47

Scheme 3.4. Trial reaction with cyclohexene to cyclohexanone using Grubbs new conditions ................................................................................................................ 47

Scheme 3.5. The reaction of 2.3a with Br₂ which results in a complex mixture ......... 49

Scheme 3.6. Epoxidation of the unsymmetrical dianthracene ......................................................................................................................................................................................... 49

Scheme 3.7. The proposed deoxygenation reaction with PPh₃ ......................................................................................................................................................................................... 54

Scheme 3.8. The scheme to functionalize the 2- or 3- position of anthracene through the epoxide intermediate .................................................................................... 54

Scheme 3.9. Product distribution after the isomerization of 3.6, with a Lewis acid ........................................................................................................................................ 56

Scheme 3.10. The reversible photochromism of the anthracene system....................... 57

Scheme 3.11. The reaction mechanism with different locked states: a) hydroboration, oxidative work up; b) dehydration; c) oxidation .............. 58
List of Figures

Figure 1.1. The light-driven reversible reaction between state A and state B............. 1
Figure 1.2. Anthracene endoperoxide (AO$_2$)................................................................. 3
Figure 1.3. The Woodward-Hoffman rules describing a) a photochemical disallowed [4+2] cycloaddition reaction and b) a photochemical allowed [2+2] cycloaddition reaction .......................................................... 4
Figure 1.4. King's$^{15}$ irradiation of anthracene derivatives to synthesize two dimensional polymers (adapted and taken from source) ..................... 5
Figure 1.5. Schluter's$^{16}$ irradiation of anthracene derivatives to synthesize two dimensional polymers (adapted and taken from source) ..................... 6
Figure 1.6. Gated photochromism with a chemical or physical change from state C to “lock” the reverse reaction .......................................................... 18
Figure 1.7. Using DNA to gate the intramolecular anthracene reaction .................. 21
Figure 2.1. Expected photoreaction of 2.1a to form the dianthracene product 2.2. ........................................................................................................... 22
Figure 2.2. Unknown products 2.3a and 2.4a from irradiation of 2.1a ................. 23
Figure 2.3. $^1$H-NMR spectrum of 2.3a............................................................................... 24
Figure 2.4. Crystal Structure of 2.3a................................................................................... 24
Figure 2.5. The observed photoproducts after irradiating 2.1a.............................. 25
Figure 2.6. The normalized UV-Vis of 2.1a (blue, 0.74mM, CH$_2$Cl$_2$) and 2.3a (red, 0.7mM, CH$_2$Cl$_2$)......................................................................................... 26
Figure 2.7. The reversion of 2.3a back to 2.1a using 285 nm light............................. 26
Figure 2.8. Thermal reversibility at 80°C of 2.3a to 2.1a........................................... 27
Figure 2.9. The distribution of photoproducts from irradiation of 2.1a in the Rayonet® (top: 2.1a in a 1 mM solution of benzene; bottom: 2.1a in a 2 mM solution of benzene)................................................................. 31
Figure 2.10. The distribution of photoproducts from irradiation of 2.1a in the Rayonet® (top: 2.1a in a 1 mM solution of acetonitrile; bottom: 2.1a in a 2 mM solution of acetonitrile)................................................................. 32
Figure 2.11. The irradiation of 2.1a at different concentrations in benzene (top) and acetonitrile (bottom).................................................................................. 34
Figure 2.12. The representation of a molecule with a flexible linker folding in solution ............................................................................................................... 36
Figure 2.13. The fluorescence of 2.1a as it photoreacts to 2.3a............................... 38
Figure 2.14. The formation of 2.3a from 2.1a by irradiation by the LED system over time................................................................................................................. 40
Figure 2.15. Concentration study of the bisanthracene with the LED system ......... 41
Figure 2.16. Proposed bisanthracene for future studies .......................................................... 43

Figure 3.1. $^1$H-NMR spectrum of 3.6 in $d^6$-DMSO before and after heating at 80°C for 1 hour .................................................................................................................................. 50

Figure 3.2. The normalized absorbance of 3.6 (black, 0.13 mM, CH$_2$Cl$_2$) compared to 2.3a (red, 0.70 mM, CH$_2$Cl$_2$) and 2.1a (blue, 0.74 mM, CH$_2$Cl$_2$) .................................................................................................................................. 51

Figure 3.3. The opening of 2.3a (top) and 3.6 (bottom) investigated by UV-Vis after irradiating at specific times .................................................................................................................. 52

Figure 3.4. The $^1$H-NMR spectra of 3.6 before and after irradiation in the Rayonet® at 300 nm .................................................................................................................................. 53
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$^1$H</td>
<td>Proton</td>
</tr>
<tr>
<td>A</td>
<td>Anthracene</td>
</tr>
<tr>
<td>$A_2$</td>
<td>Dianthracene</td>
</tr>
<tr>
<td>ANH</td>
<td>Anthracene Naphthalene Hybrids</td>
</tr>
<tr>
<td>AO$_2$</td>
<td>Anthracene Endoperoxide</td>
</tr>
<tr>
<td>cm$^{-1}$</td>
<td>Wavenumber</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation Spectroscopy</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>$d$</td>
<td>Deuterium</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DIAD</td>
<td>Diisopropyl Azodicarboxylate</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribose Nucleic Acid</td>
</tr>
<tr>
<td>Equiv</td>
<td>Equivalent</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td>hh</td>
<td>Head-to-Head</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear Multiple-bond Correlation</td>
</tr>
<tr>
<td>HOMO*</td>
<td>Excited Highest Molecular Orbital</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear Single Quantum Correlation</td>
</tr>
<tr>
<td>ht</td>
<td>Head-to-Tail</td>
</tr>
<tr>
<td>hv</td>
<td>Light</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared Spectroscopy</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem Crossing</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>M</td>
<td>Mole per Litre</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>$m$-CPBA</td>
<td>Meta-chloroperoxybenzoic Acid</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-Charge Ratio</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar Concentration</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimoles</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinide</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OAc</td>
<td>Acetate</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>qu</td>
<td>Quintet</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>sec</td>
<td>Seconds</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TBP</td>
<td>Tris(n-butyl)phosphine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
</tbody>
</table>
Chapter 1.
General Introduction

1.1. Introduction

The first focus of this thesis is to study the photochemical properties to see the possible increase in rate of the anthracene dimerization. The chemical reactivity of the alkene produced from the unusual 9, 10, 1’, 4’-dianthracene derivative will also be looked at for the possible novel way of functionalizing the 2- and 3- position of anthracene. The other goal is to investigate the possibility of using the alkene to gate the photochemical reaction. This chapter describes photochromism and gated photochromism of anthracene derivatives, with emphasis on the formation of these uncommon unsymmetrical dianthracenes and the concept of gating.

1.2. Photochromism

Photochromism is defined as a reversible transformation that uses light to change a chemical species from one structure to another (i.e., structure A to structure B). This change in structure is accompanied by a change in chemical and physical properties. This can be termed as a photoswitch (Figure 1.1). In some cases, one form (structure B) can also revert back thermally if the structure is thermodynamically unstable.¹

\[
A \xleftrightarrow[\text{hv}]{\text{hv}/\Delta} B
\]

Figure 1.1. The light-driven reversible reaction between state A and state B

There are several type of these photoswitches, which, depending on the change in physical and chemical properties, can be used for different applications which will be discussed later. Some examples include: the trans/cis isomerization of azobenzene across the N=N double bond² (Scheme 1.1a), the ring open/closing reaction of
diarylethenes\(^3\) (Scheme 1.1b) and the dimerization photoreaction of anthracene, which is the main focus of this thesis and the applications for the photochromism of anthracene will be mentioned later.

\[
\text{Scheme 1.1. a) Azobenzene and b) Diarylethene photoreaction}
\]

### 1.3. Anthracene

Anthracene photodimerization was discovered by Fritzche in 1867.\(^4\) Fritzche noticed that upon irradiation with sunlight, an anthracene solution that was distilled from coal tar formed a crystalline precipitate. This precipitate was insoluble in most organic solvents. Upon heating, the precipitate could be thermally reverted to a more soluble anthracene form.\(^4\) In 1891, Elbs, using cryoscopy, was able to determine that the precipitate was a dimer that did not fluoresce.\(^5\) It was not until 1932 that Hengstenberg determined the first crude X-ray structure of the precipitate.\(^6\) Then finally in 1966, the X-ray structure was fully characterized and the crystalline precipitate was unambiguously identified as dianthracene (Scheme 1.2).\(^6\)

\[
\text{Scheme 1.2. The photodimerization reaction of anthracene to dianthracene}
\]
1.3.1. Excitation Pathway

The mechanism of anthracene dimerization to dianthracene was first investigated by Luther and Weigert in 1905, but it was not until the 1950s that systematic attempts to study the mechanism of dimerization were undertaken (Scheme 1.3). At that time, Bowen and coworkers noticed that as the fluorescence of anthracene (A) decreased, the dimerization quantum yield to make dianthracene ($A_2$) increased. This led to the proposal that the mechanism from anthracene to dianthracene usually goes through the singlet excited state ($^1A^*$). Bowen also saw that there was a limit to this process because at high concentrations, the anthracenes aggregate causing the excited state to quench. In the presence of dioxygen, anthracenes react to form endoperoxides ($AO_2$, Figure 1.2), which result from the anthracene triplet state ($^3A^*$), due to the intersystem crossing (ISC) from the anthracene singlet excited state. In 1974 Ferguson first saw evidence of an intermediate called an excimer or excited dimer ($^1A^*A$), that can be defined as a dimer comprising of one molecule in the excited state and the other in the ground state, and as later proved by Cohen and coworkers in 1976, which collapses to form dianthracene. The discovery of the excimer, along with the development of the Woodward-Hoffman rules (Figure 1.3) in 1965, led to an increased interest in the photodimerization mechanism.

$$A \xrightarrow{hv} A^* \xrightarrow{v} A*A \xrightarrow{vi} A_2$$

Scheme 1.3. The mechanistic conversion of anthracene to dianthracene i) fluorescence, ii) non-radiative decay, iii) concentration quenching, iv) intersystem crossing, v) dissociation, vi) dimerization

**Figure 1.2.** Anthracene endoperoxide ($AO_2$)
1.3.2. Anthracene Dimers

The formation of dianthracene derivatives was initially investigated in the early 1900s. Most of these investigations focused on derivatives of anthracene with functional groups at the 9- and 10-positions because those positions are the most synthetically accessible. Moreover, substitution at any other site could cause many different regioisomers of dianthracene to form, which complicates both characterization and purification. In contrast, substitution at 9- or 10- site of anthracene typically only leads to two isomers, the head-to-head (hh) and the head-to-tail (ht) isomer. The hh isomer is more thermally labile due to steric factors and therefore 9-monosubstituted anthracenes lead to mostly ht isomers (Scheme 1.4) though there are some electronic factors that can cause the hh structures to be preferred.6

![Figure 1.3. The Woodward-Hoffman rules describing a) a photochemical disallowed [4+2] cycloaddition reaction and b) a photochemical allowed [2+2] cycloaddition reaction](image)

Scheme 1.4. Formation of the different isomers of a 9-mono-substituted photoreaction.

1.3.3. Applications

Photochromism can change molecular properties by using an external stimulus. In the case of anthracene when irradiate with light to dianthracene, the large change in dipole between the two states will be cause different guest-host interactions. This property can be used for many different applications including smart materials,11
photoactive receptor,\textsuperscript{12} and modulate magnetic properties.\textsuperscript{13} Anthracene photochromism, due to its low efficiencies and side reactions with oxygen, is not used as much as the unimolecular photoreactions of azobenzenes or diarylethenes. In recent years, the use of anthracene has increased primarily due to the fact that the anthracene reaction is a bimolecular process. This bimolecular reaction can be used to reversibly crosslink materials.\textsuperscript{14} In 2014, two papers published in Nature Chemistry by King\textsuperscript{15} (Figure 1.4) and by Schulter\textsuperscript{16} (Figure 1.5), describe anthracene single crystal photodimerization reactions to synthesize two of the first reversible two-dimensional polymers. Such materials can be used for membranes and nonlinear optics.

\textbf{Figure 1.4.} King’s\textsuperscript{15} irradiation of anthracene derivatives to synthesize two dimensional polymers (adapted and taken from source)
1.4. Intramolecular Anthracene Reaction

The dimerization process is concentration-dependent, with improved efficiencies at higher concentration. However, due to the low solubility of anthracene, the efficiency of the process is limited. To increase the efficiency of this reaction, it is common to make this bimolecular process unimolecular by linking two anthracenes together.\(^5\) When two anthracenes are linked together by a flexible chain, photodimerization will depend on the conformational dynamics of the chain, which will be explained in this section. Note that all linked system throughout this thesis will be referred to as “bisanthracene” to distinguish them from the dianthracene dimers. These bisanthracene are usually studied at low concentrations (\(\leq10^{-3}\) M) to minimize competition with intermolecular photodimerization. In the low concentration limit, the unimolecular process is independent of concentration.\(^6\)

There are many different linker systems that have been synthesized since the 1960s. These structures have shown that efficiency is strongly dependent on the length
of the linker, the nature of the linker and how this functional group is linked to the anthracene.\textsuperscript{6}

Inspection of table 1.1 sets out prototypical bisanthracene systems. Table 1.1 shows that a -CH\textsubscript{2}- linker group has higher efficiency than that of a -(CH\textsubscript{2})\textsubscript{4}-, suggesting that, beyond a certain length, longer chains decrease the efficiency of the cycloaddition reaction. Replacing one of the methylene groups with oxygen (-(CH\textsubscript{2})\textsubscript{3}- to -CH\textsubscript{2}OCH\textsubscript{2}-) leads to an increase in the efficiency of the reaction. It was suggested that the increase in efficiency is due to the oxygen reducing the rotational energy barrier.\textsuperscript{18} The addition of another oxygen further increases the efficiency. Increasing the polarity of the solvent also leads to an increase in the efficiency, as can be seen from the increase in quantum yield of the -OCH\textsubscript{2}O- linker in methanol versus methylcyclohexane (Scheme 1.5). The highest quantum yields to date were reported for the -COCH\textsubscript{2}CH\textsubscript{2}- and -COCH(Me)CH\textsubscript{2}- linked systems, with quantum yields of 0.65 and 0.72 in benzene, respectively. The author suggested that these types of linkers are the most efficient because they promote intersystem crossing to the triplet state instead of reacting through the singlet state (Scheme 1.5).

\textbf{Scheme 1.5.} The representative photoreaction of a bisanthracene with various Z (linker) from table 1
Table 1.1. Quantum yield of unimolecular photodimerization of linked bisanthracene 1.1

<table>
<thead>
<tr>
<th>Linker (-Z-)</th>
<th>Dimerization Quantum Yield</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₂⁻¹⁷</td>
<td>0.15</td>
<td>Benzene</td>
</tr>
<tr>
<td>-(CH₂)₃⁻¹⁸</td>
<td>0.14</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>-(CH₂)₄⁻¹⁹</td>
<td>0.08</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>-CH₂OCH₂⁻¹⁸</td>
<td>0.30</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>-OCH₂O⁻²⁰</td>
<td>0.36</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>-OCH₂O⁻²⁰</td>
<td>0.50</td>
<td>Methanol</td>
</tr>
<tr>
<td>-O(CH₂)₂O⁻¹⁹</td>
<td>0.22</td>
<td>Methanol</td>
</tr>
<tr>
<td>-COCH₂CH₂⁻²¹</td>
<td>0.65</td>
<td>Benzene</td>
</tr>
<tr>
<td>-COCH(Me)CH₂⁻²¹</td>
<td>0.72</td>
<td>Benzene</td>
</tr>
<tr>
<td>-COCH(Me)CH₂CH₂⁻²¹</td>
<td>0.40</td>
<td>Benzene</td>
</tr>
</tbody>
</table>

One of the limitations of trying to synthesize one- or two-membered linking groups is that anthracenes can cyclize by [4+2]-photocycloaddition to form a non-classical (9,10:1’,2’) dianthracene instead of the classical (9,10:9’10’) dianthracene (Figure 1.7). The formation of the non-classical dimerization is most likely caused when the excimer forms of the two anthracenes are not parallel.²² Therefore the -COCH₂⁻-linked system, 1.2, produces a mixture of [4+2]- and [4+4]-products, (Scheme 1.6) while -CO⁻, 1.3, linker gives only [4+2]-products, 1.4 (Scheme 1.7). From this it can be inferred that efficiency could be optimized by facilitating the spatial overlap of the two anthracenes molecules during excitation.²²
Scheme 1.6. The intramolecular reaction of bisanthracene to form [4+2]- and [4+4]-photocycloaddition products

Scheme 1.7. The intramolecular reaction of bisanthracene to form solely the [4+2]-photocycloaddition product

1.5. Unusual Dianthracenes

As mentioned above, there are non-classical ways for the anthracene to photoreact, with the previous example being the [4+2] photocycloaddition reaction. [2+2]-Photocycloaddition and [6+6]-photocycloaddition reactions are also possible (Scheme 1.8).23,24 Some unusual photoreactions involve a [4+4]-photocycloaddition reaction, where instead of the symmetrical (9,10:9',10') dianthracene, an unsymmetrical dianthracene (9,10:1',4') is formed. The focus of my research, and the next section will be on these unsymmetrical dianthracenes.
1.5.1. **Unsymmetrical Dianthracenes**

The first unsymmetrical dianthracene was reported by Felix in 1976.\(^{25}\) It was derived from the bisanthracene 1.5a that was connected by a sterically hindered linker, SiMe\(_2\)OSiMe\(_2\), between the 9- and the 9'- positions of the two anthracenes. The unusual photoproduct, 1.6a, was obtained with an isolated yield of 80% and was characterized by NMR and UV-Vis. It was hypothesized that the unsymmetrical dimerization behaviour was due to the linker causing the formation of a more unsymmetrical excimer. In 1979, Castellan synthesized the -CH\(_2\)OCH\(_2\)-linked bisanthracene, 1.7, and another bisanthracene using the same linker between the 9- and 1'-positions of the anthracenes, 1.9.\(^{26,27}\) The bisanthracene (1.7) produced a symmetrical product (1.8) while the isomeric bisanthracene (1.9) produced an unsymmetrical product (1.10). This suggests that the formation of the unsymmetrical dianthracene was due to steric constraints or imperfect overlap of the anthracenes in the excimer state. Desvergne also produced this type of unsymmetrical dianthracene when exchanging the oxygen with a CH\(_2\) group (1.5b to 1.6b) (Scheme 1.9).\(^{18}\)

![Scheme 1.8. Anthracene dimerization occurring as [6+6] and [2+2] photocycloadditions](image-url)
In 1986, Desvergne produced an unsymmetrical dianthracene from a bis(anthracene)-crown ether, 1.11 (Scheme 1.10). This bisanthracene was synthesized to study the relationship between photoreactivity and complexation of metal ions. Irradiation of the bis(anthracene)-crown ether was carried out in the presence or absence of cations that complex with the crown ether. When the crown ether 1.11 was irradiated in methanol without the metal complexation, the anthracene dimerized to yield 9,10-1′,4′ dianthracene as the sole photoproduct, 1.12. Formation of the symmetrical photoproduct was hypothesized to be unfavourable due to the repulsion of the lone pairs of the oxygen atoms at the 9-, 10-, 9′- and 10′-positions. The irradiation of the crown ether (1.11) in the presence of Na⁺ caused the cycloaddition to form the product (1.13) due to the cation decreasing the repulsion between the two oxygen lone pairs. Unfortunately, no symmetrical photoproduct (1.13) was isolated; they hypothesized that the product was the symmetrical dianthracene because there was the disappearance of
the anthracene absorbance, but the naphthalene absorption bands, characteristic of 1.12 did not appear.  

![Diagram](image)

**Scheme 1.10. The photoreaction of the bis(anthracene)-crown ether with and without metal ions**

Another example of an unsymmetrically dimerized dianthracene was synthesized by Fages in 1988 by the photodimerization of didecyloxyanthracene derivatives (Scheme 1.11).  

These electron-donating alkoxy groups were used to increase the solubility of anthracene, which would possibly increase the efficiency of dimerization as well. The alkoxy groups were placed in several different positions on the anthracene: the 2- and 6-positions (I$_{2,6}$), the 1- and 4-positions (I$_{1,4}$), the 1- and 5-positions (I$_{1,5}$), and the 1- and 8-positions (I$_{1,8}$). Each compound was irradiated in degassed THF. The photoproducts P$_{1,4}$, P$_{1,5}$, and P$_{1,8}$ were characterized by UV-Vis and $^1$H-NMR, which showed benzene absorbance and a singlet bridgehead proton respectively; these are typical features of dianthracene. The more interesting case was the P$_{2,6}$ derivative that produced two structures in a 5:2 ratio in an isolated yield by fractional distillation followed by column chromatography. The minor product, when characterized with UV-Vis and $^1$H-NMR, showed absorbance and peak signals that were similar to those of P$_{1,4}$, P$_{1,5}$, and P$_{1,8}$. The major product showed naphthalene absorbance in the UV-Vis spectrum, which suggested an unsymmetrical dimerization at the 9- and 10- positions of one anthracene and at the 1'- and 4'-positions of the other anthracene. This result was confirmed by $^1$H-NMR spectroscopy. Each of the dianthracenes products was then heated until they
decomposed to yield the monomer. The unsymmetrical dianthracene was found to be the most stable.\textsuperscript{29}

Scheme 1.11. The unsymmetrical dianthracene produced from the dimerization of the I\textsubscript{2,6} didecyloxyanthracene derivatives

In 1988, Desvargne synthesized an unsymmetrical dianthracene with a four-membered silane linker.\textsuperscript{19} The purpose was to study the effect on photoreactivity of dimerizing several different 4-membered-linked anthracenes. The different linkers that were studied were -(CH\textsubscript{2})\textsubscript{4}- (l\textsubscript{CC}), -O(CH\textsubscript{2})\textsubscript{2}O- (l\textsubscript{00}), -O(CH\textsubscript{2})\textsubscript{3}- (l\textsubscript{01}), -CH\textsubscript{2}O(CH\textsubscript{2})\textsubscript{2}- (l\textsubscript{02}), and SiMe\textsubscript{2}(CH\textsubscript{2})\textsubscript{2}SiMe\textsubscript{2} (l\textsubscript{sic}) (Scheme 1.12). The compounds, after being irradiated, formed the P\textsubscript{CC}, P\textsubscript{00}, P\textsubscript{01}, P\textsubscript{02}, and P\textsubscript{sic} photoproducts. P\textsubscript{CC}, P\textsubscript{00}, P\textsubscript{01}, and P\textsubscript{02} resulted from the cyclization through the 9-, 9'- and 10-, 10'- positions, and were the sole products from these reactions. The products were characterized by UV-Vis and NMR. UV-Vis showed no naphthalene absorbance features and the NMR showed no vinylic protons. When the symmetrical dianthracenes were heated, they reverted back to the starting materials. The P\textsubscript{sic}-linked bisanthracene formed the 9,10-1',4'-dianthracene. This was shown by naphthalene absorbance in UV-Vis and the vinylic peaks in the \textsuperscript{1}H-NMR spectrum. P\textsubscript{sic} was not isolated and the thermal stability test was inconclusive. The reason proposed for this unsymmetrical cyclization compared to the other linkers is that the SiMe\textsubscript{2} group restricted the anthracene’s ability to cyclize at the 9-, 9'- and 10-, 10'- positions because of steric hindrance.\textsuperscript{19}
Scheme 1.12. The photoreaction of anthracene containing the SiMe$_2$(CH$_2$)$_2$SiMe$_2$ linker

The dimerization of anthracene functionalized at locations other than the 9- and 10-positions has received somewhat limited attention due to the potential difficulty of separating and characterizing the various regioisomers of dianthracene that are produced from these photoreactions. In 1996, Becker studied the photoreaction of 1-acetylanthracene 1.14a and methyl 1-anthracenecarboxylate, 1.14b. 1.14a, which upon irradiation in DCM formed 5 regioisomers (Scheme 1.13a). These isomers were the syn-ht dimer (1.15), anti-ht dimer (1.16), syn-hh dimer (1.17), anti-hh dimer (1.18) and the unexpected unsymmetrical anti-ht dimer (1.19) in a ratio of 32:17:17:17:17, respectively. Each regioisomer was isolated by column chromatography and fractional crystallization. The unsymmetrical dimer was unambiguously characterized using X-ray crystallography. There was no evidence of any unsymmetrical syn-hh dimer. In the next experiment, selective excitation of 1-acetylanthracene, 1.14a, with excess anthracene led to the formation of two products: one was the acetyl-substituted dianthracene, 1.20, and the other the unsymmetrical acetyl-substituted dianthracene, 1.21, in a 1:3 ratio (Scheme 1.13b). Upon heating, the unsymmetrical dimer reverted back to starting material.

Irradiation of methyl 1-anthracenecarboxylate (1.14b) also lead to the same five regioisomers: syn-ht dimer (1.15), anti-ht dimer (1.16), syn-hh dimer (1.17), anti-hh dimer (1.18), and the unexpected unsymmetrical anti-ht dimer (1.19), but in a 34:29:19:10:8 ratio; these compounds were also isolated (Scheme 1.13a). What was especially interesting was that the unsymmetrical dimer has an absorbance close to the absorbance of the monomer (340 nm), therefore, the unsymmetrical dimer could revert under irradiation (313 nm), which was demonstrated by selectively irradiating the unsymmetrical dimer to regenerate the starting material.30
Scheme 1.13. a) The formation of products from the photoreaction of 1-acetylanthracene and methyl 1-anthracenecarboxylate. b) The formation of products of photoreacting 1-acetylanthracene with anthracene

In 1997, Noh also discovered the intermolecular unsymmetrical dianthracene, while trying to dimerize 9-methyl anthroate, 1.22.31 This photoreaction produced three different products: the symmetrical ht anthroate dimer (1.23, 83.6%), the unsymmetrical ht dimer (1.24, 8.2%), and the unsymmetrical hh dimer (1.25, 2.1%) (Scheme 1.14a). These products were characterized by ¹H-NMR. Thermolysis studies showed that 1.23 was more thermally stable than either the 1.24 or 1.25. Dimer 1.24 was more thermally stable than 1.25 and both reverted to starting material at temperatures between 79°C to 138°C. The reason stated for the formation of 1.24 and 1.25 was the slow cyclization rate of the other products due to steric effects.31

Noh observed another example of this reactivity by trying to dimerize furan (1.27) with 9-tert-butylanthracene (1.26) (Scheme 1.14b) leading to the formation of three photoproducts: the ht 9-tert-butyl dianthracene (1.28, 65.7%), the furan anthroate hybrid (1.29, 21.8%), and finally, with the smallest yield, the ht unsymmetrical 9-tert-butyl dianthracene, (1.30, 4.2%). The 1.30 dimer was less stable than the 1.28 dimer and the 1.30 dimer was less stable than the 1.26 and 1.25 dimers. The 1.30 dimer, upon heating
from 92.2°C to 109.5°C, reverts to the monomer. Photodissociation of all the photoproducts, produced the monomer forms.\textsuperscript{32}

Scheme 1.14. a) The photoproducts of the cyclization of 9-methylnanthroate and b) 9-butylanthroate with furan

1.5.2. **Anthracene-Naphthalene Hybrids**

The unsymmetrical dianthracene produces an isolated alkene group. This type of functionality can be copied by dimerizing anthracene with naphthalene, which was reported by Albinin \textit{et al} in 1987.\textsuperscript{33} He used the charge transfer complex of the acceptor 9-cyanoanthracene (1.31) with different naphthalene donor molecules (1.32 and 1.33) to attempt the synthesis of anthracene-naphthalene hybrids (ANH) (1.35 and 1.36). In order to minimize the formation of the homodimers (1.34), which forms in competition with the formation of 1.35/1.36, the 1.32/1.33 must have a higher concentration than 1.31. Upon irradiation of 1.31 and 1.32 the yield of 1.35 was 38% and that of 1.34 was 33%. Albinin also tried photodimerizing 1.31 with 1.33. This produced 1.34 in 26% yield and 1.36 in 38% yield (Scheme 1.15).
The dimerization of anthracene and naphthalene to synthesize the unsymmetrical anthracene-naphthalene hybrids

In 1995, Morie et al., synthesized and characterized many different types of linked anthracene-naphthalene systems. They noticed that some linked systems formed two products. One was the intramolecular product between naphthalene and anthracene and the other was the intermolecular product between the two anthracenes (Scheme 1.16).

Now that photochromism especially anthracene photochromism which uses light to dimerize to classical and non-classical dianthracenes is discussed, the next section is on preventing photochromism, called gated photochromism.

A chemical species that is photoactive can sometimes undergo a chemical or physical change that inhibits the reverse photochemical process. For example, if state B undergoes a change to state C, that state C, when irradiated, cannot revert back to state A. Therefore, the reverse reaction is “gated.” The forward reaction can also be gated if
state A undergoes the chemical or physical change that alters its photoreactivity (Figure 1.6).  

![Figure 1.6. Gated photochromism with a chemical or physical change from state C to “lock” the reverse reaction](image)

Gated photochromism has most commonly been reported for diarylethenes. There are two main strategies that are used. The first is where the structure is designed so that the diarylethene is photochemically inactive and can only become active when undergoing a chemical or physical change to free the conformational constraint that is inhibiting the photoreaction. The conformational constraints for diarylethene usually are due to the geometric positions of the thiopenes (Scheme 1.17). Therefore if the thiopenes are parallel, the diarylethene cannot undergo the ring closing reaction and have to equilibrate to the anti-parallel conformation for the photoreaction to ring-close. An example of this was shown by Irie, where the triene (1.37) of the diarylethene is trapped in the parallel conformer, which is photochemically inactive, by the use of a disulfide bridge (-S-S-). Adding tris(n-butyl)phosphine (TBP) reduces the disulfide bridge and allows the triene the conformational freedom to equilibrate to the anti-parallel conformer. (1.38) This becomes photochemically active and can ring close (1.39), when irradiated (Scheme 1.18).  

![Scheme 1.17 The equilibrium of the diarylethene to undergo ring-closing reaction](image)
Scheme 1.18 Using a disulphide bridge to gate the ring-closing reaction of a diarylethene

A second approach is to transform a photoactive diarylethene to an inactive state. For example, Ohsumi et al showed that an acidic alcohol on 1.40 will turn “off” the ring-closing reaction due to the competing reaction of the proton transfer with the maleimide backbone upon irradiation. The phenol can be converted to an ester via acylation (1.41), which allows the ring-closing reaction to turn “on” due to the absence of the proton transfer. The reaction then can be turned “off” again by hydrolysis of the ester to reform the phenol (Scheme 1.19).
1.6.1. Gated Anthracene

One example of a gated system involving anthracene was reported by Manchester, who added two anthracenes to a strand of DNA (S3-A). Upon irradiation, this system underwent intramolecular dimerization to form a looped DNA structure (S3-AP). When a strand of DNA (T0), which is only partially complementary to S3-A, is added then S3-A and T0 form a duplex (S3-A/T0). When the S3-A/T0 duplex is irradiated, the anthracene from the S3-A strand cannot dimerize and is therefore gated. When a third strand of DNA (S0), which is completely complementary to the T0 strand, is added, the S0 strand makes a new duplex with the T0 strand, T0/S0 duplex. This frees the S3-A strand to dimerize when irradiated (Figure 1.7).

Scheme 1.19. Changing the functional group to allow the ring-closing reaction to occur
In this thesis, the photochemical aspects of a diester linking group between two anthracenes that cyclize to form the 9,10,1,'4'-dianthracene will be investigated. I will focus on the effects of changing reaction parameters that include: the nature of the solvent, concentration, irradiation time, light source, and the length of the linking group. This is because for applications concerning switches, it is optimal to have the photoreaction occur as efficiently as possible (some example of applications are in section 1.3.3), which is the purpose of using the short diester linker. Another aspect that is investigated is the reactivity of the isolated double bond that arises from this unusual cyclization in order to explore the possibility of gating photochromism of this system. The purpose of this is to make a more photochemically and thermally stable dianthracene, which could be used for certain applications (section 3.6).

Figure 1.7. Using DNA to gate the intramolecular anthracene reaction

1.7. Research Described in this Thesis
Chapter 2. Photochromism of the Bisanthracene

2.1. Introduction

As discussed in chapter 1, anthracene photodimerization is a bimolecular reaction, and consequently it has a low efficiency. Linking two anthracenes by a flexible group convert this from a bimolecular to a unimolecular process, thus improving efficiency of the collisions between the two anthracene moieties. This is important for all applications that concern using switches so that anthracene dimerization becomes as efficient as possible. Initial studies carried out by Kevin Nickel in the Williams’ lab focused on the photochemistry of two anthracenes connected by a diester linkage. This linker was chosen because other studies indicated that aromatic diesters show a tendency to fold in solution, which could promote intramolecular photocyclization. A brief overview of his research will be presented in the following section.

2.2. Previous Research

Kevin Nickel’s original objective was to examine the photochemistry of the bisanthracene, 2.1a. It was predicted that this compound would undergo cyclization at the 9-, 9′-, 10- and 10′- positions of the two anthracenes to produce a symmetrical dianthracene 2.2 (Figure 2.1).

![Figure 2.1. Expected photoreaction of 2.1a to form the dianthracene product 2.2.](image-url)
2.2.1. Photochromism of Bisanthracene 2.1a

The photochemical behaviour of 2.1a was investigated by irradiating a 2 mM solution in benzene in a Rayonet® photochemical reactor using lamps that have an output centered at 350 nm (see appendix A). After 45 minutes of irradiation, there was no sign of a white precipitate; typically, anthracene dimers precipitate due to their low solubilities. The solvent was then removed in vacuo to yield a white solid. Analysis of the crude product by $^1$H-NMR spectroscopy indicated the presence of three species (Figure 2.2), one of which was the starting material 2.1a. The minor product was identified as the intermolecular ht-product 2.4a (Figure 2.5) because the $^1$H-NMR spectra showed the original aromatic signals of the anthracene and also the appearance of new aromatic signals at a lower chemical shift due to diminished conjugation. The $^1$H-NMR spectrum of the major compound was not consistent with the expected photoproduct 2.2. The mixture was then purified by column chromatography with a 7:3 ratio of DCM to hexanes as the eluent, followed by second column with a 3:7 ratio of ethyl acetate to hexanes. Purification was more complicated than typical for anthracene photoreactions; dianthracenes are often readily isolated from the starting material because of their much lower solubilities.

![2.1a](image)

Figure 2.2. Unknown products 2.3a and 2.4a from irradiation of 2.1a

Isolation of 2.3a yielded a product with a much more complex $^1$H-NMR spectrum (Figure 2.3) than expected for 2.2, suggesting a low symmetry product. A notable feature of this spectrum was the presence of triplets at 5.9 ppm and 6.1 ppm, which are consistent with vinylic protons. Analysis of the 1D $^1$H-NMR and $^{13}$C-NMR spectrum, as well as 2D NMR experiments (HMBC, HSQC, COSY See Appendix D) suggested that 2.3a was the result of the intramolecular [4+4]-photocycloaddition across the 9- and 10-positions of one anthracene and the 1'- and 4'- positions of the other (Figure 2.5). Based on this assignment, the isolated yield was calculated to be 63%. The structure was
confirmed by X-ray analysis of a single crystal produced by slow evaporation from an acetone solution (Figure 2.4) and the crystal structure data can be found in Appendix E.

Figure 2.3. $^1$H-NMR spectrum of 2.3a

Figure 2.4. Crystal Structure of 2.3a
The appearance of product 2.3a from the irradiation of the bisanthracene 2.1a was unexpected. Anthracene systems can produce unsymmetrical dianthracenes but usually from very sterically rigid linked systems, for example compounds 1.5 and 1.6 (Figure 1.10), which have silane linkers (other examples are in Section 1.5.1). Bisanthracene, 2.1a does not have a rigid linking group therefore it should have formed 2.2. The intermolecular product, 2.4a, was not unexpected due to the normal competition between intermolecular and intramolecular products.

**2.2.2. Photoswitching of 2.3a**

The photochemical and thermal stabilities of 2.3a of this unusual dianthracene were examined to determine if it acts as a photoswitch similar to 9, 10, 9', 10' dianthracenes. The UV-Vis absorption spectra of 2.1a and 2.3a are shown in Figure 2.6. The absorption maximum of 2.1a is at 366 nm, while that of 2.3a is blue shifted to 254 nm. This is a reasonable observation because of the diminished conjugation of 2.3a. This large shift in absorbance makes this system a potential candidate for photochromism, as both species show distinctly different absorption profiles. Thus, in principle, it should be possible selectively excite 2.3a to convert it back to 2.1a, which was analyzed by Kevin Nickel.

**Figure 2.5. The observed photoproducts after irradiating 2.1a**

![Diagram showing the photoproducts of 2.1a](image-url)
In order to examine the photochromism of 2.3a, a 1 mM solution was prepared in benzene and excited in a fluorometer using 285 nm light, and the reaction was monitored by UV-Vis spectroscopy as shown in Figure 2.7. Upon irradiation, the absorption bands of 2.3a were observed to decrease, whereas bands associated with 2.1a grew with increased irradiation times.

Figure 2.7. The reversion of 2.3a back to 2.1a using 285 nm light
Dianthracenes can also thermally revert to their corresponding monomers. In the case of dianthracene, this reaction proceeds only at very high temperatures above 250°C but substituted derivatives tend to revert at lower temperatures. To test for such behaviour, 2.3a was dissolved in $d^6$-DMSO and heated in an oil bath at 80°C. $^1$H-NMR spectroscopy was used to monitor the decomposition. Note that there was still some 2.1a present on the spectra. The vinylic proton signals at 5.9 and 6.1 ppm (triangle) decreased over time, while the signal at 8.6 ppm (circle), associated with the proton at the 10 position of compound 2.1a increased. Therefore, we can say that 2.1a and 2.3a can act as a photoswitch and that 2.3a can revert thermally as well (Figure 2.8).

![Figure 2.8. Thermal reversibility at 80°C of 2.3a to 2.1a](image)

### 2.3. Proposed Research

These preliminary studies raised the question: what effects do reaction parameters (temperature, solvent, irradiation source) have on the formation of 2.3a? My objective is to better understand and optimize these conditions in an effort to increase the yield of 2.3a. These efforts were undertaken in part to facilitate subsequent studies
(Chapter 3) aimed at exploring the chemical reactivity of this compound as well as increasing the efficiency of the anthracene photodimerization reaction for more use in applications as switches.

2.3.1. Synthesis of the Bisanthracene

The bisanthracene 2.1a was initially synthesized by Kevin Nickel according to published procedures using Mitsunobu conditions (Scheme 2.1). This involved dissolving 2 equivalents of 9-anthracene carboxylic acid, 1 equivalent of 1,3-propanediol and 2.9 equivalents of PPh₃ in THF at room temperature and followed by dropwise addition of 2.9 equivalents of DIAD. This mixture was then stirred overnight. The solvent was removed in vacuo and the solid residue was purified by column chromatography. This procedure only gave a yield of 12%. In order to obtain sufficient quantities of 2.1a to carry out detailed photochemical experiments, these reaction conditions were optimized.

The reaction was optimized by changing two conditions. First the reagents were initially mixed at 0°C in THF and then slowly allowed the mixture to warm to room temperature. The second condition that was changed was the order of reagent addition. The original conditions involved adding the carboxylic acid, the diol, and PPh₃ in THF and then slowly adding DIAD. The optimized conditions involved adding the carboxylic acid, PPh₃, DIAD in THF and then slowly adding the diol. The mixture was then allowed to warm up to room temperature and continues to stir over night. The solution was then washed in basic conditions and then purified by column chromatography, eluting with a 4:6 mixture of ethyl acetate and hexanes. The resulting solid was then recrystallized from a mixture of water and ethanol to afford 2.1a in an 83% yield.

Scheme 2.1. The optimized conditions for the formation of 2.1a
2.4. Photochemical Reactions in the Rayonet®

Preliminary tests showed that the dianthracene 2.3a is thermally unstable (see section 2.2.2.). Unfortunately, the Rayonet® photochemical reactor used to form this product produces considerable heat during irradiation and can reach temperatures up to 80°C. It was speculated that thermal effects may have been responsible for a decrease in the overall yield of 2.3a. In an effort to mitigate this issue, the Rayonet® was modified by Amir Asadirad to allow air from an external source to blow through the bottom of the apparatus; this decreased the operating temperature to around 30°C. To compare the yields of 2.3a at different temperatures, a 2 mM solutions of 2.1a in benzene was irradiated in the Rayonet® for 1 hour without cooling (80°C) and another 2mM solution of 2.1a was irradiated with air blowing through it (30°C). The two solutions were analyzed by ¹H-NMR spectroscopy and there was an increased yield of 2.3a by 5% when irradiating 2.1a with air flowing through the Rayonet®.

2.4.1. Photooxidation

Because air was being blown through the Rayonet®, the formation of endoperoxides became a concern due to anthracenes possibly reacting in the presence of O₂. To test the sensitivity of endoperoxide formation, three 2 mM benzene solutions of bisanthracene, 2.1a, were simultaneously irradiated for 1 hour. One sample was degassed through a minimum of three freeze-pump-thaw cycles; the second sample was not degassed but was irradiated under ambient conditions; and the third sample was air saturated for 5 minutes. Each sample was then sealed in a conical-bottom centrifugal tube with a screw cap and irradiated. Sample were analyzed by ¹H-NMR spectroscopy and it was determined that there was no formation of any secondary products, ruling out the formation of endoperoxides. The yields between the three samples varied by only 1-2%. Therefore 2.1a is resistant to photooxidation and can be irradiated in the presence of air.

2.4.2. Effects of Solvent and Reaction Time

Because [4+4]-photocycloaddition reactions of anthracenes are known to be sensitive to solvent polarity,¹⁷ the reaction of 2.1a in benzene and acetonitrile were
monitored as a function of time. A 2 mM benzene solution of bisanthracene, 2.1a, was prepared and divided into 4 test tubes, which were inserted into the Rayonet® carousel and each test tube was irradiated for 30, 60, 90 or 120 minutes. This procedure was repeated for a 2 mM acetonitrile solution of 2.1a. The solvent from each sample was evaporated and the residue analyzed by ¹H-NMR spectroscopy to determine the product distribution after irradiation (Figures 2.9 and 2.10). In order to assess the effect of concentration on yield and product distribution, this experiment was also repeated using 1 mM benzene and acetonitrile solutions.

It was found that within 30 minutes, using bisanthracene in 2 mM benzene, 2.3a reached a maximum yield of around 74%, with only slight fluctuations in the yield at longer irradiation times. The yield of intramolecular product 2.3a from the 1 mM benzene solution reached around 74% within 30 minutes, suggesting only minor effects of concentration on the yield of this product. The product distribution that changed the most was the proportion of the bisanthracene, 2.1a, to intermolecular product 2.4a. When a 1mM solution of 2.1a in benzene is irradiated the yield of 2.3a is 74% and that of 2.4a is 2%. In contrast, irradiation of a 2mM of 2.1a in benzene yields 74% and that of 2.4a fluctuates from 3-4%. The remainder of the material in both cases is 2.1a. The higher yield of 2.4a from 1mM to 2mM is probably due to the production of the intermolecular product being more favourable at higher concentrations.

Irradiation of 1 mM and 2 mM acetonitrile solutions led to precipitation of 2.3a. In the 1 mM solutions, the maximum yield (47%) of 2.3a was reached within 1 hour. In contrast, the yield of the unsymmetrical 2.3a from the 2 mM solution continued to increase even after 2 hours. However, the yield after 2 hours (58%) is still less than that from the 2 mM solution of benzene at 30 minutes. The precipitation should favour the forward reaction, the possible reason why the yield of 2.3a in acetonitrile never had a yield as high as in benzene is due to 2.3a never reaching saturation.

The fact that 2.1a can reach a photostationary state at such a high yield in a nonpolar solvent, especially with how long the linking group is, within 30 minutes was unexpected. This is because bisanthracenes with shorter linking groups usually dimerize more efficiently when reacted in polar solvents (see Table 1.1).
Figure 2.9. The distribution of photoproducts from irradiation of 2.1a in the Rayonet® (top: 2.1a in a 1 mM solution of benzene; bottom: 2.1a in a 2 mM solution of benzene)
Figure 2.10. The distribution of photoproducts from irradiation of 2.1a in the Rayonet® (top: 2.1a in a 1 mM solution of acetonitrile; bottom: 2.1a in a 2 mM solution of acetonitrile)
2.4.3. Concentration

The 1 mM and the 2 mM solutions in benzene (Figure 2.11) reached the photostationary state within 30 minutes and with similar yields. Moreover, there is not a large difference between the yields obtained for the intermolecular product 2.4a in either solution. This suggests that the reaction is concentration-insensitive in benzene. To study this further, solutions of bisanthracene 2.1a ranging from 1 mM to 8 mM in either benzene and acetonitrile were irradiated in the Rayonet® for 1 hour. For both the acetonitrile and benzene solutions, there was only a slight increase in 2.4a from 2% to 8% as concentration increased from 1 mM to 8 mM, demonstrating that the reaction is relatively insensitive to concentration. Interestingly, the yield of 2.1a in benzene decreases from 1 mM to 2 mM (21% to 18%) but from 2 mM to 8 mM, yield of 2.1a increases (18% to 32%); at the same time the yield of 2.3a increased from 1 mM to 2 mM (73% to 76%), but decreased from 2 mM to 8 mM (76% to 56%). It was concluded that this reaction should be carried out at lower concentrations to diminish the yield 2.4a as well as get the highest yield of 2.3a as quickly as possible. In acetonitrile, the reaction follows the same general trends as in benzene, with lower overall yields of 2.3a and higher yields for the intermolecular product 2.4a.
Figure 2.11. The irradiation of 2.1a at different concentrations in benzene (top) and acetonitrile (bottom).

2.4.4. Effects of Different Length Linkers

To investigate the effect on dimerization of changing the linker length on the reaction of tethered bisanthracenes (Scheme 2.2), the propylene bridge was replaced...
with an ethylene or a hexylene chain to afford $2.1b$ and $2.1c$, respectively. The 2 mM solutions of bisanthracenes $2.1a$, $2.1b$, and $2.1c$ in benzene were simultaneously irradiated for 1 hour and $^1$H-NMR spectroscopy was used to quantify the yields by taking the ratio of the integration of the product mixture. Consistent with earlier results, $2.1a$ was converted with a 76% yield to dianthracene $2.3a$, whereas the intermolecular product $2.4a$ was obtained with a 3% yield. In contrast, the ethylene bisanthracene $2.1b$ formed the corresponding intramolecular product $2.3b$ and the intermolecular product $2.4b$ in 58% and 13% yields, respectively. The hexylene derivative $2.1c$ produced the intra- and inter-molecular products in 7% and 16% yields respectively (Table 2.1).

![Scheme 2.2. The photodimerization of the bisanthracene with various linker lengths](image)

**Scheme 2.2.** The photodimerization of the bisanthracene with various linker lengths

<table>
<thead>
<tr>
<th>Starting Material 2.1</th>
<th>n</th>
<th>Yield of Recovered 2.1</th>
<th>Yield of 2.3</th>
<th>Yield of 2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3</td>
<td>18%</td>
<td>76%</td>
<td>3%</td>
</tr>
<tr>
<td>b</td>
<td>2</td>
<td>16%</td>
<td>58%</td>
<td>13%</td>
</tr>
<tr>
<td>c</td>
<td>6</td>
<td>61%</td>
<td>7%</td>
<td>16%</td>
</tr>
</tbody>
</table>
The interesting thing to note is that these trends parallel the effects of linker on the degree of folding in aromatic diesters previously investigated by Kevin Bozek. His research showed that dibenzophenazines linked by a flexible diester groups could fold in solution (Figure 2.12). Upfield shifts in the aromatic region of the $^1$H-NMR spectrum could be used to probe the extent of ground state folding in solution. He tested this with ethylene, propylene, and hexylene linkers, among others, and observed that the propylene-linked discotic liquid crystal spent most of its time folded, while the hexylene linker spent most of its time in the open form, whereas the ethylene was partially folded. My results parallel this, and suggest that 2.1a has the greatest yield of intramolecular product because 2.1a has a stronger tendency to fold than does 2.1b and 2.1c.

![Figure 2.12. The representation of a molecule with a flexible linker folding in solution](image)

### 2.4.5. Photoreversion Reaction

The light emitted from the Rayonet® lamp is centered at 350 nm (from 300 nm to 400 nm, see appendix A). By comparing to the UV-Vis spectra of 2.1a and 2.3a (Figure 2.6), it shows that both complexes absorb at these wavelengths. Further any heat produced by the lamps in this reactor may cause the thermally unstable product 2.3a to revert to 2.1a. Therefore, to investigate the effect of the reverse reaction (i.e., 2.3a to 2.1a), a 1 mM benzene solution of 2.3a was irradiated in the Rayonet® at the same time as a 1 mM solution of 2.1a. The dianthracene 2.3a partially reverted to 2.1a, yielding a 77:23 mixture of these compounds within 20 minutes. The same ratio was obtained for the forward reaction, confirming that this is the photostationary state of the reaction. These results were based on $^1$H-NMR spectroscopy.
2.5. Monochromatic Light

The result from section 2.4 suggests that a monochromatic light source could improve the yield of the cyclization reaction by minimizing absorption by the photoproduct. Monochromatic light from a fluorometer was used to test this hypothesis. A 2 mM solution of 2.1a in benzene was irradiated at 360 nm (25 mm slit width), with the decrease in emission of the bisanthracene 2.1a used to measure the progress of the reaction. When the emission of the bisanthracene reached the photostationary state or stopped decreasing, the sample was removed from the fluorometer (Figure 2.13). ¹H-NMR spectra of the resulting products indicated that the yield of the intramolecular product 2.3a increased from 77% in the Rayonet® to 92% in the fluorometer. The residual yield of 2.1a accounted for 7%; the remaining yield of 2.4a was less than 1%. This suggests that the broad emission of the Rayonet® is responsible for the lower yield of the intramolecular product. This experiment was repeated using a 1 mM solution under the same conditions and the time it took for the emission of the bisanthracene to reach close to zero was around half the time it took for the 2 mM solution. The yield of the 1 mM reaction (91%) was very close to that of the 2 mM solution. Both 1 mM and 2 mM solutions of 2.1a in acetonitrile were also irradiated with the fluorometer under the same conditions. The yields of the intramolecular product for the 1 mM and 2 mM solutions in acetonitrile, once they reached the photostationary state, were 77% and 85% respectively. The yields of the intermolecular product 2.4a were 2% and 3% for the 1 mM and 2 mM solution, respectively. Therefore, by increasing the flux, but still only irradiating 2.1a, the yield could increase even more.
Figure 2.13. The fluorescence of 2.1a as it photoreacts to 2.3a
2.6. LED Light Source

A limitation of the fluorometer is the relatively low photon flux. I next turned to using a LED (light emitting diode) photoreactor built in the Britton group. The LEDs emit at wavelengths higher than 345 nm (see appendix A).

A 1 mM solution of bisanthracene 2.1a in benzene was irradiated for 1 hour in the LED reactor and the proportions of the products were analyzed by $^1$H-NMR spectroscopy. The spectrum showed that the dianthracene 2.3a was formed in 97% yield. Interestingly, however, the temperature of the LEDs can reach up to 80°C, the same as the Rayonet®, but the LEDs still produce a higher yield, suggesting that temperature may not be as large of a factor as previously thought. To investigate this further, the temporal and the concentration tests were performed using the LED system to compare the results to those from the Rayonet®.

2.6.1. Reaction Time

The experiment from section 2.6 was repeated with 1 mM benzene solutions to investigate product formation at earlier times (Figure 2.14). Within 20 minutes, the bisanthracene 2.1a was almost completely converted to 2.3a, showing that under these conditions, it is possible to make relatively pure dianthracene 2.3a quickly. Also, because the reaction does not have to be irradiated for long periods, there is no build-up of heat.
2.6.2. Concentration

Different concentrations of $2.1a$ in benzene were irradiated for 20 minutes using the LED system (Figure 2.15). As the concentration increased, the amount of the intermolecular product also increased, which followed the same trend as with the Rayonet®. Another trend that followed the Rayonet® is that the amount of recovered $2.1a$ at higher concentration increases past 1 mM and the yield of $2.3a$ decreases.
2.6.3. Effects of Different Length Linkers

These experiments with the LED photoreactor suggest that the wide wavelength of the Rayonet® contributes to the lower yield of the dimerized product. In order to examine whether the same trend holds for other linking groups (Scheme 2.2), compounds containing the ethylene linking group 2.1b and the hexylene linking group 2.1c were also examined (Table 2.2). 1 mM benzene solutions of 2.1a, 2.1b and 2.1c were irradiated for 12 minutes. The yields of 2.3a and 2.4a were 87% and 2%, respectively. The yields of 2.3b and 2.4b were 74% and 9%, respectively. The yields of 2.3c and 2.4c were 14% and 5%, respectively. This demonstrates that the intramolecular product forms in higher yields in the LED system than in the Rayonet® reactor for all linked systems.

<table>
<thead>
<tr>
<th>Starting Material 2.1</th>
<th>n</th>
<th>Yield of Recovered 2.1</th>
<th>Yield of 2.3</th>
<th>Yield of 2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3</td>
<td>9%</td>
<td>87%</td>
<td>2%</td>
</tr>
<tr>
<td>b</td>
<td>2</td>
<td>8%</td>
<td>74%</td>
<td>9%</td>
</tr>
<tr>
<td>c</td>
<td>6</td>
<td>76%</td>
<td>14%</td>
<td>5%</td>
</tr>
</tbody>
</table>
2.7. Conclusion

In conclusion, the bisanthracene 2.1a was designed to fold in solution in order to increase the efficiency of dimerization. By controlling the wavelength, this dimerization can occur very quickly and in high yields in benzene, which suggests that it folds very well. Dimerization is less efficient in acetonitrile, which is a more polar solvent. This result was unexpected because in general it’s the shorter linked bisanthracene in polar solvents that dimerize more efficiently. Changing the length of the linking group can cause the proportion of products to differ. Comparison of an ethylene, a propylene, and a hexylene chain shows that the one that forms the highest intramolecular yield was the 3-carbon linked system. Due to the fact that this reaction can be driven almost to completion in 20 minutes and does not need to be deoxygenated makes this a candidate for real-world applications, such as in smart materials. The next chapter will focus on the reactivity of the isolated alkene group of this photoproduct in order to explore the ability to further control the switching of the system.

2.8. Future Work

The intramolecular photoreaction can go to almost completion quickly, it forms unsymmetrical dianthracenes, and does not need to be deoxygenated, all of which are rare properties in anthracene photochemistry. The reasons for these properties have yet to be determined and future work should seek answers to determine the factors that govern this reactivity.

The initial studies were carried out by changing the length of the linking group. While this does change the proportion of products from intramolecular to intermolecular, the unsymmetrical dianthracenes can still forms. Future work will examine the effect of changing the nature of the linking group as shown for compounds 2.5, 2.6, 2.7 and 2.8 (Figure 2.16). This will probe the causes of the photochromic properties of 2.3a, b, and c.
Figure 2.16. Proposed bisanthracene for future studies
Chapter 3.
Functionalized Dianthracene and its Photochromic Properties

3.1. Introduction

In this chapter, I will discuss attempts that were made to functionalize the isolated alkene produced from the intramolecular photoreaction of compound 2.1a. My goals are; (1) identify a new approach to add functional groups at the 2-, 3-, 6-, or 7-positions of anthracene, and (2) to investigate whether it is possible to gate the anthracene photoreaction.

Functionalization of anthracene is generally carried out at the 9- or 10- positions due to the greater reactivity of these positions towards electrophilic substitution. For example, treating anthracene with brominating agents such as NBS or Br₂, affords 9-bromoanthracene and/or 9,10-dibromoanthracene under mild conditions. On the other hand, the 2-, 3-, 6-, and 7-positions of anthracene are harder to modify and synthesis of anthracenes functionalized at these positions generally entails multistep synthesis using harsh conditions with low overall yields. 39

The dianthracene product 2.3a, described in the previous chapter has an isolated alkene moiety, which could act as a reactive site to afford functionalized anthracene derivatives. This is shown conceptually in Scheme 3.1. Because of the higher reactivity of this group towards a variety of reagents, it should be straightforward to install groups at the 2- or 3-positions. Because the resulting dianthracene should also act as a photoswitch, UV-irradiation or heating of this product should afford a new anthracene bearing substituents at the 2- and/or 3-positions.
Scheme 3.1. The pathway to functionalize the 2- or 3- position of an anthracene by substitution of the unsymmetrical dianthracene

While substitution reactions would afford a potentially photoswitchable product, addition reactions across this double bond would remove the conjugation and prevent photochemical and thermal reversion to the acyclic form (Scheme 3.2), thus “locking” the product. Conversely, restoring the double bond would “unlock” the product and allow the system to undergo photoswitching. This “locking” and “unlocking” of the photoproduct is an example of gated photochromism. Although several cases of gated photochromism have been reported for diarylethenes, I am aware of only one example where this has been reported for anthracene, as described in chapter 1. The reason why gated photochromism is being investigated is due to the possibility of increasing the thermal and photochemical stability, which can be advantageous to some applications, which is discussed later (section 3.6). This chapter will explore the reactivity of the isolated alkene of the unsymmetrical dianthracene towards substitution and addition reactions.
3.2. Substitution Reactions

The relatively low thermal stability of dianthracene 2.3a restricts the conditions that can be employed for carrying out substitution reactions on the double bond. Ideally, reactions should be conducted at or below room temperature. A substitution reaction that meets this requirement is examined and described below.

The substitution reaction that was examined is the Wacker reaction that transforms an alkene into a ketone. The Wacker reaction was chosen to form 3.1a/b from 2.3a taking advantage of the tautomerization of the 3.1a/b into an enol with 3.2a/b functionality. 3.2a/b can then revert by heat or light to reform an anthracene bearing a new alcohol group at the 2- or 3- position, 3.3a/b. Although this reaction is typically carried out at elevated temperatures, Grubbs and coworkers have recently reported a room temperature variant of the Wacker reaction. The synthesis that Grubbs developed can be carried out under mild conditions on internal alkenes and tolerates a variety of functional groups (Scheme 3.3).
Scheme 3.3. Proposed pathway to functionalize the bisanthracene via the Wacker synthesis.

The synthesis was first tested with cyclohexene (3.4), which was converted to cyclohexanone (3.5) in quantitative yield (Scheme 3.4). However, when the reaction was attempted with the dianthracene 2.3a, the reaction did not proceed, as indicated by $^1$H-NMR spectroscopy.

Scheme 3.4. Trial reaction with cyclohexene to cyclohexanone using Grubbs new conditions

One critical complication is that 2.3a is not highly soluble in acetonitrile. In order to improve the yield, other solvents were examined. After testing several solvents, it was found that the unsymmetrical dianthracene is soluble in THF, which is also miscible with the H$_2$O required for the Wacker reaction. The test reaction with the new solvent system was carried out on cyclohexene, which was converted to cyclohexanone as confirmed by $^1$H-NMR spectroscopy.
Although the dianthracene 2.3a did dissolve in the new solvent system, the reaction again only recovered starting material. This indicates that its reactivity is much lower than that of a simple cycloalkene, perhaps due to steric crowding. In particular, the benzene unit blocking one face of the double bond could prevent some of the larger molecules from binding to the unsymmetrical dianthracene. This also may prevent other substitution reactions from working. For this reason, another strategy was sought to functionalize the dianthracene. The next section will discuss addition reactions and further explore the reactivity of the double bond.

3.3. Addition Reactions

3.3.1. Bromination

The first addition reaction that was attempted was bromination in dichloromethane (Scheme 3.5). TLC of the crude mixture showed the formation of several products. The $^1$H-NMR spectrum of the crude mixture confirmed the loss of the alkene signals were absent, demonstrating that the alkene is reactive. The complexity of the mixture is probably due to a rearrangement from a carbocation intermediate. To try to reduce the number of rearranged products, bromination was carried out at 0°C (See Appendix C). The TLC still showed a complex mixture and $^1$H-NMR spectrum showed that the same products were produced but with a different distribution than the $^1$H-NMR spectrum of the room temperature bromination. Attempts to separate the components of this product mixture were unsuccessful, in part because many of the species appear to react on the silica gel column. Because the bromine reaction produced a complex mixture, this reaction was not pursued further. It does, however, show that the alkene bond is reactive and that the intermediate or product may rearrange. Therefore, an addition reaction is needed which could add to the double bond without the potential for rearrangement.
3.3.2. Epoxidation

Epoxidation reactions were carried out with \( m \)-CPBA at room temperature (Scheme 3.6). This produced an epoxide (3.6) in the endo position, in 85% yield. The endo epoxide product was identified as the structure because the epoxide proton signals appeared at a higher than usual chemical shift, attributed to the shielding effect by the adjacent phenyl group.

One reason that epoxidation was selected was because the expected product, 3.6, loses conjugation, which should be trapped in this form and not be able to revert either through heat or light to revert to the bisanthracene. This is an example of gated photochromism that was introduced earlier in the thesis. To check if the epoxide is indeed “locked”, its thermal and photochemical stability both had to be tested.

3.3.2.1. Stability of Epoxide

3.3.2.1.1. Thermal Stability

Thermal stability of 3.6 was examined by heating the sample at 80°C in \( d^6 \)-DMSO in an NMR tube for one hour in an oil bath and, at the same time, heating 2.3a as
a standard in a separate NMR tube. Thermal reversion was monitored by $^1$H-NMR spectroscopy. After heating for one hour, the $^1$H-NMR spectrum showed that there was no change to 3.6 (Figure 3.1) while 50% of 2.3a had reverted to 2.1a. This agrees with preliminary data that is represented in section 2.2.2. This result indicates that the epoxide is thermally stable under the chosen conditions.

![Figure 3.1. $^1$H-NMR spectrum of 3.6 in $d^6$-DMSO before and after heating at 80°C for 1 hour](image)

3.3.2.1.2. Photochemical Stability

To investigate the photochemical stability of the epoxide 3.6 compared to the alkene 2.3a, both were irradiated under the identical conditions. The UV-Vis absorbance of the epoxide was investigated and compared to the absorbance of 2.1a and 2.3a (Figure 3.2). The absorbance of 3.6 and 2.3a are similar, so both could be irradiated at the same wavelength (285 nm). A 1 mM solution of 2.3a in benzene was irradiated at 285 nm with a monochromatic light from a fluorometer (25 mm slit width) and monitored by UV-Vis spectroscopy (Figure 3.3, top). The reversion of 2.3a can be seen by the increase of absorbance in the anthracene region. There was still some 2.1a in both samples prior to irradiation, which was due to the purification of the dianthracene being difficult. A 1 mM solution of 3.6 in benzene was then irradiated under the same conditions and also monitored by UV-Vis spectroscopy (Figure 3.3, bottom). The absorbance of the anthracene region did increase but over the same period of time, only a very small amount reverted compared to 2.3a.

The $^1$H-NMR spectrum of the epoxide 3.6 after irradiation in the fluorometer was investigated, but was inconclusive because of the small amount of photoproduct that was generated. Therefore a new 1 mM sample of 3.6 in benzene was irradiated in the Rayonet®, which can accommodate a larger sample. The $^1$H-NMR spectrum, after the
irradiation of 3.6 in the Rayonet®, showed that the appearance of new signals (Figure 3.4), which were not identified due to the small amount generated. The major signals of the $^1$H-NMR spectrum were from 3.6. It therefore appears that the epoxide is slightly photoreactive, albeit much less so than 2.3a.

![Figure 3.2](image)

**Figure 3.2.** The normalized absorbance of 3.6 (black, 0.13 mM, CH$_2$Cl$_2$) compared to 2.3a (red, 0.70 mM, CH$_2$Cl$_2$) and 2.1a (blue, 0.74 mM, CH$_2$Cl$_2$)
Figure 3.3. The opening of 2.3a (top) and 3.6 (bottom) investigated by UV-Vis after irradiating at specific times
3.4. Deoxygenation of Epoxide

Epoxide 3.6 is largely both photochemically and thermally stable, establishing characteristic features of a “locked” form. For this to be an example of gating, I must be able to remove the oxygen. PPh$_3$ can possibly convert epoxides to alkenes due to the strong P=O bond that forms in the product.$^{43}$ Epoxide 3.6 was dissolved in CH$_2$Cl$_2$ at room temperature with 2 equivalents of PPh$_3$, but there was no sign of reversion by $^1$H-NMR. The same reaction was then repeated at 40°C and 80°C in DMSO for one hour but this still showed no sign of deoxygenation. This is potentially due to the bulkiness of the phenyl units of PPh$_3$ and the steric hindrance in 3.6 (Scheme 3.7). At this moment 2.3a can be “locked” by transforming 2.3a to 3.6 but “unlocking” the gated form is still a challenge.

Figure 3.4. The $^1$H-NMR spectra of 3.6 before and after irradiation in the Rayonet® at 300 nm
3.5. Reactions with Epoxide

In addition to providing a means to gate the photochromism of 2.6, 3.6 could also lead to alternative synthetic pathways to functionalize this dianthracene. We therefore attempted to isomerize 3.6 to the ketone (3.1a/b). Under acidic conditions, 3.1a/b could tautomerize to its enol forms (3.2a/b) restoring conjugation. That product could then be converted either thermally or photochemically to the open functionalized bisanthracene (3.3a/b) (Scheme 3.8). Because the epoxide is thermally locked, the reactions are not limited to those run at room temperature.

Scheme 3.8. The scheme to functionalize the 2- or 3- position of anthracene through the epoxide intermediate
The Meinwald rearrangement with a Lewis acid is used extensively in organic syntheses to convert epoxides to ketones or aldehydes.\textsuperscript{44} This reaction depends on the ability of the substituents on the epoxide to migrate. There are few published works with describing the isomerization of an epoxide on bicyclic systems. Boron trifluoride etherate was used because it is soluble in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{45} As well, its small size should minimize steric hindrance.

BF\textsubscript{3}\cdot\text{Et}_2\text{O} was added at 0°C to a solution of 3.6 in 5 mL of CH\textsubscript{2}Cl\textsubscript{2} (Scheme 3.9). The TLC of the resulting reaction indicated a complex mixture of products. The \textsuperscript{1}H-NMR spectrum of the mixture showed complete consumption of the epoxide resonances from 3.6. The \textsuperscript{1}H-NMR spectrum showed the appearance of multiple products, consistent with the TLC plate (See Appendix C). The purification of this mixture was attempted by column chromatography. One product that could be isolated in low yield and it was found to be 2.1a in a 5% to 10% yield. When the \textsuperscript{1}H-NMR spectrum of the purified product and a \textsuperscript{1}H-NMR spectrum of a known sample of 2.1a were superimposed on each other, the results matched. The rest of the mixture was unfortunately too difficult to purify.

The appearance of 2.1a was unexpected under these conditions, but does indicate that the oxygen can be removed, permitting reversible gating. The use of BF\textsubscript{3}\cdot\text{Et}_2\text{O} is not suggested, however, due the complexity of the products of the reaction. It would be interesting to investigate reactions of BF\textsubscript{3}\cdot\text{Et}_2\text{O with 2.3a, to see if it is possible to reverse the cyclization chemically. Using the same conditions as with 3.6, BF\textsubscript{3}\cdot\text{Et}_2\text{O was added to 2.3a; however there was no sign of any reaction, as confirmed by \textsuperscript{1}H-NMR spectroscopy. This means that the gated photochromism is reversible, but instead of unlocking to the unsymmetrical 2.3a, it unlocks to 2.1a in a minor yield (Scheme 3.9).}
3.6. Conclusion

In this chapter, the reactivity of the alkene group of the dianthracene \textbf{2.3a} was examined. Due to the poor solubility of \textbf{2.3a} and steric hindrance around the olefin, little reactivity was observed. Treatment with bromine demonstrated that the alkene can be reactive, but this reaction produced multiple products. Only when reacting with \textit{m}-CPBA did the alkene cleanly transform to a single product, the epoxide, \textbf{3.6}. Epoxide \textbf{3.6} is both thermally and photochemically more stable than \textbf{2.3a} and therefore locks the photoreaction. The deoxygenation reaction with PPh\textsubscript{3} to unlock the dianthracene was not successful, but BF\textsubscript{3}•Et\textsubscript{2}O converts \textbf{3.6} to \textbf{2.1a} as a minor product. This preliminary result suggests a means of gating the photochromism of \textbf{2.3} to \textbf{2.1a} (Scheme 3.10).
This gated system is one of the few anthracene gated photochromic systems that has been reported. This type of gating allows the unsymmetrical dianthracene to become more photochemically and thermally stable, which could be useful for certain applications like optical memory. Two of the issues with optical memory are low thermal stability and destructive read-out of the stored information. Gating the anthracene system can cause an increase in thermal stability and hence increases the retention of stored memory. The gating will also prevent destruction of the memory when using light to read out the stored information. Adding m-CPBA to gate the bisanthracene system might not be the optimal way of doing this, but it is a useful proof of concept.

**3.7. Future Work**

The epoxide 3.6 can gate photochromism, as well as potentially be used as a precursor to functionalize anthracene at the 2-, 3-, 6-, or 7- positions. The conditions explored thus far do not cleanly convert 3.6 to 2.1a, limiting its usefulness in gating. Further studies are required to identify conditions that allow the transformation of 3.6 to an unlocked state (2.3a or 2.1a) or the initially targeted ketone 3.1a/b.

Alternatively, a different addition reaction should be attempted. This could lead to a different intermediate, which could be used for gating and transformation to the ketone. For example, a hydroboration followed by an oxidative work-up to get an alcohol, 3.7 (Scheme 3.11).
Scheme 3.11. The reaction mechanism with different locked states: a) hydroboration, oxidative work up; b) dehydration; c) oxidation
Chapter 4.
Experimental

4.1. Chapter 2

4.1.1. General Procedure of Synthesizing Bisanthracenes 2.1a, 2.1b, and 2.1c

4.50 mmol of 9-anthracene carboxylic acid, 6.25 mmol of TPP and 6.25 mmol of DIAD were dissolved in 10 mL of dry THF in a round bottom flask wrapped with aluminum foil. This solution was then stirred at 0°C until an orange suspension formed. At that time, 2.25 mmol of the appropriate diol was added drop-wise over a time interval of 30 minutes, and then the solution was slowly warmed to room temperature. This was left to stir overnight or until the suspension disappeared. The solvent was then removed in vacuo and the residue was dissolved in CH₂Cl₂. The solution was washed with water (3 x 200 mL) and saturated hydrogen sodium carbonate (2 x 200 mL). The washed solvent was dried over sodium sulphate, filtered and removed in vacuo to form orange oil. This product was purified by flash column chromatography (silica gel, 40% ethyl acetate/60% hexane) and recrystallized from a mixture of hot ethanol and water to give the bisanthracene as a green powder.

2.1a: Using the general procedure above with 1,3 propanediol produced a yield of 85%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.53 (s, 2H), 8.03 (m, 8H), 7.49 (m, 8H), 4.82 (t, 4H), 2.48 (q, 2H); ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 169.72, 131.09, 129.61, 128.76, 128.58, 127.73, 127.20, 125.62, 125.00, 62.51, 28.51; UV-Vis: 0.74mM, CH₂Cl₂, λₘₐₓ = 364 nm (ε = 12,758 M⁻¹cm⁻¹); HRMS: To be submitted

2.1b: Using the general procedure above with 1,2 ethanediol produced a yield of 80%. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 8.51 (s, 2H), 8.0 (dd, 8H), 7.38 (t, 4H), 7.17 (t,4H), 5.10 (s, 4H); ¹³C-NMR (400 MHz, CDCl₃) δ (ppm): 169.47, 131.00, 129.01, 128.76,
128.65, 128.60, 127.19, 127.16, 125.60, 125.05, 63.30; m/z: 493.14 (2.1b \text{ + Na}^+); HRMS: To be submitted

\textbf{2.1c}: Using the general procedure above with 1,6 hexanediol produced a yield of 87\%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.52 (s, 2H), 8.02 (d, 8H), 7.5 (m, 8H), 4.62 (t, 4H), 1.92 (m, 4H), 1.6 (m, 4H); $^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 169.91, 131.16, 129.42, 128.79, 128.55, 128.23, 127.11, 125.03, 125.12, 65.87, 28.84, 25.99, 18.60; m/z: 549.20 (2.1c \text{ + Na}^+); HRMS: To be submitted

\textbf{4.1.2. Photochemical Experiments for 2.1a}

2 mmol (24.2 mg) of the bisanthracene was dissolved in 25 mL of reagent-grade benzene. There was no removal of oxygen unless stated otherwise. The sample was then irradiated for 2 h with the appropriate light source. After irradiation, the solvent was removed at RT \textit{in vacuo}. The resulting residue was then purified using silica gel chromatography and a 7:3 mixture of dichloromethane with hexanes followed by another purification through a 2:8 mixture of ethyl acetate to hexanes to give a white powder at 66\% yield of 2.3a.

\textbf{2.3a}: $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.75 (d, 1H), 7.60 (d, 1H), 7.38 (m, 2H), 7.27 (m, 5H), 6.98 (d, 1H), 6.88 (m, 1H), 6.68 (m, 2H), 6.18 (t, 1H), 5.905 (t, 1H) 5.47 (d, 1H), 5.39 (m, 1H), 5.25 (t, 1H) 4.60 (d, 1H), 4.43 (m, 2H), 4.23 (t, 1H), 2.6 (m, 1H), 2.34 (m, 1H); $^{13}$C-NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ (ppm): 173.47, 169.42, 138.74, 135.41, 128.47, 128.38, 127.94, 127.90, 127.52, 127.47, 126.83, 126.80, 126.77, 126.68, 126.49, 125.61, 125.50, 66.17, 66.075, 54.02, 48.93, 28.13; UV-Vis: 0.74 mM, CH$_2$Cl$_2$, $\lambda_{\text{max}}$ = 270 nm ($\varepsilon$ = 8765 M$^{-1}$cm$^{-1}$)

\textbf{2.4a}: $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.57 (s, 2H), 8.04 (m, 8H), 7.54 (m, 8H), 7.00 (dt, 4H), 6.84 (m, 8H), 6.68 (dd, 2H), 6.59 (dd, 2H), 5.71 (dt, 2H), 4.59 (t, 4H), 4.34 (t, 4H), 2.25 (qu, 4H)
4.1.3. **Photochemical Experiments for 2.1b and 2.1c**

2 mmol (23.5 mg of 2.1b or 26.3 mg of 2.1c) were dissolved in 25 mL of reagent-grade benzene. There was no removal of oxygen through degassing by freeze-pump-thaw cycles. The sample was then irradiated for 1 h with the appropriate light source. There was no further purification and yields were derived from the $^1$H-NMR spectra.

4.1.4. **Rayonet® Irradiation**

Usually the bisanthracene was dissolved in benzene or acetonitrile from 1 mM to 8 mM concentration. About 5 mL of the solvent was typically used for irradiation in a disposable test tube and no degassing techniques were used. A Rayonet® photochemical reactor with 16 RPR3500A (350 nm) was used for irradiation with a plastic tube blowing air through the bottom. The irradiation could last up to 2 h after which the solvent was removed *in vacuo* at RT. The resulting product mixture was then analyzed by $^1$H-NMR spectroscopy.

4.1.5. **Fluorometer Irradiation**

The bisanthracene was dissolved in benzene or acetonitrile from 1 mM to 2 mM concentration. About 3 mL of the solvent was usually used for irradiation in a glass cuvette with a 1 cm path length and no degassing techniques were used. The fluorometer with the slit width set to 25 nm was used as a light source. The solvent was then removed *in vacuo* and the product mixture was analyzed by $^1$H-NMR spectroscopy.

4.1.6. **LED Irradiation**

The bisanthracene was dissolved in benzene at 1 mM concentration. About 5 mL of the solvent was usually used for irradiation in a disposable test tube and no degassing techniques were used. The sample was usually irradiated for 20 minutes unless stated otherwise. The LED flexible strip light with SMD3528 was used for irradiation. The solvent was then removed *in vacuo* and the product mixture was analyzed by $^1$H-NMR spectroscopy.
4.2. Chapter 3

4.2.1. Wacker Reaction

The general procedure comes from Grubbs et al.41 Palladium acetate (5 mol\%) and benzoquinone (1 equiv) were added to a 25-mL round-bottom flask. Then a ration of 3.5:3.5:1 of dimethyl acetamide, acetonitrile, and water were added to the round bottom flask into which 0.27M of 48% HBF$_4$ was added. The cyclohexene (1 equiv) was then added and the solution stirred for at least 16 hours. The solution was diluted with brine (30 mL) and ether (30 mL) and the different phases were separated. Ether was used again to extract the aqueous phase. The organic phases were combined and dried with sodium sulphate, filtered and removed \textit{in vacuo}. The oil was then analyzed by $^1$H-NMR spectroscopy.

The new procedure was changed by adding all components in THF and adding 1 equivalent of H$_2$O instead of excess.

**Test Reaction:** When adding 1 mmol of cyclohexene to the general procedure or new produced a yield of 70\% of cyclohexanone as an oil. $^1$H –NMR spectrum matched reference.41

2.3a: Adding 1 mmol of 2.3a to the general or new procedure only recovered starting material.

4.2.2. Typical procedure for Bromination of Alkene

25 mg (0.05 mmol) of 2.3a was dissolved in dichloromethane. 0.05 mmol of bromine was then added and was stirred with a mechanical stir bar for 30 min at room temperature. The solution was washed with sodium thiosulphate (50 mL) and the organic layer was dried over sodium sulphate, filtered, and removed \textit{in vacuo} at room temperature. The crude mixture was analyzed by $^1$H-NMR spectroscopy. The crude mixture was then purified by column chromatography with silica gel with a variety of different solvent mixtures and the isolated fractions were analyzed by $^1$H-NMR spectroscopy. The above conditions were repeated at 0°C in an ice bath.
4.2.3. Typical procedure for Epoxidation of Alkene

25 mg (0.05 mmol) of 2.3a was dissolved in dichloromethane. 0.06 mmol of meta-chloroperoxybenzoic acid was then added and was stirred with a mechanical stir bar over night at room temperature during which time a white precipitate formed. The precipitate was removed by vacuum filtration, and the filtrate was washed with sodium thiosulfate (50 mL). The washed solvent was dried over sodium sulphate, filtered and removed in vacuo. This yielded a white product that was washed several times with acetonitrile to yield a white solid in 85% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.74 (m, 1H), 7.57 (m, 1H), 7.45 (m, 1H), 7.34 (m, 3H), 7.27 (m, 2H), 6.97 (d, 1H), 6.85 (d, 1H), 6.6 (m, 3H), 5.42 (m, 2H), 5.22 (dt, 1H), 4.633 (d, 1H), 4.41 (m, 2H), 3.10 (t, 1H), 2.93 (t, 1H), 2.59 (m, 1H), 2.35 (m, 1H); \(^{13}\)C-NMR (400 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) (ppm): 172.12, 168.26, 141.53, 140.91, 140.15, 131.76, 128.5, 128.18, 127.46, 127.07, 126.93, 126.35, 126.3, 125.61, 125.60, 125.00, 61.92, 53.6, 52.58, 44.85, 44.67, 30.69, 25.12; m/z: 501.17 (3.1 +H\(^+\)); IR: (epoxy stretch: 1239 cm\(^{-1}\)); UV-Vis: 0.13mM, CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) = 270 nm (\(\varepsilon = 5231\) M\(^{-1}\)cm\(^{-1}\)) HRMS: To be submitted

4.2.4. Deoxygenation of Epoxide

The original reaction was done by adding 0.05 mmol of 3.6 in dichloromethane with 0.1 mmol of TPP and stirring at room temperature overnight. This was washed with water and the wash was dried with sodium sulphate, filtered and the solvent was removed in vacuo. This yielded a white substance that was analyzed by \(^1\)H-NMR spectroscopy. The reactions carried out at 40°C or 80°C in an oil bath were done in \(d^6\)-DMSO and analyzed directly by \(^1\)H-NMR spectroscopy, which showed that no reaction occurred.

4.2.5. Typical procedure with Boron Trifluoride Etherate

25 mg (0.05 mmol) of 3.6 was dissolved in dichloromethane which was cooled in an ice bath for 20 minutes to get to 0°C. 0.05 mmol of boron trifluoride etherate was then added and was stirred with a mechanical stir bar for 5 minutes. This was washed with hydrogen sodium carbonate (50 mL) and the wash was dried over sodium sulphate, filtered and removed in vacuo. The solvent was then removed in vacuo at room temperature and the crude mixture was analyzed by \(^1\)H-NMR spectroscopy. This
was then purified through silica gel chromatography with a 2:8 mixture of ethyl acetate to hexanes, which isolated two separate products; the minor product was green while the major product was colourless. The major product when analyzed by $^1$H-NMR spectroscopy showed to be a complex mixture.

**The green product:** $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.53 (s, 2H), 8.03 (m, 8H), 7.49 (m, 8H), 4.82 (t, 4H), 2.48 (q, 2H)
References


15) Kissel, P.; Murray, D. J.; Wulftange, W. J.; Catalano, V. J.; King, B. T. Nat. Chem. 2014, 6 (9), 774–778.


Appendix A.

Emission of Devices

Emission of the Rayonet

Emission of the Fluorometer
Appendix B.

Beer-Lambert plots

2.1a

![Graph 2.1a showing Beer-Lambert plots for different wavelengths.]

2.3a

![Graph 2.3a showing Beer-Lambert plots for different wavelengths.]

---

70
Appendix C.

$^1$H-NMR spectra of Reactions Resulting in Complex Mixtures

Figure. C.1. $^1$H-NMR spectrum of the complex mixture from reacting 2.3a with Br$_2$

Figure. C.2. $^1$H-NMR spectrum of the complex mixture from reacting 3.6 with BF$_3$•Et$_2$O
Appendix D.

2D-NMR spectra of 2.3a

Figure D.1. COSY spectra of 2.3a
Figure D.2. HSQC spectra of 2.3a

Figure D.3. HMBC spectra of 2.3a
Appendix E.

Crystal Stucture Data of 2.3a

<table>
<thead>
<tr>
<th></th>
<th>2.3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{33}$H$</em>{24}$O$_4$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>484.55</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P 2$_1$/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>16.6809(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>10.1264(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>14.6053(3)</td>
</tr>
<tr>
<td>α, °</td>
<td>90</td>
</tr>
<tr>
<td>β, °</td>
<td>100.754(2)</td>
</tr>
<tr>
<td>γ, °</td>
<td>90</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>2423.76</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>T, K</td>
<td>293</td>
</tr>
<tr>
<td>$\rho$$_{\text{calculated}}$</td>
<td>1.328</td>
</tr>
</tbody>
</table>