Formal Intramolecular Photoredox Reactions of Anthraquinones Mediated by Water

by

Yunyan Hou
B.Sc., Jilin University, 1995
M.Sc., Jilin University, 1998

A Dissertation Submitted in Partial Fulfillment
of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in the Department of Chemistry

© Yunyan Hou, 2010
University of Victoria

All rights reserved. This thesis may not be reproduced in whole or in part, by photocopy
or other means, without the permission of the author.
Formal Intramolecular Photoredox Reactions of Anthraquinones Mediated by Water

by

Yunyan Hou
B.Sc., Jilin University, 1995
M.Sc., Jilin University, 1998

Supervisory Committee

Dr. Peter Wan, (Department of Chemistry)
Supervisor

Dr. Natia Frank, (Department of Chemistry)
Departmental Member

Dr. Alexandre G. Brolo, (Department of Chemistry)
Departmental Member

Dr. Michel Lefebvre, (Department of Physics and Astronomy)
Outside Member
Abstract

Supervisory Committee

Dr. Peter Wan, (Department of Chemistry)
Supervisor
Dr. Natia Frank, (Department of Chemistry)
Departmental Member
Dr. Alexandre G. Brolo, (Department of Chemistry)
Departmental Member
Dr. Michel Lefebvre, (Department of Physics and Astronomy)
Outside Member

The formal intramolecular photoredox reaction initially discovered for the parent 2-(hydroxymethyl)-9,10-anthraquinone (HMAQ) in aqueous solution was extended to a variety of anthraquinone derivatives 2.1-2.9, biphenyl anthraquinones 3.1-3.4 and acenequinones 4.1-4.4. The purpose of the study was to explore the generality of the unique photochemical reaction involving HMAQ, understand the mechanism of the reaction and develop potential applications.

All the anthraquinones studied (except for 2.4) undergo the formal intramolecular photoredox reaction with a range of quantum yields (Φ = 0.02-0.7). Mechanistic studies based on the parent compound HMAQ were carried out by product studies, isotope effects, solvent deuterium isotope effects, pH effect, triplet quenching studies, and laser flash photolysis. It was found that the formal intramolecular photoredox reaction involves a highly polarized triplet excited state in which the electron density of the benzylic CH₂OH moiety is transferred to the central anthraquinone ring. This highly polarized triplet excited state is subsequently trapped adiabatically by protonation at the anthraquinone carbonyl oxygen.
Designed anthraquinones 2.2, 2.3, 2.5 and 2.6 successfully photoreleased "protected" alcohol, aldehyde, or ketone with good yields (80-90 %), respectively, and shows that the anthraquinon-2-yl chromophore is potentially useful for photocaging in aqueous solution. In addition, diketone 2.9 undergoes an analogous photoredox reaction but only in acid (Φ = 0.003, pH < 1), to give the formal redox product diphenylisobenzofuran 2.29, thereby demonstrating that other aromatic diketones can react in an analogous fashion.

Biphenyl and terphenyl analogs 3.1-3.4 in which the oxidizable benzyl alcohol group is significantly further away from the anthraquinone moiety were designed to explore the effect of the distance between CH₂OH and carbonyl group on the efficiency of the intramolecular photoredox reaction. All of these compound undergo a clean and efficient formal intramolecular photoredox reaction in water catalyzed by acid (Φ = 0.1-0.6). Triplet quenching studies and laser flash photolysis support a mechanism involving reactive triplet excited states. Laser flash photolysis also detected a long-lived and pH dependent transient which might be assigned to an enol intermediate.

A number of acenequinones were also designed to explore the intramolecular photoredox reaction for higher benzannelated systems. In particular, we were interested in whether the photoredox reaction could be applied to 2-(hydroxymethyl)-6,13-pentacenequinone (4.1) which would result in 2-formyl-6,13-dihydroxypentacene (4.5) and hence offer a photochemical method for synthesizing a pentacene derivative. Whereas a number of related acenequinones displayed a range of photoredox reactivity, photolysis of 4.1 in acidic aqueous solution (pH < 3) resulted in a clean intramolecular Photoredox reaction, via an enol intermediate, to give 4.5 (green compound; Φ ~ 0.2 at pH 1). Thus the photoredox reaction is reasonably general for acenequinones.
## Table of Contents

Supervisory Committee .................................................................................. ii
Abstract ........................................................................................................... iii
Table of Contents ............................................................................................ v
List of Tables .................................................................................................... viii
List of Figures ................................................................................................... ix
List of Schemes ................................................................................................ xi
List of Numbered Compounds-Names ............................................................ xii
List of Numbered Compounds-Structures ...................................................... xv
List of Abbreviations ....................................................................................... xvii
Acknowledgments ........................................................................................... xx
Dedication ......................................................................................................... xxii

1. Introduction .................................................................................................. 1
   1.1 Redox Reactions ....................................................................................... 1
   1.2 Basic Photophysical and Photochemical Processes .................................. 2
   1.3 Photoredox Reactions .............................................................................. 5
   1.4 Photoredox Reactions of Nitroaromatic Compounds .................................. 6
   1.5 Classical Photochemistry of Aromatic Ketones ......................................... 12
   1.6 Excited State Acid-Base Properties of Aromatic Compounds ................. 17
   1.7 Photoredox Reactions of Benzophenones ............................................... 21
   1.8 Photochemistry of Anthraquinones ........................................................ 23
      1.8.1 Photoreduction .................................................................................. 24
      1.8.2 Photoinduced Electron Transfer ...................................................... 25
      1.8.3 Intramolecular Photoredox Reaction ............................................. 26
   1.9 Photodeprotecting Groups ....................................................................... 27
   1.10 Proposed Research ................................................................................. 33

2. Intramolecular Photoredox Reaction of Anthraquinones and Its Potential Utility as a Photodeprotecting Group ......................................................... 35
   2.1 Introduction ............................................................................................. 35
   2.2 Syntheses ................................................................................................ 38
      2.2.1 α-D-2-(Hydroxymethyl)-9,10-anthraquinone (HMAQ-αD) ................. 38
      2.2.2 Anthraquinone Ethers 2.2 and 2.3 ...................................................... 38
      2.2.3 Anthraquinone Alcohols 2.1 and 2.7 ................................................. 39
      2.2.4 Anthraquinones Acetals .................................................................. 40
      2.2.5 Anthraquinone Acetate Ester 2.4 and Diketone 2.9 ......................... 40
   2.3 Product Studies ....................................................................................... 41
      2.3.1 Photoredox Chemistry of 2.1, 2.7 and 2.8 .................................... 41
      2.3.2 Photodeprotection via the Intramolecular Photoredox Chemistry of 2.2-2.6 .. 49
      2.3.3 Photochemistry of Diketone 2.9 ...................................................... 59
   2.4 Mechanistic Studies ................................................................................. 61
      2.4.1 Isotope Effects on the Photoredox Reaction .................................... 61
      2.4.2 pH Effects on the Photoredox Reaction ......................................... 65
      2.4.3 Solvent Effects on the Photoredox Reaction .................................... 66
2.4.4 Nanosecond Laser Flash Photolysis (LFP) of HMAQ ........................................ 70
2.4.5 Quenching of Triplet HMAQ ......................................................................... 73
2.4.6 HOMO/LUMO Calculations ........................................................................... 75
2.4.7 Proposed Reaction Mechanisms ....................................................................... 77
2.5 Summary ............................................................................................................. 80
2.6 Experimental ...................................................................................................... 82
2.6.1 General ............................................................................................................ 82
2.6.2 UV-Vis Studies ............................................................................................... 82
2.6.3 Product Studies ............................................................................................... 82
2.6.4 Quantum Yield Measurements ........................................................................ 83
2.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ ..................................... 83
2.6.6 Synthesis of Anthraquinone Derivatives HMAQ-αD, 2.1-2.9 ....................... 84
2.6.7 Photolysis Procedures for HMAQ-αD, 2.1-2.9 and Characterization of Products ............................................................ 90
2.6.8 Trapping of Photolysis Product of HMAQ ...................................................... 93
2.6.9 pH Effects on Photolysis Efficiency of HMAQ .............................................. 94
2.6.10 Quenching of Triplet HMAQ ......................................................................... 95

3. Long-Range Intramolecular Photoredox Reaction of Biphenyl Anthraquinones Mediated by Water .................................................................................. 96
3.1 Introduction ......................................................................................................... 96
3.2 Syntheses ............................................................................................................ 97
3.2.1 Synthesis of 3.1-3.3 ....................................................................................... 97
3.2.1 Synthesis of 3.4 ............................................................................................ 98
3.3 Product Studies .................................................................................................. 99
3.3.1 Photoredox Chemistry of 3.1-3.3 ................................................................ 99
3.3.2 Photoredox Chemistry of 3.4 ......................................................................... 107
3.4 Mechanistic Studies .......................................................................................... 109
3.4.1 pH Effects on Photolysis Efficiency of 3.1-3.4 ............................................. 109
3.4.2 Evidence for Unimolecular Reaction in Anthraquinone .............................. 110
3.4.3 Solvent isotope Effect on Photoredox Reaction ........................................... 112
3.4.4 Nanosecond Laser Flash Photolysis (LFP) of 3.1 ....................................... 113
3.4.5 Quenching of Triplet 3.1 ............................................................................... 117
3.4.6 HOMO/LUMO Calculations ......................................................................... 119
3.4.7 Proposed Mechanism ..................................................................................... 120
3.5 Summary ............................................................................................................ 122
3.6 Experimental .................................................................................................... 122
3.6.1 General ........................................................................................................... 122
3.6.2 UV-Vis Studies ............................................................................................... 122
3.6.3 Product Studies ............................................................................................... 123
3.6.4 Quantum Yield Measurements ...................................................................... 123
3.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ ................................. 123
3.6.6 Syntheses of 3.1-3.4 ...................................................................................... 124
3.6.7 Photolysis Procedures for 3.1-3.4 and Characterization of Products .......... 131
3.6.8 Trapping of Photolysis Product of 3.1 ........................................................... 133
3.6.9 Concentration Effects on Photolysis Conversions of 3.1 ............................. 134
3.6.10 pH Effects on Photolysis Efficiency of 3.1-3.4 ............................................ 134
3.6.11 Quenching of Triplet 3.1-3.3 .................................................................................. 134
4. A Pentacene Intermediate via Intramolecular Photoredox of a 6,13-Pentacenequinone in Aqueous Solution ................................................................. 136
4.1 Introduction ................................................................................................................. 136
4.2 Synthesis ...................................................................................................................... 137
4.3 Product Studies ........................................................................................................... 139
  4.3.1 Photoredox Chemistry of 4.1 .................................................................................. 139
  4.3.2 Photoredox Chemistry of 4.2 ................................................................................. 143
  4.3.4 Photoredox Chemistry of 4.3 and 4.4 ................................................................. 146
4.4 Mechanistic Studies of Photoredox Reaction of Pentacenequinone 4.1 .............. 148
  4.4.1 pH Effects on the Photoredox Reaction ............................................................... 148
  4.4.2 Nanosecond laser flash photolysis (LFP) of 4.1 ................................................... 149
  4.4.3 HOMO/LUMO Calculations .................................................................................. 151
  4.4.4 Proposed Mechanism ............................................................................................ 153
4.5 Summary ...................................................................................................................... 156
4.6 Experimental .............................................................................................................. 157
  4.6.1 General .................................................................................................................... 157
  4.6.2 UV-Vis Studies ....................................................................................................... 157
  4.6.3 Product Studies ....................................................................................................... 157
  4.6.4 Quantum Yield Measurements ............................................................................. 158
  4.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ ....................................... 158
  4.6.6 Syntheses of 4.1-4.4 ............................................................................................. 158
  4.6.7 Photolysis Procedures for 4.1-4.4 and Characterization of Products ............... 160
  4.6.8 Trapping the Photoredox Product of 4.2 ............................................................. 162
  4.6.9 pH Effects of Photolysis of 4.1 and 4.2 ............................................................... 163
5. Summary ...................................................................................................................... 164
5.1 Intramolecular Photoredox Reaction of Anthraquinones ....................................... 164
5.2 Potential Applications of the Intramolecular Photoredox Reaction of Anthraquinones ........................................................................................................ 164
  5.2.1 Photodeprotecting group ....................................................................................... 164
  5.2.2 Oxygen Sensor ....................................................................................................... 165
  5.2.3 Manufacture of H₂O₂ ............................................................................................ 165
  5.2.3 Solar Energy Storage ............................................................................................. 166
Bibliography ..................................................................................................................... 167
Appendix A: ¹H, ¹³C NMR Spectra ............................................................................... 178
Appendix B: UV-Vis Traces ......................................................................................... 214
Appendix C: Excitation and Fluorescence Spectrum ................................................ 218
Appendix D: Others ......................................................................................................... 220
List of Tables

Table 2.1 Quantum yields for the formation of photoredox products of anthraquinone derivatives .................................................................................................................. 81
Table 3.1 Quantum yields for the formation of photoredox products of biphenyl anthraquinones 3.1-3.3 in 1:1 H₂O-CH₂CN .............................................................................. 106
List of Figures

Figure 1.1 Photophysical processes as shown in a simplified Jablonski diagram ........................................... 3
Figure 1.2 Redox potentials in ground and excited states .................................................................................... 6
Figure 1.3 Förster Cycle .................................................................................................................................. 18
Figure 2.1 UV-Vis traces of the photoredox reaction of 2.1 ................................................................................. 42
Figure 2.2 UV-Vis traces of the photoredox reaction of 2.7 ................................................................................. 44
Figure 2.3 UV-Vis traces of the photoredox reaction of 2.14 .............................................................................. 47
Figure 2.4 UV-Vis traces of the photoredox reaction of 2.8 ................................................................................. 48
Figure 2.5 UV-Vis traces of the photoredox reaction of 2.2 ................................................................................ 51
Figure 2.6 Yields of CH₃CH₂OH and CH₃OH from photolysis of 2.2 and 2.3 ....................................................... 54
Figure 2.7 UV-Vis traces of photoredox reaction of 2.5 ..................................................................................... 57
Figure 2.8 UV-Vis traces observed on photolysis of diketone 2.9 ....................................................................... 60
Figure 2.9 Effect of H₂O and D₂O content (in CH₃CN) on photoredox efficiency of HMAQ ......................... 64
Figure 2.10 pH Dependence of intramolecular photoredox efficiency for HMAQ ............................................. 66
Figure 2.11 Solvent effect on the competition between intramolecular photoredox and simple photoreduction on photolysis of HMAQ in H₂O-2-propanol mixtures ........................................... 70
Figure 2.12 Triplet-triplet absorption spectra of HMAQ in neat CH₃CN ............................................................ 73
Figure 2.13 Triplet-triplet absorption spectra of HMAQ in 1:1 H₂O-CH₃CN ....................................................... 73
Figure 2.14 Stern-Volmer plot of quenching of the photoredox reaction for HMAQ in the presence of sorbic acid .................................................................................................................................................... 75
Figure 2.15 Calculated HOMO and LUMO for HMAQ ..................................................................................... 76
Figure 3.1 UV-Vis traces for photolysis of 3.1 in 1:1 H₂O-CH₃CN ................................................................. 101
Figure 3.2 Proton NMR studies of photolysis of 3.1 in 10% D₂O-CD₃CN ........................................................... 102
Figure 3.3 UV-Vis traces of photolysis of 3.2 in 1:1 H₂O-CH₃CN ................................................................. 104
Figure 3.4 Proton NMR studies of photolysis of 3.2 in 10% D₂O-CD₃CN ....................................................... 105
Figure 3.5 UV-Vis traces of photolysis of 3.4 ................................................................................................. 108
Figure 3.6 pH Dependence of intramolecular photoredox efficiency for 3.1, 3.2 and 3.3 .............................. 110
Figure 3.7 Effect of concentration of 3.1 on the observed reaction rate of photoredox reaction .................. 111
Figure 3.8 Solvent isotope effect on the photoredox efficiency of 3.1 ............................................................... 113
Figure 3.9 Triplet-triplet absorption spectra of 3.1 in neat CH₃CN ............................................................... 114
Figure 3.10 Triplet-triplet absorption spectra of 3.1 in 1:1 H₂O-CH₃CN .......................................................... 116
Figure 3.11 Triplet-triplet absorption spectra of 3.1 in 1:1 H₂O-CH₃CN (pH 1, nitrogen-saturated) ......... 117
Figure 3.12 Stern-Volmer plots of quenching of photoredox reactions for 3.1, 3.2 and 3.3 in the presence of sorbic acid ........................................................................................................................................ 118
Figure 3.13 Calculated (AM1) HOMO and LUMO for 3.2 .............................................................................. 120
Figure 3.14 Calculated (AM1) HOMO and LUMO for 3.4 .............................................................................. 120
Figure 4.1 UV-Vis traces observed on photolysis of pentacenequinone 4.1 ................................................... 140
Figure 4.2 Decay of photogenerated dihydroxypentacene 4.5 ........................................................................ 141
Figure 4.3 UV-Vis traces observed on photolysis of naphthoquinone 4.2 ..................................................... 144
Figure 4.4 Dramatic differences in observed colors in the photolysis of 4.2, HMAQ, and 4.1 in 1:1 H₂O-CH₃CN ............................................................................................................................................. 145
List of Schemes

Scheme 1.1 Proposed mechanism for the intramolecular photoredox reaction of 1.1 ..... 8
Scheme 1.2 Proposed mechanism for the photoredox reaction of 1.5.................... 9
Scheme 1.3 Proposed mechanism for the intramolecular photoredox reaction of 1.14 .. 11
Scheme 1.4 Simplified n,π' Transitions of the carbonyl chromophore.................. 12
Scheme 1.5 Norrish Type II photoelimination of aliphatic ketones...................... 14
Scheme 1.6 Proposed mechanism for photoreduction of 1.27............................ 15
Scheme 1.7 Synthesis of 1.34 via an initial photoenolization of 1.30................. 16
Scheme 1.8 Proposed mechanism for the photohydration of benzophenone 1.47......... 21
Scheme 1.9 Proposed mechanism for the intramolecular photoredox reaction of 1.51 .. 23
Scheme 1.10 Manufacture of H₂O₂ via the autoxidation of anthraquinone 1.56........ 24
Scheme 1.11 Proposed mechanism for photoreduction of anthraquinone 1.58........... 25
Scheme 1.12 An overall process from initial syntheses to the eventual photorelease.... 28
Scheme 1.13 Proposed mechanism for photolysis of o-nitrobenzyl derivative 1.63 to release ATP........................................ 30
Scheme 1.14 Photolysis of anthraquinone 1.67 to release acetophenone.................. 32
Scheme 1.15 Proposed mechanism for ortho substituted anthraquinone 1.70 to release benzaldehyde........................................ 33
Scheme 2.1 Proposed mechanism for the intramolecular photoredox reaction of 2.7.... 45
Scheme 2.2 Proposed mechanism of reaction for 2.2.................................... 53
Scheme 2.3 Proposed mechanism for photolysis of 2.22 to release benzoic acid........ 56
Scheme 2.4 Proposed mechanism for photolysis of 2.5 to release benzaldehyde........ 59
Scheme 2.5 Deprotonation of the excited anthraquinone HMAQ-αD...................... 63
Scheme 2.6 Trapping of photoredox products (DHA and 2.33) of HMAQ.................. 68
Scheme 2.7 Proposed mechanism for the intramolecular photoredox reaction of HMAQ .................................................. 77
Scheme 2.8 Alternative mechanistic pathway for the photoredox reaction of HMAQ...... 79
Scheme 3.1 Syntheses of phenyl-substituted anthraquinones 3.1-3.3..................... 98
Scheme 3.2 Synthesis of biphenyl anthraquinone 3.4.................................. 99
Scheme 3.3 Photolysis of 3.1 and trapping of the photoredox product 3.11 of 3.1...... 103
Scheme 3.4 Proposed mechanism for the intramolecular photoredox reaction of 3.1 .. 121
Scheme 4.1 Syntheses of acenequinones 4.1 and 4.4.................................. 138
Scheme 4.2 Attempts to trap the photoredox product 4.5................................ 143
Scheme 4.3 Photolysis of 4.2 and trapping of the photoredox product 4.7 of 4.2...... 146
Scheme 4.4 Proposed mechanism for the intramolecular photoredox reaction of 4.1 .. 155
List of Numbered Compounds-Names

HMAQ    2-(hydroxymethyl)-9,10-anthraquinone
DHA     2-formyl-9,10-dihydroxyanthraquinone
FAQ     2-formyl-9,10-anthraquinone
HMAQ-αD α-D-2-(hydroxymethyl)-9,10-anthraquinone
HMAQ-a  2-methyl-9,10-anthraquinone
2.1     2-(1-hydroxyethyl)-9,10-anthraquinone
2.2     2-(ethoxymethyl)-9,10-anthraquinone
2.3     2-(1-methoxyethyl)-9,10-anthraquinone
2.4     2-(acetoxyethyl)-9,10-anthraquinone
2.5     9-phenyl-7,11-dihydro-8,10-dioxa-cyclohepta[b]anthracene-5,13-dione
2.6     9-methyl-9-phenyl-7,11-dihydro-8,10-dioxa-cyclohepta[b]anthracene-5,13-dione
2.7     2,3-di(hydroxymethyl)-9,10-anthraquinone
2.8     2-[1,3]dioxolan-2-yl-9,10-anthraquinone
2.9     1,2-dibenzoyl-4-methylbenzene
2.11    2-acetyl-9,10-anthraquinone
2.14    1-hydroxy-1,3-dihydro-anthra[2,3-c]furan-5,10-dione
2.16    3H-anthra[2,3-c]furan-1,5,10-trione
2.18    9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid 2-hydroxy-ethyl ester
2.29    1,3-diphenyl-isobenzofuran-5-carbaldehyde
2.30    1,2-dibenzoyl-4-formylbenzene
<table>
<thead>
<tr>
<th>2.34</th>
<th>2-formyl-9,10-diaceotoxyanthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>2-(hydroxymethyl)-9,10-diaceotoxyanthracene</td>
</tr>
<tr>
<td>3.1</td>
<td>2-(o-hydroxymethylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.1a</td>
<td>2-(o-methylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.2</td>
<td>2-(m-hydroxymethylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.2a</td>
<td>2-(m-methylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.3</td>
<td>2-(p-hydroxymethylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.3a</td>
<td>2-(p-methylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.4</td>
<td>2-(p-hydroxymethylbiphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.4a</td>
<td>2-(p-methylbiphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.8</td>
<td>2-(o-formylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.9</td>
<td>2-(m-formylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.10</td>
<td>2-(p-formylphenyl)-9,10-anthraquinone</td>
</tr>
<tr>
<td>3.11-OAc</td>
<td>2-(p-formylbiphenyl)-9,10-diaceotoxyanthracene</td>
</tr>
<tr>
<td>3.14</td>
<td>2-(p-formylphenyl)-9,10-diaceotoxyanthracene</td>
</tr>
<tr>
<td>4.1</td>
<td>2-(hydroxymethyl)-6,13-pentacenequinone</td>
</tr>
<tr>
<td>4.1a</td>
<td>2-methyl-6,13-pentacenequinone</td>
</tr>
<tr>
<td>4.2</td>
<td>6-(hydroxymethyl)-1,4-naphthoquinone</td>
</tr>
<tr>
<td>4.2a</td>
<td>6-methyl-1,4-naphthoquinone</td>
</tr>
<tr>
<td>4.3</td>
<td>6-(hydroxymethyl)-1,4-anthraquinone</td>
</tr>
<tr>
<td>4.3a</td>
<td>6-methyl-1,4-anthraquinone</td>
</tr>
<tr>
<td>4.4</td>
<td>2-(hydroxymethyl)-5,12-naphthacenequinone</td>
</tr>
<tr>
<td>4.6</td>
<td>2-formyl-6,13-pentacenequinone</td>
</tr>
</tbody>
</table>
4.7-OAc  6-formyl-1,4-diacetoxynaphthalene
4.8      6-formyl-1,4-naphthoquinone
4.9      6-formyl-1,4-anthraquinone
List of Numbered Compounds-Structures

HMAQ

DHA

FAQ

HMAQ-αD

HMAQ-a

2.1 R = H; R' = CH₃
2.2 R = CH₂CH₃; R' = H
2.3 R = R' = CH₃
2.4 R = COCH₃; R' = H

2.5 R = H, R' = Ph
2.6 R = CH₃, R' = Ph

2.7

2.8

2.9

2.11

2.14

2.16

2.18

2.29
3.1  X = CH₂OH; Y = Z = H  
3.1a X = CH₃; Y = Z = H  
3.2  X = Z = H; Y = CH₂OH  
3.2a X = Z = H; Y = CH₃  
3.3  X = Y = H; Z = CH₂OH  
3.3a X = Y = H; Z = CH₃  
3.8  X = CHO; Y = Z = H  
3.9  X = Z = H; Y =CHO  
3.10 X = Y = H; Z = CHO

3.4  X = CH₂OH  
3.4a X = CH₃  
3.14 X = CHO

3.11-OAc

4.1  X = CH₂OH  
4.1a X = CH₃  
4.6  X = CHO

4.2  X = CH₂OH  
4.2a X = CH₃  
4.8  X = CHO

4.3  X = CH₂OH  
4.3a X = CH₃  
4.9  X = CHO

4.4
List of Abbreviations

A       absorbance
AQ      9,10-anthraquinone
Ac₂O    acetic anhydride
cm⁻¹     units of wavenumber
conc.   Concentrated
DME     dimethylethane
DMSO    dimethylsulfoxide
EtOAc   ethyl acetate
eV      electron volt
g       gram
h       hours
HOMO    highest occupied molecular orbital
HRMS    high resolution mass spectrometry
Hz      Hertz
IR      infrared
ISC     intersystem crossing
J       coupling constant
LUMO    lowest unoccupied molecular orbital
m       meta
M⁺      molecular ion
mg      milligram
| min | minutes |
| mL | milliliter |
| mmol | millimoles |
| M | molarity |
| MO | molecular orbital |
| mp. | melting point |
| MS | mass spectrometry |
| m/z | mass per charge |
| nm | nanometer |
| NBS | $N$-bromosuccinimide |
| NMR | nuclear magnetic resonance |
| $p$ | para |
| Ph | phenyl |
| ppm | parts per million |
| q | quartet (NMR descriptor) |
| t | triplet (NMR descriptor) |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| UV-Vis | ultraviolet-visible |
| °C | degree Celsius |
| $\delta$ | chemical shift in parts per million |
| $\lambda_{\text{max}}$ | maximum absorption wavelength |
| $\lambda_{\text{ext}}$ | excitation wavelength |
$\lambda_{em}$

emission wavelength (fluorescence)
Acknowledgments

I would like to express the deepest gratitude to my supervisor, Dr. Peter Wan, for his encouragement, patience, guidance and support from the initial to the final stages of my studies at the University of Victoria. I am impressed by his prudence in science and enthusiasm in research. As a result, my research life has been smooth and rewarding.

All the lab workers in Dr. Wan’s group (past: Nicola Basaric, Erin Dallin, Devin Mitchell; current: Niloufar Behin Aein, Alfredo Franco Cea) made a friendly and convivial environment to work in. I especially thank Dr. Nikola Basaric for his help and inspiration in my study and research.

A special thank goes to Dr. Cornelia Bohne, her group members and Luis Netter for their technical support on LFP and fluorescence measurements. I would also like to thank Dave McGillivary for MS and Chris Greenwood for NMR.

Finally, thanks to my family for their encouragement and support.
Dedication

To my mother and my husband
1. Introduction

1.1 Redox Reactions

Oxidation-reduction (also called redox reaction), a simple and important chemical process, involves the loss and gain of electrons within molecules that result in their overall oxidation and reduction. Redox reactions are very common and essential to life. They occur frequently, such as in the rusting of iron, combustion of coal, and in the photosynthesis of plants. In organic synthesis, redox reactions are widely employed to prepare a large variety of organic compounds.\(^1\) Redox reactions also play an important role in biological processes for the storage and release of energy.\(^2\)

Due to the importance of the redox reaction, it is not surprising that there is great interest on the details of this process and countless papers have been published. A number of reviews\(^3\) have also been published on the redox process, either initiated thermally, e.g. enzyme or metal catalyzed, or photochemically. For example, methanol is not harmful, but ingestion of methanol could result in blindness. This is because the oxidation of methanol catalyzed by alcohol dehydrogenase (an enzyme) generates toxic formaldehyde\(^4\). The biochemical process involves oxidization of methanol via an important coenzyme-NAD\(^+\) (oxidizing reagent) catalyzed by dehydrogenase, to produce formaldehyde (eqn. 1.1). To treat methanol ingestion, ethanol\(^5\) or fomepizole\(^6\) is given to the patient by intravenous injection. Alcohol dehydrogenase has a much bigger affinity for ethanol or fomepizole than it has for methanol. Thus, there is less of a chance for methanol to be oxidized due to the fact that most of alcohol dehydrogenase will be loaded with ethanol or fomepizole.
1.2 Basic Photophysical and Photochemical Processes

An organic molecule might undergo photophysical and/or photochemical processes after excitation to an electronic excited state. Photophysical processes result in no net chemical change and are further classified as a radiative or radiationless transition. As shown in Figure 1.1 (simplified Jablonski diagram), a molecule in the ground state \( S_0 \) absorbs a photon and is promoted to an excited singlet state \( S_1 \) at different vibrational levels. The electronic excited state undergoes an isoenergetic radiationless process, internal conversion \( \text{IC}(\rightarrow) \) followed by vibrational relaxation to arrive at the lowest level \( S_1 \) \( \text{(→)} \). The molecule in the \( S_1 \) state may then undergo internal conversion followed by vibrational relaxation or radiative emission (fluorescence) back to the ground state \( S_0 \). The former emits heat \( (\rightarrow) \) and the latter emits light \( (\rightarrow) \). A change in spin multiplicity on the excited state results in transformation from the singlet excited to the triplet excited state \( T_1, T_2, \ldots \) via intersystem crossing \( \text{ISC}(\rightarrow) \). The triplet excited state \( T_1 \) relaxes to the ground state \( S_0 \) via phosphorescence \( (\rightarrow) \) or intersystem crossing \( \text{ISC} \) followed by vibrational relaxation \( (\rightarrow) \).
Different from photophysical processes, photochemical processes result in net chemical change due to formation of photoproducts. The reactant in the ground state ($R$) absorbs photons to create an electronic excited state ($^1R$) which transforms to products ($P$)(eqn. 1.2). Due to the operation of photophysical processes that compete with the photochemical pathway, in order to observe photochemistry, the photochemical processes must be faster (as measured by their respective rate constants) than the sum of all deactivative photophysical processes, $k_p > \Sigma k$ ($k_p$: the rate constant for formation of products, $\Sigma k$: the sum of all the rate constants for photophysical decay). Many photochemical reactions proceed from triplet excited states rather than singlet excited states because the former is much longer lived than the latter, although singlet excited states can be photochemically reactive as well.
Chemists are also interested in how photochemical processes occur by understanding mechanisms of reactions. Photochemical processes may involve many possible pathways to form products, and many of these involve formation of intermediates such as radical pairs, biradicals, carbenes, zwitterions, etc.

Studying a photochemical reaction may include preparative irradiations as well as mechanistic studies. Preparative irradiation requires light sources and photochemical reactors. Light sources such as mercury arc lamps, deuterium lamps, and xenon lamps emit over certain wavelengths. The proper irradiation wavelength is chosen by measuring the absorption spectra of compounds.

A photochemical reactor consists of lamps, a reaction vessel, a cooling system and a degassing system. The reaction vessel should be transparent to the wavelength of excitation. A cooling system is used to prevent any competing thermal reaction. A degassing system is used for the removal of oxygen which is known to quench triplet excited states and react with free radicals and other intermediates.⁸

Photoproducts generated by preparative irradiation are directly characterized by NMR, IR, UV-Vis spectroscopy and mass spectrometry.⁹ Mechanistic studies involve measuring quantum yields, and studying various pH and solvent effects.⁹ In addition, direct information regarding mechanism, including the possibility of a reactive triplet excited state and existence of short-lived intermediates, may be gathered by time-resolved spectroscopy such as nanosecond laser flash photolysis (LFP).⁹ Additional information
about triplet state reactions may also be obtained by using triplet quenching and sensitization experiments.9

1.3 Photoredox Reactions
Redox reactions initiated by electronic excitation are called photoredox reactions. The most important example is photosynthesis. The Earth is a huge chemical factory and most of its energy is derived from solar irradiation. In this huge chemical factory, photosynthesis is the most important process that produces two essential compounds for living organisms: oxygen and carbohydrates. Photosynthesis involves the well-known photochemical redox reaction in which electron transfer induced by light results in the oxidation of H₂O and the reduction of CO₂. The former generates O₂ and the latter generates carbohydrates (glucose).¹⁰

An electronic excited molecule is more reactive than its ground state because of the promotion of an electron from the HOMO to a higher energy LUMO. Occupancy of the LUMO results in a lower oxidation potential (Pox) and a larger reduction potential (Presd) in the excited state than in the ground state (Fig. 1.2). Consequently, the electronically excited molecule is both easier to lose or gain an electron than its ground state. Thus, it is not hard to understand that electronic excited molecules are both strong oxidants and reductants and in principle can readily undergo photoredox reactions.
This Thesis focuses on intramolecular photoredox reactions which involve oxidation of one functional group and reduction of another functional group on the same molecule. To accomplish this, a molecule should have both an oxidizing moiety (electron acceptor) such as NO$_2$ or C=O, and a reducing moiety (electron donor) such as NH$_2$ or OH.

1.4 Photoredox Reactons of Nitroaromatic Compounds
Nitroaromatic compounds have played very important roles in organic synthesis and are also important precursors of dyes and explosives.$^{11}$ Although the first paper of photoinduced reactions of nitroaromatic compounds was published more than one century ago, studies on their photoactivity have gradually increased since 1960s due to the unique character and utility of the nitro group in organic photochemistry.$^{12}$
The nitro group provides low-lying triplet excited states which enhance intersystem crossing.\textsuperscript{12} Consequently, many of photochemical reactions of nitroaromatic compounds proceed via triplet excited states, of either $\pi-\pi^*$ or $n,\pi^*$ configuration.\textsuperscript{13}

The intramolecular photoredox reaction of nitroaromatic compounds is a class of reactions resulting in the overall reduction of the nitro group, to give nitroso, and the oxidation of another functional group in the same molecule. Most of the known examples\textsuperscript{13,14,15} involve ortho substituted nitrobenzyl derivatives and their primary mechanistic step is believed to involve hydrogen atom abstraction by the triplet excited nitro group (usually of the $n,\pi^*$ configuration).

The well-known intramolecular photoredox reaction of o-nitrobenzaldehyde (1.1) gives o-nitrosobenzoic acid (1.4) in neat acetonitrile ($\Phi \sim 0.5$).\textsuperscript{16} The proposed mechanism involves an intramolecular hydrogen atom transfer from the aldehyde in the triplet excited nitro group, to generate ketene 1.2. Cyclization of 1.2 gives 1.3 which eventually undergoes rearrangement to lead to an overall reduction of the nitro group and oxidation of the aldehyde, to form the final photoredox product o-nitrosobenzoic acid (1.4) (Scheme 1.1). Picosecond LFP studies of 1.1 showed that the triplet excited state has a lifetime of 0.6 ns and that the intermediate ketene 1.2 has an absorption band centered at 440 nm.\textsuperscript{16}
Scheme 1.1 Proposed mechanism for the intramolecular photoredox reaction of 1.1

Consistent with the above mechanism, both meta- and para-substituted isomers were not expected to undergo photoredox reaction because the two functional groups are too far away to react via hydrogen atom abstraction and this is indeed the case when organic solvents are used. However, p-nitrobenzaldehyde (1.5) is the first example of a nitroaromatic compound that is not ortho-substituted but still undergoes a formal intramolecular photoredox reaction, but only in water. In the presence of water, photolysis of 1.5 gave p-nitrobenzoic acid (1.9) (Φ ~ 0.034 in 99:1 H₂O-CH₃CN) with the quantum yield dependent on the concentration of water. The proposed mechanism (Scheme 1.2) involves electron transfer from water to the nitrophenyl triplet n,π* state, to generate the radical ion pair 1.6, which undergoes quick proton transfer to generate the radical pair 1.7. Subsequent hydrogen abstraction from the aldehyde hydrogen results in formation of quinoid ketene intermediate 1.8, which ultimately gives the photoredox product p-nitrobenzoic acid (1.9).
Scheme 1.2 Proposed mechanism for the photoredox reaction of 1.5

It is well-known that the electron donating or withdrawing ability of functional groups attached to benzene and other aromatic rings can be considerably enhanced on electronic excitation.\(^1\) Therefore, it is perhaps not surprising for meta- and para-nitrobenzyl alcohols to undergo intramolecular photoredox reaction since the benzyl alcohol moiety is readily oxidized. For instance, \(p\)-nitrobenzyl alcohol (1.10) in basic aqueous solution undergoes intramolecular photoredox reaction to form \(p\)-nitrosobenzaldehyde (1.13) (\(\Phi < 0.01, \text{pH } 14\)).\(^2\) The mechanism involves benzylic C-H bond deprotonation of triplet excited 1.10 by hydroxide ion with proton transfer from solvent water to the nitro group oxygen, to generate aci-nitro intermediate 1.11, which undergoes ketonization to give hydrated nitroso 1.12, which upon final loss of water gives 1.13 (eqn. 1.3).
The mechanism of intramolecular photoredox reaction of meta-nitrobenzyl alcohol (1.14) is more complicated. Photolysis of 1.14 produces two products: meta-nitrobenzaldehyde 1.15 ($\Phi \sim 0.25$, pH -1.4) and meta-azoxybenzaldehyde 1.16 ($\Phi \sim 0.079$, pH -1.4), via intramolecular photoredox reaction, without detectable formation of $m$-nitrosobenzaldehyde (eqn. 1.4). The photochemical reaction requires water and is dependent on pH. The authors proposed a mechanism similar to that of the para isomer in the initial steps. Deprotonation of the benzylic carbon by water of triplet excited 1.14* excite generates intermediate 1.17, which subsequently gives rise to the initial unstable photoredox product 1.18. Products 1.15 and 1.16 are proposed to arise by subsequent dark reactions. Disproportionation of two molecules of 1.18 generates nitrobenzaldehyde 1.15 and the hydroxylamine 1.19. The latter then reacts with with 1.18 to give observed azoxy product 1.16 via a condensation reaction (Scheme 1.3).
Scheme 1.3 Proposed mechanism for the intramolecular photoredox reaction of 1.14

The authors commented that both reactions proceeded via $\pi,\pi^*$ triplets instead of $n,\pi^*$ triplets. Generally, simple nitrobenzenes are believed to have the lowest $n,\pi^*$ triplets which are not known to activate the benzene ring. However, the above reactions clearly involve activation of the benzene ring. A reasonable explanation is that $\pi,\pi^*$ triplets are involved. The above reactions are only observed in water but not in common organic solvents. It is known that solvents of high dielectric constant stabilize $\pi,\pi^*$ and destabilize $n,\pi^*$ configurations. Water has a higher dielectric constant ($\varepsilon = 80$) than all the common organic solvents ($\varepsilon \leq 40$). Thus, in water, the lowest triplets might be of $\pi,\pi^*$ character which would lead to the above reactions.
1.5 Classical Photochemistry of Aromatic Ketones

As this Thesis focuses on the photochemistry of aromatic ketones, it is necessary to discuss general photochemical properties of the carbonyl chromophore. Thus, a brief review of the photochemistry of aromatic ketones is provided below.

In organic photochemistry, compounds bearing the carbonyl (C=O) chromophore are the most widely and intensively investigated. It is well-known that in thermal chemistry, the carbonyl group is easily attacked by nucleophiles at the carbonyl carbon. However, in photochemistry, completely different behaviour is observed.

\[ \pi^* \searrow \pi, \pi^* \nearrow n, \pi^* \newline \parallel \parallel \parallel \parallel \]

Scheme 1.4 Simplified n,\( \pi^* \) Transitions of the carbonyl chromophore

The oxygen in the carbonyl group has two non-bonding electron pairs in non-bonding molecular orbitals (Scheme 1.4). An electron in the non-bonding molecular orbital (\( n \)) is excited to the lowest anti-bonding orbital (\( \pi^* \)) to form the lowest energy excited state. Consequently, the electron in the \( \pi^* \) orbital is shared between both carbon and oxygen atoms, which results in lower electron density at the oxygen atom than in the ground state. This electronic feature readily leads to the species 1.20 as the representative of the excited state, which is resemblant to alkoxy radicals. Therefore, it is not surprising that electronically excited carbonyl compounds undergo the following reactions:

a) Photoreduction via hydrogen abstraction to form ketyl radicals 1.21;\(^{21}\)

b) \( \alpha \)-Cleavage or Norrish Type I reaction to form radicals 1.22;\(^{22}\)
c) Norrish Type II elimination reaction via 1,4-biradicals 1.23 which are formed via 1,5-hydrogen abstraction\(^\text{23}\).

d) Photocyclization via intramolecular hydrogen abstraction\(^\text{24}\).

e) \([2 + 2]\) Photocycloaddition to form oxetanes (eqn. 1.5), via one of 1.24, 1.25, or 1.26\(^\text{25}\).

\[\begin{align*}
\text{1.20} & \quad \text{1.21} & \quad \text{1.22} & \quad \text{1.23} \\
\end{align*}\]

\[\begin{align*}
\text{3} \quad \left[ \begin{array}{c}
\text{R} \quad \text{R'} \\
\text{R} \quad \text{R'}
\end{array} \right]^+ & \quad \text{\textequiv} & \quad \text{1.24} \\
\text{or} & \quad \text{1.25} & \quad \text{or} & \quad \text{1.26} \\
\end{align*}\]

Compared with the aliphatic ketones, aromatic ketones exhibit somewhat different features. For example, aromatic ketones such as benzophenone do not undergo Norrish Type I (\(\alpha\)-cleavage). Vibrational energy for the bond cleavage must come from the electronic excitation energy. Thus, in order to cleave a bond, the initial electronic energy must be high enough. However, electronically excited benzophenone, due to its lower triplet (and singlet) energy, has less available electronic excitation energy to be converted to vibrational energy for bond breaking than aliphatic ketones such as acetone\(^\text{26}\).

Norrish Type II photoelimination of aliphatic ketones proceeds via hydrogen abstraction to generate 1,4-biradical 1.23, followed by \(\gamma\)-cleavage to give rise to alkenes.
and enols, the latter being readily converted to ketones (Scheme 1.5). However, aromatic ketones such as 1.27 can only undergo the initial hydrogen abstraction from the alkyl group at the ortho position, but not the subsequent elimination since that would lead to fragmentation of the aromatic ring. The overall result is photoenolization.\textsuperscript{24a,27}

\begin{equation}
\text{1.23} \rightarrow \text{1.27}
\end{equation}

\textbf{Scheme 1.5} Norrish Type II photoelimination of aliphatic ketones

One of most common pathways of reaction of photoexcited aromatic ketones is hydrogen atom abstraction. The process may occur in a bimolecular or unimolecular reaction, to generate semi-pinacol radicals resulting in overall reduction of the carbonyl group. The reactive excited state can be either singlet or triplet.\textsuperscript{28}

Upon photolysis, aromatic carbonyl compounds with an alkyl group in the ortho position are known to readily produce the corresponding enols. The mechanism involves the triplet excited state 1.29 that generates a triplet biradical $^3E$ via intramolecular hydrogen abstraction. Subsequently, $^3E$ leads to formation of two isomeric enols, $E$ and $Z$. Singlet excited state 1.28 produces only enol $Z$. The short-lived $Z$ is quickly converted back to starting molecule 1.27. The longer-lived $E$ isomer has a lifetime of up to seconds (for ketonization)(Scheme 1.6).\textsuperscript{29}
Scheme 1.6 Proposed mechanism for photoreduction of 1.27

In the presence of a trapping reagent such as a dienophile, the long-lived enol $E$ can undergo Diels-Alder reaction. Meador and coworkers reported the synthesis of phenanthrene 1.34 via the initial photoenolization of 3,6-dibenzoyl-o-xylene (1.30) followed by subsequent Diels-Alder trapping.$^{30}$ In the photochemical preparation, 1.30 in nitrogen saturated benzene was irradiated (450 W medium pressure Hg lamp equipped with a Pyrex filter) and the enols trapped with $N$-phenylmaleimide (1.31), to give rise to bisadduct 1.32 in good yield (65%). Subsequently, phenanthrene 1.34 was synthesized by initial acid-catalyzed dehydration of 1.32 followed by aromatization of 1.33 with DDQ (Scheme 1.7). The key step in the synthesis is the hydrogen abstraction by the carbonyl oxygen of 1.30, to generate triplet biradical 1.35 which undergoes enolization to give o-xylylenol 1.36 (eqn. 1.6).
Scheme 1.7 Synthesis of 1.34 via an initial photoenolization of 1.30

If there is a good leaving group such as a carboxylate at an appropriate position, the long lived enol $E$ can undergo elimination to release a caged group such as an alcohol or a carboxylic acid. Thus, photoenolization can be widely used for photodeprotection. For example, the 2,5-dimethylphenacyl chromophore serves as a good photodeprotecting group for carboxylic acids. The carboxylate leaving group, on the $\alpha$-carbon of the 2,5-
dimethylphenacyl compound 1.37, is photoreleased to form indanone 1.38 via the enol $E'$ (Φ ~ 0.2) (eqn. 1.7).  

\[ \text{1.37} \quad \xrightarrow{\text{hv benzene}} \quad \text{enol } E' \]

\[ \text{1.38} \]

\[ + \quad \text{PhCOOH} \]

(1.7)

1.6 Excited State Acid-Base Properties of Aromatic Compounds

Just as Section 1.3 noted that redox behaviour of molecules changes significantly on going from ground to excited states, the acid-base properties of molecules also change considerably. A simple explanation is that there is significant migration of electron density in molecules upon electronic excitation. This affects acid-base properties of molecules.\(^{33,34,35,36}\) Thus, it is not surprising that some electronically excited molecules readily undergo proton transfer but the corresponding ground state molecules do not.

Phenols are known to be more acidic in the $S_1$ state than in the $S_0$ state. The enhancement of acidity may be simply explained with an energy level diagram involving the different electronic states of the phenol (HA) and its conjugated base ($A^-$), as shown in the Förster Cycle (Figure 1.3).\(^{20}\) Note that phenols (HA) in general have a higher energy ($\Delta G_{HA}$) for the HA-HA* transition than for the $A^- - A'^*$ transition of the
conjugated base ($\Delta G_A$). Thus, the dissociation of $HA^+$ is more favourable than that of HA. In another words, $HA^+$ is more acidic than HA.

![Diagram showing a Förster Cycle](image)

**Figure 1.3** Förster Cycle

Benzyl alcohol 1.39 undergoes photodissociation (loss of hydroxide ion) to generate benzyl cation 1.40 (eqn. 1.8). Photodissociation of $\sigma$-hydroxybenzyl alcohol (1.41) ($\Phi \sim 0.3$) is 5 times more efficient than 1.39. This is rationalized by the higher acidity of the phenol of 1.41 in $S_1$ ($pK_a^+ \sim 3$), which leads to a concerted intramolecular proton transfer pathway that results in the elimination of water (eqn. 1.9). The first step leads to photodehydration, to generate $\sigma$-quinoemethide 1.42, which then undergoes methanolysis to give 1.43.

```
1.39
\[ \text{CH}_2\text{OH} \]
\[ \text{OMe} \]
\[ \rightarrow \]
\[ \text{H}_2\text{O-MeOH} \]
\[ \text{H}^+ \]
\[ 1.40 \]
\[ \text{CH}_2\text{OH} \]
\[ \text{OMe} \]
\[ \rightarrow \]
\[ \text{MeOH} \]
\[ \text{CH}_2\text{OMe} \]
\[ 1.43 \]
\[ \text{OMe} \]

(1.8)
```
Suberene (1.44) is the first example of an excited state carbon acid.\(^{39}\) Photolysis of 1.44 in D\(_2\)O-CH\(_3\)CN results in deuterium exchange at the benzylic position (Φ ~ 0.035), to give 1.46 via carbanion 1.45 (eqn. 1.10). The mechanism involves the deprotonation at the 5-position by water acting as the general base, which is consistent with the much higher acidity of 1.44 in S\(_1\) (pK\(_a\) ~ -1) than that in the ground state (pK\(_a\) ~ 31-38).

Aromatic ketones also exhibit significantly different acid-base properties in the excited state. As opposed to phenols or suberene, electronically excited aromatic ketones are more basic.\(^{40}\) For example, benzophenone 1.47 in the triplet excite state is more basic than in the ground state. This has been experimentally verified by measurement of the pK\(_a\) of protonated benzophenone 1.48, in the triplet excited state, pK\(_a\) (T\(_1\)) ~ 0.4 whereas
in the ground state, \( pK_a(S_0) = -5.7 \).\textsuperscript{41} Additionally, the reactive triplet states in these protonations are believed to be of \( \pi,\pi^* \) character rather than \( n,\pi^* \) character.

Consequently, triplet excited benzophenone 1.47 undergoes adiabatic proton transfer to oxygen, resulting in the formation of triplet excited conjugate acid 1.48.

![Chemical Structures]

Indeed, Wirz and co-workers have reported the photohydration of benzophenone via this type of proton transfer.\textsuperscript{41} Triplet excited benzophenone 1.47 undergoes initial protonation of the carbonyl oxygen in the presence of acid, to generate triplet excited 1.48 which has substantial positive charge at the ortho and meta positions of the benzene ring (Scheme 1.8. In this and future schemes, for simplicity, not all open shell structures are explicitly shown except in representative cases). Attack by water at these positions leads to the transiently observed unusual hydration products 1.49 and 1.50. Both hydration products readily return to 1.47 by dehydration.
Scheme 1.8 Proposed mechanism for the photohydration of benzophenone 1.47

1.7 Photoredox Reactions of Benzophenones

With respect to photochemistry, benzophenone is one class of aromatic ketone that has been studied most widely.\textsuperscript{22a,23a,42,43,44} Benzophenone (1.47) undergoes efficient intersystem crossing\textsuperscript{45} and hence has a non-fluorescence and very short-lived (10\textsuperscript{-11}s) singlet state.\textsuperscript{44} In addition, benzophenone has a higher triplet energy than many compounds. The above properties make benzophenone and derivatives useful as triplet sensitizers.

Like most aromatic ketones, the most common primary photochemical reaction of benzophenone and its substituted derivatives is photoreduction via hydrogen atom abstraction in the presence of hydrogen donors.\textsuperscript{46,47,48} However, recently, an unusual intramolecular photoredox reaction involving the benzophenone chromophore was reported by Wan and coworkers.\textsuperscript{49} In neutral aqueous solution,
3-(hydroxymethyl)benzophenone (1.51) undergoes only photoreduction. Under acidic conditions, an intramolecular photoredox reaction was observed. The reaction requires water and is very efficient in the presence of acid (Φ ~ 0.6, pH < 3, H₂O-CH₃CN), to generate the formal photoredox product 1.52 (eqn. 1.11). Nanosecond laser flash photolysis of 1.51 showed two absorption bands (λₒ = 325 nm and λₓ = 525 nm) assignable to triplet excited benzophenone with a lifetime of 0.6 μs.

![Chemical Structure](image)

When the hydroxymethyl group is replaced by a methyl group, under the above experimental conditions, no photoredox reaction was observed.

The proposed mechanism involves an excited state carbocation 1.53 and is very similar to the acid-catalyzed photohydration of benzophenone 1.47 previously explored by Wirz.⁴¹ Protonation of the carbonyl oxygen of triplet excited 1.51 gives rise to 1.53 in which the positive charge is strongly localized at the meta position. This enhances the acidity of the benzylic C-H bond (of the CH₂OH moiety) sufficiently that it is deprotonated by solvent water, giving rise to a biradical dienol 1.54. The dienol 1.54 undergoes intersystem crossing and electron pairing, to give a zwitterionic intermediate 1.55 that subsequently results in an overall intramolecular photoredox reaction (Scheme 1.9).
Scheme 1.9 Proposed mechanism for the intramolecular photoredox reaction of 1.51

1.8 Photochemistry of Anthraquinones

As this Thesis primarily studies anthraquinones, a subset of aromatic ketones, it is necessary to briefly review the general applications and photochemistry of anthraquinones. In nature, anthraquinones are found in plants (e.g. rhubarb), and in some fungi and insects (e.g. coccids). All of these anthraquinones serve as the basic skeleton for pigments.\(^5\) In industry, many anthraquinone derivatives are used as dyes. Alizarin, which is extracted from the root of the madder plant, is the first natural pigment to be synthesized from anthracene by Graebe and Liebermann in 1869.\(^5\) Anthraquinones are also used as catalysts for the production of wood pulp to enhance fiber potency.\(^5\) They are also used as effective bird repellents on seeds.\(^5\) In addition, in the manufacture of \(\text{H}_2\text{O}_2\), the autoxidation of anthraquinones is the first and still a major method.\(^5\) In this process, 2-ethyl-9,10-dihydroxyanthracene (1.56) is autoxidized in air to generate \(\text{H}_2\text{O}_2\)
and anthraquinone 1.57, which is reduced back to the dihydroxy compound using hydrogen gas with metal catalysts (Scheme 1.10).

Scheme 1.10 Manufacture of H₂O₂ via the autoxidation of anthraquinone 1.56

The photochemistry of anthraquinones has been extensively investigated due to their widespread use as photosensitizers and antennas for solar energy conversion.⁵⁵ Anthraquinones undergo efficient intersystem crossing (Φ_{ISC} ~ 0.9), to form a long-lived triplet excited state, which can lead to efficient photochemical reaction competing with physical radiative and radiationless decay.⁵⁶,⁵⁷ Anthraquinones are also good electron acceptors and efficient hydrogen abstractors (via the carbonyl oxygen).⁵⁶ Thus, electronically excited anthraquinones may undergo photoreduction and photoinduced electron transfer, some of which will be further elaborated below.

1.8.1 Photoreduction

The well-known photoreduction of anthraquinone was reported by Wilkinson and coworkers.⁵⁸ Photoexcited anthraquinone 1.58 is reduced by isopropanol (hydrogen donor), to dihydroxyanthracene 1.60 via hydrogen atom abstraction. More recently, the mechanism has been investigated in detail using time-resolved transient spectroscopy by Görner.⁵⁹ These studies suggest that hydrogen abstraction by the carbonyl oxygen of triplet excited anthraquinone 1.58 gives rise to the corresponding semi-quinone radical 1.59 (“ketyl”) ultimately leading to reduced anthraquinone 1.60 (Scheme 1.11).⁵⁹ This
reaction involves the addition of external hydrogen atoms and hence involves an overall bimolecular process.

Scheme 1.11 Proposed mechanism for photoreduction of anthraquinone 1.58

1.8.2 Photoinduced Electron Transfer

Pal and coworkers reported bimolecular photoinduced electron transfer in an anthraquinone-amine system. The proposed mechanism involves photoinduced electron transfer from the amine donor (1.61) to the singlet excited anthraquinone acceptor (1.62). The process was observed by time-resolved fluorescence quenching. The intensity of fluorescence of the singlet excited anthraquinone is significantly quenched by aromatic amines ($k_q \approx 2.4 \times 10^{10}$ M$^{-1}$s$^{-1}$). The free energy change ($\Delta G_{el}$) for the photoinduced electron transfer reaction is -0.964 eV.
In recent years, photoredox reactions (via electron transfer) in DNA and peptides have attracted considerable attention. Schuster and coworkers\textsuperscript{61} reported selective oxidative damage of DNA via photoinduced electron transfer. In a complex of an anthraquinone conjugated to a duplex DNA, the DNA base is an electron donor and electronically excited anthraquinone is the electron acceptor. An electron transfer from the DNA base to the excited anthraquinone results in the formation of a radical cation in the DNA. This then leads to a mutation of DNA.

1.8.3 Intramolecular Photoredox Reaction

The first intramolecular photoredox reaction involving an anthraquinone chromophore was reported by Wan and coworkers.\textsuperscript{62} 2-(Hydroxymethyl)anthraquinone (HMAQ) undergoes a highly efficient photoredox reaction in aqueous solution ($\Phi \sim 0.8$) (eqn. 1.12).\textsuperscript{62} Photolysis of HMAQ in neutral aqueous solution gave an orange 2-formyl-9,10-dihydroxyanthracene (DHA), which is oxidized to give 2-formyl-9,10-anthraquinone (FAQ) when exposed to air. When the hydroxymethyl group was replaced by a methyl group, no photoredox reaction was observed, even upon prolonged irradiation. The reaction requires water and no reaction was observed in neat acetonitrile. The observed concentration ($10^{-6}$-$10^{-4}$ M) independence of the substrate on quantum yield of reaction suggests that the photoredox reaction is unimolecular in anthraquinone. A detailed mechanism of this reaction will be presented in Chapter 2 of this Thesis since a number of related substrates will be studied as part of continuing work on this reaction.
1.9 Photodeprotecting Groups

Photodeprotecting groups have attracted considerable interest due to their wide application in organic synthesis and biochemistry. Photodeprotecting groups are designed to protect functional groups and to be removed by a trigger, namely light to release the protected functionality. In organic synthesis, protecting groups play an important role in chemical selectivity of reaction when two or more functional groups are present. Generally, in thermal chemistry, removal of a protecting group is carried out by acid or base, but these cannot be used for some sensitive compounds. Compared with many protecting groups that are removed thermally, photochemical deprotecting groups are more convenient and can be removed efficiently without the addition of more chemicals. This has added benefit in biology.

In the design of a photodeprotecting group, one should consider many factors, such as the synthesis of photoprotected compounds AB and the photorelease process, etc. Scheme 1.12 shows the overall process from initial syntheses to the eventual photorelease.
Scheme 1.12 An overall process from initial syntheses to the eventual photorelease

A good photodeprotecting group should meet the following criteria:

a) The photoprotected compound AB is easily synthesized in high yield;
b) AB should have good photosensitivity and good solubility, and especially in biology, AB should be water-soluble and bioinert.
c) It should be easy to remove the deprotecting group B', to release the protected molecule A in high yield upon irradiation.
d) In biology, the excitation wavelength for AB should be above 300 nm in order to prevent damage to biological tissue.
e) There should be few or no by-products. The photodeprotected compound A should be readily recoverable.
f) The by-product B' should be photoinert and transparent at the excitation wavelength. In biology, the by-product B' should be bioinert.

The most common and also commercially available photodeprotecting groups are based on o-nitrobenzyl derivatives. They are low cost, compatible with most functional groups and have high releasing yields.\(^{65}\) Currently, o-nitrobenzyl derivatives are used to protect alcohols,\(^{66}\) ketones (aldehydes),\(^{67}\) amines,\(^{68}\) carboxylic acids,\(^{69}\) phosphates,\(^{70,71}\) etc. The reaction mechanism involves hydrgen atom abstraction by the nitro group, to give the aci-tautomers (E-aci and Z-aci) as shown for the parent o-nitrotoluene (eqn. 1.13). The E-aci tautomer is reactive in photorelease.

![Reaction Mechanism](image)

As an example, the 1-(2-nitrophenyl)ethyl ester of ATP 1.63 photoreleases ATP anion (RO\(^{-}\)) in aqueous solution in high yield (\(\Phi \sim 0.63\), pH 6~10)\(^{70,71}\) (Scheme 1.13). The proposed mechanism involves hydrogen atom abstraction by electronically excited 1.63, to give aci-nitro form 1.64, followed by a series of thermal steps, to give 1.65. The ATP anion is released by elimination/ketonization of 1.65.\(^{72}\)
Scheme 1.13 Proposed mechanism for photolysis of o-nitrobenzyl derivative 1.63 to release ATP

However, nitro compounds are toxic and their photochemical by-products (nitroso compounds) compete for light absorption. Their release rate (after excitation) is relatively slow in most cases ($> 10^{-3}$ s). Consequently, other photodeprotection groups such as $p$-hydroxyphenacyl derivatives, benzoin and coumarinyl derivatives have been developed to address these shortcomings.

Anthraquinone derivatives as a new chromophore for photodeprotection was first reported by Iwamura and coworkers. Anthraquinone 1.66 photoreleases the protected galactose derivative in good quantum yield ($\Phi = 0.10$) (eqn. 1.14). However, the authors neither reported the nature of the by-products nor explored the mechanism of reaction.
Recently, an anthraquinone photodeprotecting group for aldehydes and ketones was reported by Song and coworkers.\textsuperscript{77} Compound 1.67 photoreleases acetophenone ($\Phi = 0.038$ for disappearances of the caged compound) (Scheme 1.14). Besides acetophenone, two other products A and B were also formed. The authors suggested that they might be generated from the photolysis of 1.68. The photodeprotection mechanism was proposed to arise via heterolytic bond cleavage, to generate zwitterionic intermediate 1.69. This is subsequently trapped by water to give a hemi-acetal. Breakdown of the acetal would be expected to give acetophenone and 1.68
Scheme 1.14 Photolysis of anthraquinone 1.67 to release acetophenone

All of the above anthraquinone photodeprotecting groups are based on *meta* substituted compounds. Blankespoor and coworkers reported the use of *ortho* substituted anthraquinones, 1-alkoxy-9,10-anthraquinone (1.70) as a photodeprotecting group for aldehydes. The mechanism involves intramolecular hydrogen abstraction of electronically excited 1.70, to generate biradical 1.71, which subsequently undergoes single electron transfer (SET), giving zwitterion 1.72. Trapping of 1.72 by CH₃OH gives dihydroxyanthacene 1.73 (Scheme 1.15). Upon oxidation in air, anthraquinone 1.74 is produced, which upon hydrolysis in aqueous acetic acid produces 1-hydroxyanthraquinone (1.75) and the corresponding aldehyde in high yield (68%).
Scheme 1.15 Proposed mechanism for ortho substituted anthraquinone 1.70 to release benzaldehyde

1.10 Proposed Research

The initial work on the intramolecular photoredox reaction of anthraquinones such as HMAQ (eqn. 1.12) was reported by Wan and coworkers in 2002. Prior to that, the intramolecular photoredox reactions of nitro compounds were of interest in this area. The work on anthraquinones may be regarded as an extension of the work on the m- and p-nitrobenzyl alcohols. The goal of the present research is to further explore intramolecular reactions of aromatic ketones using the anthraquinone chromophore as the platform.

In this Thesis, the intramolecular photoredox reaction of anthraquinone HMAQ will be extended to a number of anthraquinone derivatives with the goal of better understanding the clean and efficient intramolecular photoredox reaction displayed by the parent compound. To study the generality of the photoredox reaction, we will design a variety of substituted derivatives on the basic backbone of the anthraquinon-2-yl moiety,
including alcohols, ethers, acetics, esters as well as related chromophores (Chapter 2), to explore whether these derivatives undergo the intramolecular photoredox reaction discussed above. In addition, a new photodeprotecting group will be designed and investigated with possibility of releasing several protected functionalities. Chapter 2 will also focus on mechanistic studies of parent compound HMAQ exploring isotope, solvent, pH effects as well as the use of laser flash photolysis (LFP) to investigate mechanism of reaction.

In Chapter 3, studies will explore whether or not the above formal intramolecular photoredox reaction could occur for substrates in which the benzyl alcohol moiety is far away from the anthraquinone. Thus, new anthraquinones with phenyl and biphenyl “spacers” between the two potentially reactive functional groups will be synthesized and their photochemistry investigated in detail.

The photoredox reaction will also be extended (Chapter 4) to acenequinones, by removing or adding benzene rings to the anthraquinone system but still preserving the planarity and conjugation. The designed compounds will include a naphthoquinone, an anthraquinone, a naphthacenequinone and a pentacenequinone. A photochemical method involving an intramolecular redox process to prepare a pentacene derivative will also be detailed.
2. Intramolecular Photoredox Reaction of Anthraquinones and Its Potential Utility as a Photodeprotecting Group*

2.1 Introduction
Previous studies of 2-(hydroxymethyl)anthraquinone (HMAQ) in water suggest a different and unusual sort of photochemical reactivity for a simple anthraquinone derivative. The highly efficient reaction (Φ = 0.8) of HMAQ is observed only in the presence of water with clean formation of the formal intramolecular redox product DHA. On exposure to air or oxygen, the anthraquinone chromophore is regenerated in product FAQ. We wondered whether this efficient photoredox reaction is only a special case reaction for HMAQ or it is a general one for HMAQ analogs.

Previous studies of HMAQ also suggested that the photoredox reaction might proceed via protonation of the anthraquinone carbonyl oxygen and deprotonation of the benzylic C-H. In addition, the alcohol group is apparently a key substituent in the photoredox reaction because no photoredox reaction was observed for 2-methyl-9,10-anthraquinone. Thus, to examine the generality of the photoredox reaction, a variety of appropriate anthraquinones (2.1-2.8) were designed (Chart 2.1). All of these anthraquinones have one common character: an anthraquinone or related chromophore and a “distal” substituent bearing a benzylic oxygen moiety. Diketone 2.9 was prepared to examine whether or not other aromatic diketones could react in an analogous fashion.

The design of 2.2-2.6 has a dual purpose. One is to examine the generality of the photoredox reaction as noted above; the other is to examine the possible application of

the anthraquinon-2-yl moiety acting as a photodeprotecting group for alcohols, carboxylic acids, and ketones/aldehydes. The details of this application are presented in Section 2.3.2.

![Chart 2.1]

Since the photoredox reaction of HMAQ exhibits a significant colour change upon excitation,\textsuperscript{62} UV-Vis spectroscopy was firstly employed to explore the possible long-lived transients and the presence of photoredox products for all the designed anthraquinone derivatives.

Since all anthraquinones (2.1-2.8) are an extension of HMAQ, HMAQ could be considered as a basic model for studying the photoredox reaction. However, no detailed
mechanistic studies of the photoredox behaviour of HMAQ had been reported. Thus, it is necessary to explore the mechanism of the photoredox reaction of HMAQ itself.

The photoredox reaction of HMAQ most likely involves the protonation of the carbonyl oxygen and the deprotonation of the benzylic C-H bond. In order to examine the effect of the bond breaking on formation of the photoredox product, the α-deuterated anthraquinone HMAQ-αD was prepared, to measure the isotope effect on the deprotonation of the benzylic C-H bond. The isotope effect can be obtained by comparing the formation of deuterated or non-deuterated product yields. Protonation of carbonyl oxygen can be studied by photolysis in D₂O/H₂O and the effect of pH. Results are presented in Section 2.4.1.

Although HMAQ exhibits an efficient photoredox reaction in neutral aqueous solution, previous studies showed that the analogous photoredox reaction of benzophenone 1.51 is pH dependent and that no photoredox reaction was observed in neutral aqueous solution. In addition, the photoreduction of benzophenone 1.51 competes with its photoredox reaction. It is well-known that anthraquinones also undergo photoreduction in the presence of hydrogen donors. Thus, the details concerning pH effects (Section 2.4.2) and hydrogen donor solvent effects (Section 2.4.3) on the photoredox behaviour of HMAQ will be presented. These results reveal interesting differences between photoreduction and photoredox behaviour.

Nanosecond laser flash photolysis (LFP) will be employed to explore the nature of reactive excited states of HMAQ and the existence of intermediates that lead to photoredox product for the parent HMAQ. The results are presented in Section 2.4.4. Anthraquinones tend to react via triplet excited states due to their efficient intersystem
crossing ($\Phi = 0.9$). Confirmation of triplet state reactivity for HMAQ photoredox chemistry will also be performed through triplet quenching methods (Section 2.4.5).

### 2.2 Syntheses

#### 2.2.1 $\alpha$-D-2-(Hydroxymethyl)-9,10-anthraquinone (HMAQ-$\alphaD$)

Synthesis of the monodeuterated derivative HMAQ-$\alphaD$ was readily achieved via the reduction of FAQ with NaBD$_4$ in CH$_3$OH, and purified by column chromatography in 90% yield. FAQ itself was synthesized using the photochemical reaction shown in eqn. 1.12. The presence of one deuterium at the benzylic position was confirmed in HMAQ-$\alphaD$, by comparison of the integration of the methylene proton signal at $\delta$ 4.86 with the aromatic proton signal with three protons at $\delta$ 7.82-7.20. A ratio of 1:3 indicated that one deuterium has been incorporated into the methylene position. The MS also indicated the required mass ($M^+ = 238 \text{ m/z}$) and its purification was $>98\%$.

#### 2.2.2 Anthraquinone Ethers 2.2 and 2.3

The synthetic pathway of 2.2 is shown in eqn. 2.1. The commercially available starting material HMAQ-a was first converted to the bromo derivative HMAQ-b. After solvolysis in CH$_3$CH$_2$OH and purification by column chromatography, 2.2 was obtained in 56% yield. Synthesis of 2.3 followed a similar procedure via 2.1a and 2.1b, to give 2.3 in 74% yield.
2.2.3 Anthraquinone Alcohols 2.1 and 2.7

The synthetic pathway of 2.7 is shown in eqn. 2.2. The commercially available bismethyl compound 2.7a was first converted to the dibromo derivative 2.7b via NBS bromination in 90% yield. After hydrolysis, recrystallization from toluene gave 2.7 in 30% yield. Synthesis of 2.1 followed a similar synthetic protocol starting from 2.1a, to give 2.1 in 75% yield.
2.2.4 Anthraquinones Acetals

The synthetic procedure for acetal 2.8 is shown in eqn. 2.3. FAQ is reacted with ethylene glycol in refluxing toluene in the presence of H₂SO₄ catalyst (1% v/v) to give 2.8 via an overall dehydration. After column chromatography, 2.8 was obtained in 74% yield. Synthesis of acetals 2.5 and 2.6 followed a similar synthetic procedure, by reacting benzaldehyde and acetophenone (acid-catalyzed acetal formation) with diol 2.7, to give the pure target compounds in 49% and 30% yield, respectively.

![Chemical structure of eqn. 2.3](image)

2.2.5 Anthraquinone Acetate Ester 2.4 and Diketone 2.9

Acetate ester 2.4 was readily prepared by esterification of HMAQ with acetyl chloride in the presence of pyridine (eqn. 2.4). After column chromatography, pure 2.4 was obtained in 70% yield. Diketone 2.9 (eqn. 2.5) was readily prepared by the hydrolysis of the corresponding bromomethyl precursor, which itself was made from the known methyl derivative 2.9a.⁷⁹ Purification by column chromatography gave an overall yield of 65% for 2.9.

![Chemical structure of eqn. 2.4 and 2.5](image)
2.3 Product Studies

2.3.1 Photoredox Chemistry of 2.1, 2.7 and 2.8

Initial studies were carried out on anthraquinone 2.1, 2.7 and 2.8 because these compounds may be regarded as the simplest extensions of the parent HMAQ, and which photoredox reaction does not result in photodeprotection of a separate molecule (which is discussed in 2.3.2).

Previous studies have shown that the photoredox reaction of anthraquinone HMAQ forms a new anthracene chromophore which can be readily observed by UV-Vis spectroscopy.\(^{62}\) In addition, the oxygen sensitive initial photoredox product DHA cannot be isolated by simple experimental methods. Thus, UV-Vis spectroscopy is a very useful tool to monitor the photoredox reaction. In addition, UV-Vis spectroscopy is time-saving and solvent-saving compared to product work-up. Therefore, it was the first tool used to study the photoredox behaviour of all the anthraquinones in this Thesis.

The first studied compound was 2.1 in which the CH\(_2\)OH group of HMAQ was replaced by CH\(_3\)CHOH. Since the chemical structure of 2.1 is so similar to that of HMAQ, 2.1 was expected to undergo the photoredox reaction much like that observed for HMAQ. Initial UV-Vis studies were carried out for 2.1 in 1:1 H\(_2\)O-CH\(_3\)CN
(deaerated with argon). Short time exposure to 300 nm (10 s) resulted in the formation of an intense band at 281 nm and two weaker and broad bands at 396 and 433 nm, respectively (Figure 2.1). With continued photolysis (up to 50 s), these bands gradually increased in intensity. The presence of several isosbestic points indicates that all these new bands belong to the same product(s) with the absence of secondary reactions. After aeration, all of these bands disappeared quickly, to give a spectrum almost identical to that of the starting material 2.1.

![UV-Vis traces](image)

**Figure 2.1** UV-Vis traces of the photoredox reaction of 2.1 in 1:1 H₂O-CH₃CN (λₑₓ = 300 nm). Each trace represents 10 s of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 2.1) at 257 and 326 nm with formation of 2.10 (281, 396 and 433 nm). Inset: ten-fold expansion of the long wavelength region.

All of these observations are very similar with that reported for the parent compound HMAQ, which suggests that 2.1 undergoes the photoredox reaction to give a UV-Vis observable product 2.10. When the solution is exposed to air, 2.10 is readily oxidized to
the final stable compound 2.11, which has a similar absorption spectrum with that of 2.1 (eqn. 2.6).

Direct photolysis in an NMR tube under argon was subsequently employed to study the photochemistry of 2.1 (10⁻³ M, 10% D₂O-CD₃CN, pH 7, λₑₓ = 350 nm), so that all potential primary photoproducts could be monitored without work-up or oxidation by oxygen. This experiment showed the formation of 2.10-OD (40% yield, distinctive singlet at δ 8.96 due to aromatic proton Hₐ and a singlet at δ 2.71 due to the methyl protons next to the carbonyl group) (eqn. 2.6). After aeration, the NMR spectrum is entirely consistent with the quantitative formation of 2.11, with the Hₐ proton shifted upfield to δ 8.67 and the methyl peak upfield to δ 2.68. All of these observations indicate that 2.1 does undergo a clean photoredox reaction in aqueous solution.

\[
\text{O} \quad \text{CH₃} \quad \xrightarrow{\text{hv}} \quad \text{OH} \quad \text{H₂O-CH₃CN} \quad \text{or} \quad \text{D₂O-CD₃CN} \\
\text{2.1} \quad \rightarrow \quad \text{2.11} \quad \text{(D)HO} \quad \text{Hₐ} \quad \text{CH₃} \quad \rightarrow \quad \text{2.10-OD} \quad \text{(D)HO} \quad \text{Hₐ} \quad \text{CH₃}
\]

Semi-preparative photolyses were carried out to confirm the reactivity of all compounds (based on initial UV-Vis studies as above) and to isolate, characterize and in some cases trap initial photoproducts. Semi-preparative photolysis of 2.1 (10⁻⁴ M, 1:1 H₂O-CH₃CN, pH 7) was carried out in a large quartz tube. Exposure to 300 nm gave a yellow solution. When worked-up in air, the solution was bleached quickly to cleanly give 2.11 (>90%). Using the photoredox reaction reported for HMAQ as a secondary
actinometer ($\Phi = 0.8$, pH 7), we estimated a quantum yield of photoredox for 2.1 to be about 0.7.

When the anthraquinone bears two CH$_2$OH substituents at the 2 and 3 positions, will it behave in the manner observed for 2.1 or HMAQ? Thus, diol 2.7 was synthesized to explore this question. Exposure of 2.7 to 300 nm excitation resulted in the formation of an intense sharp band at 268 nm with a shoulder band at 286 nm, and less intense but broad bands at 395 nm and 450 nm (Figure 2.2). Although the intense new absorption bands are different from those observed for HMAQ, the long wavelength bands are entirely consistent with those of DHA. After aeration, all new bands disappeared quickly to give a spectrum almost identical to that of 2.7. These observations indicate that diol 2.7 gives a photoproduct bearing an oxidizable anthracene chromophore prior to aeration.

**Figure 2.2** UV-Vis traces of the photoredox reaction of 2.7 in 1:1 H$_2$O-CH$_3$CN ($\lambda_{ex} = 300$ nm). Each trace represents 10 s of photolysis. Photolysis resulted in loss of absorption (due to the photoreaction of 2.7) at 259 and 326 nm with formation of 2.13 (268 nm, 286 nm, 395 nm and 450 nm). Inset: seven-fold expansion of the long wavelength region.
Due to the low solubility of 2.7 in CH$_3$CN, the photochemistry of 2.7 could not be carried out in a small amount (1 mL) of D$_2$O-CD$_3$CN. Instead, semi-preparative photolysis of 2.7 ($10^{-4}$ M, 1:1 H$_2$O-CH$_3$CN, pH 7) was employed. Photolysis of 2.7 ($10^{-4}$, 1:3 H$_2$O-CH$_3$CN, pH 7, deaerated with argon) was carried out in a large quartz tube (100 mL). Exposure to 300 nm gave an orange yellow solution which was bleached when worked-up in air. Finally, the major product, cyclic hemiacetal 2.14 (65%), and a minor product, lactone 2.16 (7%), were isolated (combined quantum yield, $\Phi \sim 0.5$) (Scheme 2.1).

![Scheme 2.1 Proposed mechanism for the intramolecular photoredox reaction of 2.7](image)

Although the anticipated photoredox product 2.12 was not observed, the above results are readily rationalized by the proposed mechanism shown in Scheme 2.1. Anthraquinone 2.7 undergoes an intramolecular photoredox reaction in the manner observed for HMAQ...
or 2.1, to generate the expected initial redox product aldehyde 2.12, which exists as the
cyclic hemiacetal 2.13. Subsequently, 2.13 is oxidized in air to give 2.14 as the major
isolated product. In the semi-preparative photolysis of 2.7, 2.16 was also isolated albeit in
low yield. One possibility is that during photolysis of 2.7, the product 2.13 is oxidized to
give 2.14 due to the presence of residual oxygen. Subsequently, 2.14 undergoes a
secondary photoredox reaction, give 2.15, which on work-up gives lactone 2.16.

To gain further evidence for the secondary photoredox reaction of 2.14, UV-Vis studies
of 2.14 were carried out in 1:1 H2O-CH3CN. Exposure to 300 nm resulted in the
enhancement of the intense sharp band at 258 nm and formation of a less intense but
broad band at 476 nm which was assignable to 2.15 (Figure 2.3). After aeration, all new
bands disappeared quickly to give a spectrum identical to that of 2.16. These observations
further show that 2.14 is photoredox active.
Figure 2.3 UV-Vis traces of the photoredox reaction of 2.14 in 1:1 H₂O-CH₃CN (λₑₓ = 300 nm). Each trace represents 10 s of photolysis. Photolysis resulted formation of 2.15 (258 nm and 476 nm). Inset: ten-fold expansion of the long wavelength region.

Finally, semi-preparative photolysis of 2.14 (10⁻⁴, 1:3 H₂O- CH₃CN, pH 7, deaerated with argon) was carried out in a 100 mL quartz tube. Exposure to 300 nm gave an orange yellow solution which was bleached when worked-up in air. Lactone 2.16 was isolated in 50% yield.

Cyclic acetal 2.8 has no alcohol moiety so there is no prior information as to whether a photoredox reaction would occur or not. Fortunately, UV-Vis studies of 2.8 in 1:1 H₂O-CH₃CN showed formation of a new chromophore with absorption bands at 278 nm and 455 nm (Figure 2.4). The long wavelength band is consistent with that observed for DHA. After aeration, all new bands disappeared quickly to give a spectrum almost
identical to that of 2.8. These observations suggest that photolysis of cyclic acetal 2.8 gives a primary product bearing an anthracene chromophore. In addition, the presence of several isosbestic points indicates that all of these new bands belong to the same product.

![Absorbance vs Wavelength](image)

**Figure 2.4** UV-Vis traces of the photoredox reaction of 2.8 in 1:1 H₂O-CH₃CN (λₑₓ = 300 nm). Each trace represents 20-60 s of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 2.8) at 253 nm and 328 nm with formation of 2.17 (278 nm and 455 nm). Inset: eight-fold expansion of the long wavelength region.

Direct photolysis of 2.8 (10⁻³ M, 10% D₂O-CD₃CN, pH 7, λₑₓ = 350 nm) in a NMR tube resulted in formation of 2.17-OD (10% yield, singlet at δ 9.11 due to aromatic proton Hₛ). After aeration, the NMR spectrum is entirely consistent with the quantitative formation of 2.18, with the Hₛ proton shifted upfield to δ 8.74 (eqn. 2.7).
Photolysis of 2.8 \((10^{-4} \text{ M}, 1:1 \text{ H}_2\text{O}-\text{CH}_3\text{CN}, \text{pH} 7, \lambda_{ex} 300 \text{ nm})\) in a large quartz tube gave a highly coloured intermediate that is assignable to 2.17, which on treatment with oxygen gives hydroxyester 2.18 in up to 70% yield \((\Phi \sim 0.3)\). This anthraquinone system is closely related to one reported by Song and coworkers\(^{77}\) for the photodeprotection of aldehydes and ketones (also in \(\text{H}_2\text{O}-\text{CH}_3\text{CN}\)) (Scheme 1.14). However, no molecular mechanisms of the photochemical reaction were given in their paper. It is assumed that the chemistry observed in their work is closely related but not identical to the intramolecular redox reaction observed for 2.8.

### 2.3.2 Photodeprotection via the Intramolecular Photoredox Chemistry of 2.2-2.6

Photolabile protecting groups have received considerable attention in recent times, as attested by reviews of Pelliccioli and Wirz\(^{65}\) and Bochet.\(^{80}\) New systems that are efficiently photolabile only in aqueous solution with good absorption characteristics (as is inherent in the anthraquinone chromophore) in the long wavelength UV region are always of interest for application in biological systems.

Anthraquinones have been employed in the past for photodeprotection. Blankespoor and coworkers\(^{78}\) have employed 1-alkoxy-substituted anthraquinones for the photorelease...
of aldehydes and ketones via initial intramolecular hydrogen abstraction to generate a radical pair. Both Iwamura and coworkers\textsuperscript{76} and Song et al.\textsuperscript{77} have employed an anthraquinone-2-yl system for the photodeprotection of alcohols, aldehydes, and ketones. However, these latter studies make no attempts at uncovering the mechanism for the reaction, which may or may not be related to the intramolecular photoredox reaction studied in this work.

In Wan and coworkers' original report of the photoredox chemistry of HMAQ,\textsuperscript{62} it was noted that when the CH$_2$OH side chain was replaced with CH$_2$OCH$_3$, the photoredox chemistry was still observed, with one of the products being CH$_3$OH, although with an attenuation in yield (the reaction was not observed with a simple CH$_3$ side chain).\textsuperscript{62}

Further explorations of the possibility of using the anthraquinone-2-yl moiety for the photorelease of alcohols and other functional groups (e.g., aldehydes and ketones) are warranted. Thus, anthraquinones 2.2-2.6 are designed for this purpose, all of which were anticipated to undergo intramolecular photoredox reaction with the release of alcohols (2.2 and 2.3), acetic acid (2.4), aldehyde (2.5) and ketone (2.6).

Initial UV-Vis studies were carried out for 2.2 in 1:1 H$_2$O-CH$_3$CN (deaerated with argon). Short time exposure to 300 nm (< 60 s) resulted in the formation of an intense sharp band at 260 nm and a less intense but broad band at 370 nm that absorbs up to 450 nm (Figure 2.5). When left in the dark (over a 10 min period) or with continued photolysis, this species transforms to a species with bands at 274, 392 and 451 nm which are associated with DHA. After aeration, all new bands disappeared quickly to give the spectrum almost identical to that of 2.2. These observations suggest that the
intramolecular photoredox chemistry of 2.2 gives rise to an observable intermediate on the way to DHA. Similar behaviour was observed for 2.3.

![UV-Vis traces of the photoredox reaction of 2.2 in 1:1 H₂O-CH₃CN (λₑx = 300 nm). Each trace represents 20s - 60s of photolysis. Early photolysis resulted in loss of absorption (due to photoreaction of 2.2) at 250 and 325 nm with formation of an observable intermediate 2.19 (260 and 370 nm). This is subsequently transformed to DHA (over a 10 min period; loss of 260 nm band, formation of 274, 392 and 451 nm bands). Inset: ten-fold expansion of the long wavelength region.]

Figure 2.5 UV-Vis traces of the photoredox reaction of 2.2 in 1:1 H₂O-CH₃CN (λₑx = 300 nm). Each trace represents 20s - 60s of photolysis. Early photolysis resulted in loss of absorption (due to photoreaction of 2.2) at 250 and 325 nm with formation of an observable intermediate 2.19 (260 and 370 nm). This is subsequently transformed to DHA (over a 10 min period; loss of 260 nm band, formation of 274, 392 and 451 nm bands). Inset: ten-fold expansion of the long wavelength region.

The photochemistry of 2.2 (10⁻³ M, 10% D₂O-CD₃CN, pH 7, λₑx 350 nm) was studied by direct photolysis in an NMR tube under argon. This experiment showed formation of DHA-OD (30% yield, singlet at δ 10.07 due to the aldehyde proton and a singlet δ 8.90 due to aromatic proton H₆) as well as formation of CH₃CH₂OD (characteristic triplet and quartet at δ 1.10 (J = 7.3) and δ 3.52 (J = 7.3), respectively (eqn. 2.8). After aeration,
the NMR spectrum is entirely consistent with quantitative formation of FAQ, with the aldehyde proton shifted downfield to δ 10.15 and the Hₐ proton upfield to δ 8.67.

Similar results were obtained for 2.3, which gave photoproduct 2.10-OD (40% yield, singlet at δ 9.02 due to aromatic proton Hₐ and a singlet δ 2.72 due to the methyl protons next to the carbonyl group), and photoreleased the corresponding CH₃OD (characteristic singlet at δ 3.24), respectively. After aeration, the NMR spectrum is entirely consistent with the quantitative formation of 2.11, with the Hₐ proton shifted upfield to δ 8.72 and the methyl protons upfield to δ 2.69.

![Chemical Structures](image)

A proposed mechanism of reaction for 2.2 (and 2.3) is shown in Scheme 2.2. Excited 2.2 undergoes carbonyl oxygen protonation with benzyl C-H bond deprotonation, to give a quinone dimethide intermediate 2.19 (also an enol or enol ether). Further reaction requires nucleophilic attack by water (with protonation at the remaining ketone) to generate dihydroxyanthrancene 2.20, which is expected to quickly release CH₃CH₂OH to give DHA, followed by transformation to FAQ when exposed to oxygen. Evidence for formation of 2.19 is provided in Figure 2.5 in which an intermediate absorbing at 260 nm
and 370-450 nm was observed prior to formation of DHA. Gritsan and coworkers reported a related \( \sigma \)-quinone dimethide 2.21 at 380 and 590 nm generated via intramolecular hydrogen abstraction of triplet excited 1-methylantraquinone (it is not possible using this method to photogenerate the isomer that directly corresponds to 2.19 in which the OCH\(_2\)CH\(_3\) is replaced by H). Since 2.19 is cross-conjugated whereas 2.21 is not (it has a longer linearly conjugated system), it is expected to have a longer wavelength absorption band. Therefore, we have tentatively assigned the observed intermediate at 260 nm and 370-450 nm as quinone dimethide 2.19.

![Chemistry Diagram]

**Scheme 2.2** Proposed mechanism of reaction for 2.2

\[ 2.21 \ (\lambda_{\text{max}} \ 380, 590 \text{ nm}) \]
Finally, semi-preparative photolyses of 2.2 and 2.3 were carried out in 100 mL quartz vessels (10^{-4} M, 1:1 H2O-CH3CN, pH 7, argon purged). Upon work-up in air, 2.11 and FAQ were obtained in up to 90% yield. In these runs, the formation of the corresponding photoreleased CH3CH2OH and CH3OH was not observed due to the work-up procedure which involved drying under vacuum. In order to follow the photorelease of CH3CH2OH and CH3OH, photolyses were carried out in 10% D2O-CD3CN (pH 7) using 3 mL quartz cuvettes (under argon purge) and monitored by ^1H NMR at various time intervals (Figure 2.6). The plot shows that conversions as measured by released alcohol reached up to 90%. Quantum yield measurements showed that both 2.2 and 2.3 were about equally efficient, with Φ ~ 0.4 in 1:1 H2O-CH3CN.

![Figure 2.6](image)

**Figure 2.6** Yields of CH3CH2OH (▲) and CH3OH (■) from photolysis of 2.2 and 2.3, respectively, in 10% D2O-CD3CN (λex 300 nm), as determined by ^1H NMR (relative to the starting material). Measurement error is ± about 5%.
Acetate ester 2.4 was expected to undergo similar photoredox chemistry as observed for 2.2 and 2.3, which would offer a method for the photorelease of carboxylic acids. However, to our great surprise, 2.4 proved to be photoinert under conditions in which extensive (> 90%) photoredox was observed for HMAQ and 2.1-2.3. In these runs, 2.4 was recovered unchanged after photolysis. Extended photolysis led only to photodecomposition with no evidence of any photoredox reaction. We were puzzled at the complete lack of photoredox chemistry since one would not have anticipated a great deal of difference with respect to electronic character between a CH$_3$O and a CH$_3$(C=O)O group at the benzylic position of the anthraquinone chromophore. On closer analysis, one would argue that the (ester) oxygen on the acetyl group is less able (via electron withdrawing inductive effects) to stabilize a developing positive charge (which is presented in the proposed mechanism in Section 2.4.7) at the benzylic position compared to an oxygen on a simple alkyl group. Since it is known that a simple methyl group on the anthraquinone leads to an unreactive compound (with respect to photoredox reaction)$^{62}$ it would appear that such a small change could lead to lack of reaction. Another possibility is that the carbonyl oxygen of the acetyl group is able to deprotonate (or partially deprotonate) the benzylic proton in the excited state, via a cyclic transition state. If this is completely reversible, only non-productive deactivation of the excited state would result. However, photolysis in D$_2$O resulted in no observable deuterium incorporation in recovered 2.4 indicating that there is no reversible proton transfer either to solvent water or to the acetyl group. Since 2.4 was completely unreactive, related derivatives were not studied further until a better understanding of the lack of reaction is available.
Recently, Song and coworkers reported a similar anthraquinone system for the photodeprotection of carboxylic acids.\textsuperscript{82} In 1:1 H\textsubscript{2}O-CH\textsubscript{3}CN, 2-(1'-hydroxyethyl)-anthraquinone (2.22) was photoinert, which is consistent with our observations with 2.4. However, photolysis of 2.22 in neat CH\textsubscript{3}OH photoreleases the corresponding benzoic acid (\(\Phi = 0.077\)) (Scheme 2.3). The authors suggested that the proposed mechanism involves a photoreduction via hydrogen abstraction step. Thus, triplet excited 2.22 is reduced by CH\textsubscript{3}OH, to give dihydroxyanthracene 2.23. Subsequently, 2.23 undergoes a photoreaction to release benzoic acid, and give enol 2.24. Ketonization of 2.24 gives 2.25. The photodeprotection reaction observed for 2.22 in CH\textsubscript{3}OH has significant differences compared to the pathways for 2.2 and 2.3. Compound 2.22 reacts via initial photoreduction whereas 2.2 and 2.3 react via overall intramolecular photoredox reaction.

\begin{center}
\includegraphics[width=\textwidth]{scheme2_3.png}
\end{center}

\textbf{Scheme 2.3} Proposed mechanism for photolysis of 2.22 to release benzoic acid
Based on positive results observed for 2.2 and 2.3, we anticipated that compounds 2.5 and 2.6 will undergo an analogous photoredox reaction, which would release the corresponding benzaldehyde and acetophenone, respectively as shown in Scheme 2.4. Initial UV-Vis studies of 2.5 showed the requisite formation of a coloured intermediate on photolysis at 300 nm (absorptions at 269, 391 and 450 nm) in 1:3 H$_2$O-CH$_3$CN, (bleached on introduction of air), which is assignable to redox product 2.13 (Figure 2.7). The same behaviour was observed for 2.6.

Figure 2.7 UV-Vis traces of photoredox reaction of 2.5 in 1:1 H$_2$O-CH$_3$CN ($\lambda_{ex}$ = 300 nm). Each trace represents 10 s of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 2.5) at 258 and 326 nm with formation of 2.13 (269 nm, 391 nm and 450 nm). Insert: ten-fold expansion of the long wavelength region.
The low solubilities of both 2.5 and 2.6 prevented studies in sealed NMR tubes (preventing oxidation of initial photoproduts) which would have been more ideal for the analysis of released benzaldehyde and acetophenone. Instead, semi-preparative photolyses were carried out in 100 mL quartz vessels with work-up in air. In these runs, up to 80% yield of 2.16 was obtainable with formation of the corresponding benzaldehyde (characteristic aldehyde singlet at δ 10.00) and acetophenone (characteristic methyl singlet at δ 2.59). The expected initial redox product 2.13 was not observed. Since the quantum yield for reaction of 2.5 and 2.6 were the lowest observed for this series of compounds (Φ ~ 0.02), long photolysis times were required to achieve significant conversion. One possibility is that initially formed redox product 2.13 was oxidized in situ to 2.14 during these long photolysis runs, which on further photolysis (subsequent photoredox reaction) would lead to 2.15 and subsequently 2.16 (Scheme 2.4). This is consistent with the photoredox reaction of 2.14 discussed in Section 2.3.1.
Scheme 2.4 Proposed mechanism for photolysis of 2.5 to release benzaldehyde

2.3.3 Photochemistry of Diketone 2.9

Finally, the potential photoredox chemistry of diketone 2.9 was explored. The compound is related to anthraquinone HMAQ except for the lack of “annelation” of the second ring, as well as possessing all of the structural features of benzophenone 1.51, which is known to undergo efficient photoredox reaction in acid (pH < 3) (eqn. 1.11).\textsuperscript{49} We were disappointed initially since no reaction was observed on photolysis of 2.9 in 1:1 H\textsubscript{2}O-CH\textsubscript{3}CN, pH 1-7 (reported pH is of the aqueous portion). However, at pH ~ 0 (about 5% H\textsubscript{2}SO\textsubscript{4}), significant changes were observed in the UV-Vis spectrum on photolysis (Figure 2.8), namely, the formation of two distinct bands at 316 and 426 nm which were unchanged on introduction of air to the solution.
Figure 2.8  UV-Vis traces observed on photolysis of diketone 2.9 in 1:1 H₂O-CH₃CN (λₓ 300 nm; pH 0; argon purged). Each trace represents 10 min of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 2.9) at 259 nm with formation of 2.29 (316 nm and 426 nm). Insert: eight-fold expansion of the long wavelength region

Semi-preparative photolysis of 2.9 in 1:1 H₂O-CH₃CN, pH ~ 0 gave diphenylisobenzofuran 2.29 (50%) and diketone aldehyde 2.30 (30%) (combined Φ ~ 0.003) (eqn. 2.9). Consistent with the above UV-Vis traces, isobenzofuran 2.29 has absorption bands at 316 and 426 nm (see Appendix B). Indeed, 2.29 would be the logical acid-catalyzed condensation product of the initially formed intramolecular redox product 2.28 (or an alternate isomer obtained by interchange of the ketone and benzhydrol moieties). Independent photolysis of 2.29 in the presence of oxygen gave 2.30 quantitatively consistent with the literature on the photochemistry of diphenylisobenzofurans.¹³
Consistent with its isobenzofuran chromophore, 2.29 in CH$_3$CN displayed the expected absorption bands from 350 nm to 500 nm ($\lambda_{em} = 550$ nm), and long wavelength fluorescence with a broad band between 460 nm and 710 nm ($\lambda_{ex} = 440$ nm). Photolysis of 2.29 in the presence of air resulted in the significant decrease of both absorption and fluorescence emission. These observations are rationalized by the photochemical formation of 2.30, which is not fluorescent, and has very different UV-Vis absorption characteristics compared to 2.29.

2.4 Mechanistic Studies

2.4.1 Isotope Effects on the Photoredox Reaction
The proposed mechanism$^{62}$ of the intramolecular photoredox reaction of anthraquinone HMAQ involves two key proton transfer steps. One is protonation of the ketone and the other is deprotonation of the C-H bond of the benzylic CH$_2$OH moiety. To probe the importance of the C-H bond breaking step, compound HMAQ-$\alpha$$D$ was made as this substrate offers the choice between a C-H vs. a C-D bond at the CH$_2$OH moiety. We had also intended to study the $\alpha$,\$-dideutero compound (in direct comparison experiments with HMAQ) but were unable to readily synthesize the required
compound. In any event, compound HMAQ-\(\alpha D\) proved to be just as useful as the C-H vs. C-D bond breakage occurs from the *same* reactive excited state.

Photolysis of HMAQ-\(\alpha D\) (10\(^{-5}\) M, 1:1 H\(_2\)O-CH\(_3\)CN, pH 7, argon purged, 300 nm) was carried out at 1-4 min intervals and gavex oxidized products FAQ-D and FAQ in overall conversions of 25-85% when solutions were worked-up in air, *via* the initially formed redox products 2.31 and DHA, respectively (eqn. 2.10). The proportion of FAQ-D vs. FAQ was calculated based on the integration of the aldehyde proton of FAQ vs. aromatic proton H\(_a\) of FAQ and FAQ-D. The product ratio was further confirmed by MS analysis. The ratio of yield for FAQ-D: FAQ was 2.1 ± 0.1 which can be equated to an isotope effect for quantum yield of photoredox reaction, \(\Phi_H/\Phi_D = 2.1 ± 0.1\). That is, there is a preference for breaking the C-H bond compared to the C-D bond in this reaction. Indeed, since both C-H and C-D bonds come from the same excited state, this ratio is also equable to a kinetic isotope effect for deprotonation, \(k_H/k_D\).

![Chemical diagram](image)

Kinetic isotope effects for the deprotonation of C-H vs. C-D are not well reported in organic photochemistry since only a few well-defined excited state carbon acids are known.\(^{18b}\) We have reported a primary kinetic isotope effect \((k_H/k_D)\) of 2.8 ± 0.4 for the
deprotonation of the benzylic protons of dibenzosuberene,\textsuperscript{84} a very strong carbon acid in $S_1$, and a primary isotope effect for reaction (at the benzylic position) of $1.9 \pm 0.2$ for a related photoredox reaction of a nitro biphenyl alcohol.\textsuperscript{85} These values are remarkably similar to the value observed for the anthraquinone system under study. This result is consistent with a mechanism in which the rate limiting step probably involves C-H bond breaking (at the CH$_2$OH moiety) of a prior protonated substrate (at the carbonyl oxygen). This is illustrated in Scheme 2.5 where the excited anthraquinone deprotonation undergoes either loss of the C-H to give $2.32$-$\alpha D$ and then $2.31$, or loss of the C-D to give $2.32$ and then DHA. Remarkably, recovered HMAQ-$\alpha D$ did not lose deuterium content in exhaustive photolyses carried out in H$_2$O indicating that the deprotonation step is irreversible.

Scheme 2.5 Deprotonation of the excited anthraquinone HMAQ-$\alpha D$
To explore the effect of H₂O vs. D₂O on photoredox reaction of anthraquinone HMAQ, photolysis of HMAQ was carried out in 3 mL quartz cuvettes (deaerated by argon purge) as a function of H₂O/D₂O content (in CH₃CN). The extent of the photoredox reaction was monitored at 280 nm (formation of DHA or deuterated DHA in D₂O) and the observed ΔA (which is directly proportional to quantum yield for the reaction) plotted vs. water content (Figure 2.9).

![Graph showing ΔA vs. % (v/v) H₂O (D₂O) in MeCN](image)

**Figure 2.9** Effect of H₂O (■) and D₂O (▲) content (in CH₃CN) on photoredox efficiency of HMAQ (λₑₓ = 300 nm) monitored at 280 nm (formation of DHA). Measurement error is about ± 5%.

The photoredox reaction is very sensitive to water content especially at the lower water region noting that no reaction was observed in neat CH₃CN. It reaches a plateau region (in efficiency) at about 20% (v/v) water. Note also that use of D₂O results in a lower quantum yield in most water contents, by as much as 20% at 15% (v/v) H₂O(D₂O). In low and high water regions, we were unable to detect a significant difference in relative
efficiency using the technique employed although in most cases, reaction in the presence of D$_2$O was always less efficient. It seems reasonable to assume that the details of the photoredox mechanism change with water content since the span of water concentrations converted ranges from mostly CH$_3$CN to 40% water. An analysis of solvent isotope effects over this range of water content is beyond the scope of this work but it seems clear that proton transfer to the carbonyl oxygen is intimately involved in the reaction mechanism. The generally small solvent isotope effects observed are consistent with fast rates of proton transfer from the solvent to the carbonyl oxygen and this is entirely consistent with excited state proton transfers.

2.4.2 pH Effects on the Photoredox Reaction

Previous studies of benzophenone 1.51 showed that no photoredox reaction was observed for 1.51 in neutral aqueous solution. But when the pH of the solution was lower than 3, an efficient photoredox reaction was observed. This indicates that the photoredox behaviour of benzophenone 2.51 is acid catalyzed. Although HMAQ has an efficient photoredox in neutral aqueous solution (Φ ~ 0.8), we wondered whether or not the photoredox of HMAQ can be acid catalyzed as was observed for 1.51.

To explore the effect of pH on the efficiency of the intramolecular photoredox reaction of HMAQ, photolyses of HMAQ (10$^{-4}$ M, 1:1 H$_2$O- CH$_3$CN, argon purged, $\lambda_{ex}$ = 300 nm, pH 13-1) were carried out in 100 mL quartz vessels. After irradiation, all solutions were worked up in air. Conversion yields (%) of the photoredox product were determined with proton NMR. The results are plotted as a function of pH in Figure 2.10. No acid catalysis for this reaction was observed between pH 9 and pH 1. Instead, the reaction displayed a base inhibition above pH 9. These observations strongly suggest that the
proton (or hydroxide ion) concentration plays an important role in the photoredox reaction. Isotope effect on the photoredox reaction as shown in Section 2.4.1 suggests that the rate limiting step might involve a C-H bond breaking (at the CH₂OH moiety) of a prior protonated substrate (at the carbonyl oxygen). Although basic solution is favourable for the benzyllic C-H bond breaking, it is unfavourable for the protonation of the carbonyl oxygen. Alternatively, there may be an unproductive photophysical or a photochemical quenching pathway as hydroxide ion is increased. The details of this quenching pathway were not further investigated.

![Conversion Yield vs pH](image)

**Figure 2.10** pH Dependence of intramolecular photoredox efficiency for HMAQ in 1:1 H₂O-CH₃CN, ~10⁻⁴M, N₂ (pH refers to the aqueous portion). Measurement error is about ±5%.

### 2.4.3 Solvent Effects on the Photoredox Reaction

It has been noted⁶² that HMAQ does not undergo photoredox in neat CH₃CN but upon increasing H₂O content, the photoredox reaction is observed and becomes more efficient. The role of H₂O in the photoredox reaction is believed to be as a mediating solvent and as a catalytic source of protons and weak base, but not as a reducing agent. On the other
hand, it is well-known that alcohols function as efficient direct reducing agents (*via* initial hydrogen abstraction from the alcohol) for a variety of photoexcited anthraquinones and related compounds.\(^{59}\) To explore the effect of an alcoholic solvent on the intramolecular photoredox reaction, photolyses of **HMAQ** were carried out in H\(_2\)O-CH\(_3\)CH\(_2\)OH mixtures.

Initial photolysis of **HMAQ** in neat CH\(_3\)CH\(_2\)OH (argon saturated, not water-free) followed by work-up in air gave only oxidized aldehyde product **FAQ** up to 25% yield without any photoreduction product. It has been reported\(^ {59}\) that anthraquinones undergo photoreduction in CH\(_3\)CH\(_2\)OH to give dihydroxyanthracenes which readily react with oxygen to restore the starting materials (anthraquinones). Thus, in principle, photoreduction product \(^{2.33}\) was probably generated and oxidized quickly to **HMAQ** in the presence of air (Scheme 2.6).

To obtain evidence for the formation of \(^{2.33}\), a method of trapping \(^{2.33}\) was developed to give a stable product that could be isolated and subjected to NMR and MS analyses. Since \(^{2.33}\) is an aromatic alcohol, a viable trapping method is to convert it to its acetyl ester, by a reaction with Ac\(_2\)O using base, which would give diacetoxyanthracene alcohol \(^{2.35}\).

The same idea was also used to trap the photoredox product **DHA**, to form diacetoxyanthracene aldehyde \(^{2.34}\). Isolation of \(^{2.34}\) would provide additional evidence that an anthracene moiety is formed in the photoredox reaction. A solution of **HMAQ** (10\(^{-4}\) M, 1:1 H\(_2\)O-CH\(_3\)CN, pH 7, argon purged) was photolyzed in the usual way as described above. After photolysis, sufficient solid NaOH was added to the photolysate to basicify the solution to pH > 10. The solution turned blue upon basification, consistent
with formation of the dianion of a dihydroxyanthracene. Excess \( \text{Ac}_2\text{O} \) were then added, which quenched the blue colour. Upon work-up, diacetoxyanthracene aldehyde 2.34 (up to 85\% yield) was isolated (Scheme 2.6). Consistent with its anthracene chromophore, 2.34 exhibits the expected structured five-finger excitation band from 310 to 420 nm and long wavelength fluorescence, with \( \lambda_{\text{em}} = 461 \text{ nm} \) in addition to the standard NMR data.

![Chemical diagram]

**Scheme 2.6** Trapping of photoredox products (DHA and 2.33) of HMAQ

Photolysis of HMAQ in neat \( \text{CH}_3\text{CH}_2\text{OH} \) followed by the above trapping protocol gave a mixture of diacetoxyanthracene alcohol 2.35 (75\%) and diacetoxyanthracene aldehyde 2.34 (25\%) (Scheme 2.6). Formation of 2.34 is evidence for an intramolecular photoredox pathway which is minor in neat \( \text{CH}_3\text{CH}_2\text{OH} \). The dominant pathway is
simple photoreduction to give 2.33, which is subsequently trapped by Ac₂O to form 2.35. Thus in the presence of a weak hydrogen donor such as CH₃CH₂OH, simple photoreduction via initial hydrogen abstraction\(^{59}\) dominates. However, the fact that the intramolecular photoredox reaction occurred is in direct contrast to the complete lack of reaction observed in neat CH₃CN. This is consistent with the requirement of a hydroxyl solvent to mediate the intramolecular photoredox reaction. When water was added (1:1 (v/v) H₂O- CH₃CH₂OH), photolysis of HMAQ resulted in 70% yield of 2.34 and 30% yield of 2.35. Interestingly, photolysis of HMAQ in neat CH₃CH₂OH under oxygen gave only 2.34 suggesting that only intramolecular photoredox reaction occurred. However, the simple photoreduction product 2.33 would be oxidized quickly to HMAQ in the presence of oxygen which on further photolysis would eventually give rise to the intramolecular photoredox product DHA, which is sufficiently long-lived in oxygen (due to the electron withdrawing aldehyde substituent on the anthracene ring) to be trapped by Ac₂O to give 2.34.

We have found that it is also possible to follow the competition between simple photoreduction vs. intramolecular photoredox using UV-Vis spectrophotometry. UV-Vis studies of HMAQ on photolysis in 1:1 H₂O-CH₃CN (only intramolecular redox) showed the formation of dihydroxyanthracene DHA with \(\lambda_{\text{max}}\) 280, 380 and 450 nm. Photolysis in neat 2-propanol (only photoreduction) resulted in dihydroxyanthracene 2.33 with \(\lambda_{\text{max}}\) 267 and 440 nm. By following the OD of the sharper 280 and 267 nm bands, it is possible to qualitatively monitor the competition between simple photoreduction vs intramolecular photoredox of HMAQ in H₂O-2-propanol mixtures (Figure 2.11). In 50% H₂O-2-propanol, the major pathway is simple photoreduction. When 2-propanol was replaced
with CH₃CH₂OH, the major pathway in 50% H₂O-CH₃CH₂OH was intramolecular photoredox. These observations are consistent with the better hydrogen donating ability of 2-propanol compared to CH₃CH₂OH.

![Graph showing solvent effect on the competition between intramolecular photoredox (formation of DHA) and simple photoreduction (formation of 2.33) on photolysis of HMAQ in H₂O-2-propanol mixtures. ■ absorption due to DHA at 280 nm; ▲ absorption due to 2.33 at 267 nm. Measurement error is about ±5%.]

**Figure 2.11** Solvent effect on the competition between intramolecular photoredox (formation of DHA) and simple photoreduction (formation of 2.33) on photolysis of HMAQ in H₂O-2-propanol mixtures; ■ absorption due to DHA at 280 nm; ▲ absorption due to 2.33 at 267 nm. Measurement error is about ±5%.

### 2.4.4 Nanosecond Laser Flash Photolysis (LFP) of HMAQ

LFP was employed to gain a better understanding of reaction mechanism, in particular to confirm triplet state reactivity and the possibility of observing critical intermediates which would be expected to be formed by the formal photoredox reaction.

The triplet-triplet absorption spectrum of HMAQ (10⁻⁵ M in neat CH₃CN, flow cell, nitrogen purged) showed an intense absorption band centered at 380 nm (Figure 2.12). The signal decayed with first order kinetics (1.7 ± 0.1 × 10⁵; τ ~ 6 μs). The intensity and lifetime of this transient was significantly reduced in the presence of oxygen (τ ~ 0.39
μs). Similar observations were made for 9,10-anthraquinone, namely, an intense absorption band centered at 380 nm in neat CH$_3$CN ($\tau \sim$ 7 μs in nitrogen saturated solution) that is quenched by oxygen ($\tau \sim$ 0.6 μs). All of these observations are consistent with an excited triplet 9,10-anthraquinone (an intense 380 nm absorption, $\tau \sim$ 6 μs in nitrogen saturated solution, $\tau \sim$ 10 ns in oxygen saturated solution) as reported by Görner.$^{59a}$ Based on the above, we assign the 380 nm transient observed for HMAQ to the triplet state.

![Absorbance vs Wavelength](image)

**Figure 2.12** Triplet-triplet absorption spectra of HMAQ in neat CH$_3$CN (nitrogen-saturated) after the 266 nm pulse, 1.44 μs ($\sigma$), 4.26 μs ($\circ$), 16.3 μs ($\Delta$), 38.8 μs ($\times$). Insets: triplet decay ($\tau \sim$ 5.9 μs, at 380 nm). Measurement error is about ±10%.

In the presence of water, LFP of HMAQ ($10^{-5}$ M, 1:1 H$_2$O-CH$_3$CN, pH 7, nitrogen purged) showed an intense band at 390 nm and a shoulder band at 440 nm. The two signals gradually decayed to give a steady transient with two absorption bands at 390 and
460 nm (the absorption spectrum at 78 μs in Figure 2.13), which is almost identical to the UV-Vis spectrum of DHA. Since the photoredox product could be observed in general UV-Vis spectroscopy, it can also be observed by LFP. Thus, the steady transient must be the photoredox product DHA. The decay of the signal could not be fitted to a single exponential function, suggesting a presence of more than one species (τ ~ < 0.1 μs and 11 μs). In the presence of oxygen, both absorption bands at 390 and 440 nm also gradually decayed (τ ~ < 0.1 μs and τ ~ 9 μs) to give DHA in almost same yield as that in nitrogen saturated solution. Photolysis of 9,10-anthraquinone under the same experimental condition showed only a triplet transient (τ ~ 0.6 μs) with a broad absorption band ranging from 340 nm to 500 nm (λ_{max} = 400 nm). Thus, the two absorption bands at 390 and 440 nm are assigned to be a combination of a short-lived triplet excited state (τ < 0.1 μs), and a long-lived intermediate state (τ ~ 10 μs). The latter is not quenched by oxygen.
Figure 2.13  Triplet-triplet absorption spectra of HMAQ in 1:1 H$_2$O-CH$_3$CN (nitrogen-saturated) after the 266 nm pulse, 0.1 us (*), 2 µs (○), 8 µs (○), 33 µs (Δ), 78 µs (×). Inset: triplet and intermediate decay at 450 nm. Measurement error is about ±10%.

2.4.5 Quenching of Triplet HMAQ

The above LFP studies gave evidence that photolysis of HMAQ generates a triplet excited state but not conclusive evidence that triplet HMAQ is photoreactive in the photoredox reaction. If the triplet HMAQ is reactive, we expect it may be quenched using a triplet quencher, which would result in a significantly lower overall yield of the photoredox product.

An efficient quencher should have a lower triplet energy than the triplet state energy of the substrate (the triplet energy of 9,10-anthraquinone: $^3\Delta E \sim 62$ kcal/mol)$^{86}$. Sorbic acid (a conjugated diene) has $^3\Delta E \sim 60$ kcal/mol and is an excellent quencher of triplet excited states,$^{44,87}$ and is water soluble. Thus, sorbic acid was employed to study the reactivity of triplet HMAQ.
Photolyses of HMAQ (10^{-4} M, 1:1 H2O- CH3CN, pH 7, argon purged, \lambda_{ex} 350 nm) were carried out in 100 mL quartz vessels in the presence of sorbic acid (0 \sim 0.02 M). After work-up in air, the yields (the formation of FAQ, 8 \sim 35\%) were determined with NMR. A Stern-Volmer plot (\Phi_0 / \Phi = 1 + k_q \tau [Q]) for the photolysis of HMAQ was made (\Phi_0 / \Phi vs. the concentration of sorbic acid, where \Phi_0 / \Phi refers to the ratio of the conversion yields in the absence and presence of sorbic acid, k_q refers to the triplet quenching rate constant, \tau refers to the lifetime of the triplet excited state, [Q] refers to the concentration of the quencher). The biphasic plot (Figure 2.14) showed initial linear quenching at low concentrations of sorbic acid (< 0.08 M) and a plateau region with \Phi_0 / \Phi \sim 4 at the high concentrations of sorbic acid (0.01-0.02 M). These values can be interpreted to mean that with respect of the photoredox reaction, about 25\% of HMAQ of the reaction cannot be quenched by sorbic acid. This means that about 75\% of the photoredox reaction of HMAQ proceeds via the triplet excited state. The remaining “unquenchable” fraction (the flat region) is most likely due to the singlet excited state reaction although one cannot rule out the possibility of reaction via another short-lived triplet state. From the initial linear region of the plot, the slope (k_q \tau) was 295 M^{-1}.

Assuming that the bimolecular triplet quenching rate constant is diffusion-controlled in water (5 \times 10^{-9} M^{-1}s^{-1}), it was estimated that the reactive triplet lifetime of HMAQ was 60 ns. This result is consistent with the observations for LFP studies that indicates that the reactive triplet HMAQ is short-lived (\tau < 0.1 \mu s) in the presence of water.
Figure 2.14 Stern-Volmer plot of quenching of the photoredox reaction for HMAQ in the presence of sorbic acid. Measurement error is about ±5%.

Oxygen is also a very efficient quencher ($^3\Delta E \sim 30$ kcal/mol) of triplet excited states. We expected oxygen could quench the triplet HMAQ as well. Photolysis of HMAQ ($10^{-4}$ M) was carried out in oxygen saturated solution (1:1 H$_2$O-CH$_3$CN, pH 7). After work-up in air, the conversion yield of FAQ in the absence and presence of oxygen was $\Phi_0/\Phi \sim 1.05$. Since the bimolecular triplet quenching rate constant of oxygen for anthraquinone in benzene is $1.4 \times 10^9$ M$^{-1}$s$^{-1}$, one can estimate that the reactive triplet lifetime of HMAQ is 50 ns. The result is consistent with the triplet quenching studies using sorbic acid.

2.4.6 HOMO/LUMO Calculations
As Section 1.3 noted, an excited state may be thought of as originating when an electron is promoted from the HOMO to the LUMO. To gain additional insights into the
possible underlying reasons for the photochemical behaviour of HMAQ, the HOMO and LUMO of HMAQ were calculated at the AM1 level using Chem 3D.

**Figure 2.15** Calculated HOMO (left) and LUMO (right) for HMAQ (Chem 3D, AM1)

Shown in Figure 2.15 are the results for the HOMO and LUMO of HMAQ, which is typical for most of the anthraquinones studied in this work. If one assumes that the electronic distribution of the excited singlet or triplet state can be approximated by the change in MO coefficients on promotion of an electron from the HOMO to the LUMO, then it is clear that the excited state will gain electron density at the central ring and in particular at the carbonyl carbon and oxygen atoms, and lose electron density from the ring with the attached substituent. Note in particular the loss of electron density from the ArCH₂ protons. These predictions in change in electron density corroborates the proposed mechanism in which protonation of the carbonyl oxygen is required along with deprotonation of one of the ArCH₂ protons (details are presented in Section 2.4.7). Interestingly, the same calculations showed that the loss of electron density from the benzene ring containing the CH₂OH group in 2.9 would be minor, and this correlates with the low photoredox reactivity observed for this compound.
2.4.7 Proposed Reaction Mechanisms

LFP and triplet quenching studies (Section 2.4.4 and 2.4.5) gave evidence that the triplet excited state is reactive. Although we can not rule out reaction via a short-lived singlet excited state, that the triple state is reactive is consistent with much of the known photochemistry of anthraquinones. Isotope effect studies of HMAQ-\textit{aD} (Section 2.4.1) are consistent with a reaction limiting step involving deprotonation of the benzylic C-H. Based on the above mechanistic studies, a postulated mechanism is shown in Scheme 2.7.

\begin{equation*}
\text{HMAQ} \quad \begin{array}{c}
\text{1) hv} \\
\text{2) ISC} \\
\text{3) H}_2\text{O-CH}_3\text{CN} \\
\text{pH 7}
\end{array} \rightarrow \begin{array}{c}
\text{[1]} \\
\text{[2]} \\
\text{2.36a}
\end{array}
\end{equation*}

\begin{equation*}
\text{DHA} \quad \begin{array}{c}
\text{CHO} \\
\text{ketonization/enolization}
\end{array} \rightarrow \begin{array}{c}
\text{[2.37]} \\
\text{2.36b}
\end{array}
\end{equation*}

\text{Scheme 2.7 Proposed mechanism for the intramolecular photoredox reaction of HMAQ}

The photoredox reaction requires water. Not only does water act as the proton source and base for deprotonation necessary for the photoredox reaction, but it provides a polar environment for the reaction. Increasing the percent of water in the solvent mixture (H\textsubscript{2}O-CH\textsubscript{3}CN) increases the polarity of the solvent mixture. Change of solvent polarity has a
significant effect on the efficiency of the photoredox reaction. Just as Section 2.4.2 noted, when the percent of water was lower than 15%, the yield of redox product dropped dramatically with the decrease of the amount of water. However, note that even at the lowest percent of 1%, there is still 1.7 mM water. Compared with the concentration (10^{-5} M) of anthraquinone HMAQ, there is still a large excess of water for the photoredox reaction. Thus, we suggest that the photoredox reaction proceeds via the π−π* lowest triplet state because polar solvents stabilize the π−π* triplet state. Lack of water may result in a switch between the π−π* triplet state and n−π* triplet state. This is favourable for hydrogen abstraction which leads to photoreduction. This is consistent with the observation of photoreduction products when a hydrogen donor solvent is used as shown in Section 2.4.3.

Simple HOMO/LUMO calculations (Section 2.4.6) shows that the LUMO has a high electron density on the center ring of the anthraquinone moiety and low electron density on the benzylic carbon. Thus, anthraquinone ketone should exhibit enhanced basicity. Upon protonation (2.36a), assuming the compound is still in the excited state and the charge distribution does not change, the benzene ring with the attached hydroxymethyl group is still electron deficient since its previous charge has been transferred to the central ring on the anthraquinone moiety. This results in a net positive charge localized at the 2-position of benzene ring. Deprotonation by water at the benzylic position gives the dienol 2.37, which upon ketonization/enolization gives DHA (Scheme 2.7).

One may postulate that the first protonation of carbonyl oxgen might occur at the 9 position instead of the 10 position as shown in the alternative mechanistic pathway of the Scheme 2.8. Indeed, simple HOMO/LUMO calculations do not show any difference of
electron density between these two positions. Thus, the proton transfer from water to carbonyl oxygen may occur at the 9-position. The possible mechanism is very similar to that of the photoredox reaction observed for benzophenone 1.51,49 which generates a biradical dienol 1.54 (Scheme 1.9). Note that in this case, 2.38 is the anologue of 1.54. Thus, 2.38 will transfer to 2.39, which ultimately will give DHA.

Scheme 2.8 Alternative mechanistic pathway for the photoredox reaction of HMAQ

As noted before, the photoexcited compound is highly polarized with enhanced electron density on the central ring of the anthraquinone moiety and low electron density on the benzene ring with the attached hydroxymethy group. Thus, one may also postulate
that the deprotonation of the benzylic C-H might occur first (eqn. 2.11), to form benzylic
carbonanion 2.40 and eventually 2.41, which has a net negative charge on the carbonyl
oxygen. This would undergo protonation by water and follow the same steps as shown in
Scheme 2.7, to give photoredox product DHA.

\[
\begin{align*}
\text{2.40} \\
\text{2.41}
\end{align*}
\]

However, the effect of pH on the efficiency of the photoredox reaction of HMAQ
(Section 2.4.2) shows that at pH > 9, the yield of photoredox product DHA dropped
dramatically. These observations suggest that the protonation of carbonyl oxygen is most
likely the first step. At pH > 9, protonation of carbonyl oxygen by water or hydronium is
highly unlikely. This would inhibit the subsequent deprotonation of the benzylic C-H,
resulting in a low overall yield of the photoredox reaction.

2.5 Summary
Results presented in this chapter showed that the intramolecular photoredox reaction
observed for HMAQ is a reasonably general reaction for a variety of anthraquinones 2.1-
2.9 (except 2.4) in aqueous solution (Table 2.1). Some of these derivatives have potential
as photoprotecting agents, releasing their protected moieties via intramolecular
photoredox reaction. Diketone 2.9 also undergoes an analogous photoredox reaction in acidic aqueous solution ($\Phi = 0.003$, pH 0), demonstrating that other aromatic diketones can react in an analogous fashion.

**Table 2.1 Quantum yields for the formation of photoredox products of anthraquinone derivatives**

<table>
<thead>
<tr>
<th>Anthraquinone derivatives</th>
<th>Photoredox products</th>
<th>Photoreleased products</th>
<th>Quantum yield ($\Phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>2.11</td>
<td>/</td>
<td>0.7$^a$</td>
</tr>
<tr>
<td>2.2</td>
<td>FAQ</td>
<td>Ethanol</td>
<td>0.4$^a$</td>
</tr>
<tr>
<td>2.3</td>
<td>2.11</td>
<td>Methanol</td>
<td>0.4$^a$</td>
</tr>
<tr>
<td>2.5</td>
<td>2.16</td>
<td>benzaldehyde</td>
<td>0.02$^b$</td>
</tr>
<tr>
<td>2.6</td>
<td>2.13</td>
<td>acetophenone</td>
<td>0.02$^b$</td>
</tr>
<tr>
<td>2.7</td>
<td>2.13</td>
<td>/</td>
<td>0.5$^b$</td>
</tr>
<tr>
<td>2.8</td>
<td>2.18</td>
<td>/</td>
<td>0.3$^a$</td>
</tr>
</tbody>
</table>

$^a$ Solvent is 1:1 H$_2$O-CH$_3$CN, pH 7. $^b$ Solvent is 1:3 H$_2$O-CH$_3$CN, pH 7.

The intramolecular photoredox reaction is different from simple photoreduction, which is a well-known primary reaction for aromatic ketones. The photoredox reaction requires water, a solvent in which simple photoreduction cannot occur. It is known that photoreduction of aromatic ketones goes via the $n,\pi^*$ triplet state, whereas the photoredox reaction most likely proceeds via the $\pi,\pi^*$ triplet state. The photoredox reaction is unimolecular with respect to the anthraquinone moiety whereas photoreduction must be bimolecular involving substrates and reducing agents. The essential steps in the photoredox mechanism include (a) protonation of the carbonyl oxygen of the triplet excited state; (b) deprotonation of the benzylic carbon; (c) thermal ketonization and enolization of a dienol to form the photoredox product. In the following chapters of this Thesis, the photoredox reaction will be extended to substrates in which
the reduced and oxidized moieties are separated by greater molecular distances (further apart), demonstrating further generality and applicability of the photoredox reaction.

2.6 Experimental

2.6.1 General

NMR spectra were recorded on Bruker instruments, 300 or 500 MHz for $^1$H, and 75 or 125 MHz for $^{13}$C. IR spectra were recorded on a Perkin-Elmer 283 instrument. UV-Vis spectra were taken on a Cary 1 spectrophotometer. Mass spectra were obtained on a Kratos Concept H spectrometer. All solvents for synthesis (ACS grade) were purchased from Aldrich and used as received. CH$_3$CN (HPLC grade) and distilled water were used in photolyses. CDCl$_3$, D$_2$O and acetone-$d_6$ were purchased from Cambridge Isotope laboratory and D$_2$SO$_4$ was obtained from Aldrich. Preparative TLC was carried out on 20 cm × 20 cm silica gel GF Uniplates (Analtech). All readily available organic and inorganic reagents required in the synthesis and photolyses were purchased from Aldrich and used as received.

2.6.2 UV-Vis Studies

UV-Vis studies (~$10^{-5}$ M in H$_2$O-CH$_3$CN, pH 7) were carried out in 3.0 mL quartz cuvette (1 cm). Solutions were bubbled using a fine needle with argon for 5 min to remove any dissolved oxygen. Parafilm was then used to seal the open side of the cuvette. Solutions were then irradiated at 300 nm or 350 nm in a Rayonet photochemical reactor. UV-vis spectra were recorded before and after each photolysis.

2.6.3 Product Studies

Compounds were photolyzed in 100 mL quartz tubes using a Rayonet RPR 100 photochemical reactor equipped with 300 nm or 350 nm lamps. Typically, a solution of
the compound \((10^{-4}, 10^{-5}) \text{ M}, \text{H}_2\text{O-CH}_3\text{CN (1:1 or 1:3), pH7 or 0})\) was bubbled with argon for 15 min and then irradiated under argon purge. The irradiated solution was extracted by \(3 \times 50 \text{ mL CH}_2\text{Cl}_2\) in air and the collected organic extracts was dried over anhydrous MgSO\(_4\). The solvent was removed under reduced pressure and the photolysate analyzed by NMR, MS and IR.

In order to monitor the initially formed redox product, photolyses were carried out in NMR tubes which allowed characterization of the first formed redox products. NMR tubes were filled with 1 mL of the appropriate solution \((10^{-3} \text{ M, 10\% D}_2\text{O-CD}_3\text{CN})\). Solutions were bubbled using a fine needle through rubber stoppers with argon for 15 min before irradiation then irradiated with 300 nm or 350 nm lamps.

2.6.4 Quantum Yield Measurements

Quantum yields were measured using NMR and the reaction of 2-(hydroxymethyl)anthraquinone (HMAQ) as a secondary actinometer \((\Phi = 0.8)\).\(^{62}\) A solution of the compound \((2.1-2.9, 10^{-4} \text{ M}, \text{in H}_2\text{O-CH}_3\text{CN (1:1 or 1:3), pH 7 or 0})\) was purged with argon for 15 min and irradiated for 1 min at 300 nm (2 lamps) under argon purge. After irradiation, the conversion to product was determined by \(^1\text{H} \text{NMR}\) and compared to an identical run using HMAQ. All converions were kept below 30% and repeated twice.

2.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ

LFP studies were conducted at the University of Victoria LFP facility employing a Spectra Physics Quanta-Ray YAG laser, model GSR-11, with a pulse width of \(\sim 10 \text{ ns}\) and excitation wavelength 266 nm. The energy of the laser pulse was less than 20 mJ / Pulse, with a repetition rate of 1 Hz. Quartz flow cells were used and solutions were
purged with nitrogen or oxygen for 20 min prior to measurement. Optical densities at 266
nm were ~ 0.6.

2.6.6 Synthesis of Anthraquinone Derivatives HMAQ-αD, 2.1-2.9
α-D-2-(Hydroxymethyl)-9,10-anthraquinone (HMAQ-αD)

NaBD₄ (0.023 g, 2.4 mmol) in 20 mL of anhydrous CH₃OH was added dropwise to 2-
formylanthraquinone (FAQ, 0.14 g, 0.6 mmol) in 20 mL of anhydrous CH₃OH under N₂.
The mixture was stirred in an ice water bath for 2 h. After reaction, 20 ml of saturated
NH₄Cl was added and the resulting solution extracted by 2 × 25 mL of CH₂Cl₂. The
collected extractions were dried over anhydrous MgSO₄ and the solvent was removed.
The residue was purified by column chromatography with silica gel using 5% EtOAc in
CH₂Cl₂ as an eluent, to give HMAQ-αD (white powder, 0.13 g, m.p 183-185°C) in 90%
yield. ¹H NMR (CDCl₃, 300 MHz) δ 8.31-8.20 (m, 4H), 7.82-7.20 (m, 3H), 4.86 (s, 1H),
2.0 (s, broad OH peak); MS (EI), m/z 239 (M⁺, 100), 238 (20), 237 (32), 235 (42).

The 2-formylanthraquinone (FAQ) was prepared by photolysis of 2-
(hydroxymethyl)anthraquinone (HMAQ) which was purchased from Aldrich. A solution
(100 mg of HMAQ in 1:1 H₂O-CH₃CN, argon purged, in 300 mL of photolysis quartz
tube) was irradiated for 10 min and extracted with 3 × 50 mL CH₂Cl₂. The combined
extractions were dried over anhydrous MgSO₄ and solvent was removed. The same
procedure was repeated three times. The combined material was purified by column
chromatography with silica gel using CH₂Cl₂ as an eluent, to give FAQ (pale yellow
powder, 0.24 g) in 80% yield. ¹H NMR (CDCl₃, 300 MHz) δ 10.20 (s, 1H), 8.74 (s, 1H),
8.41 (d, 1H, J = 8.1 Hz), 8.37-8.25 (m, 2H), 8.26 (d, 1H, J = 8.1 Hz), 7.90-7.77 (m, 2H);
¹³C NMR (CDCl₃, 75 MHz) 191.0, 182.6, 182.3, 140.1, 137.1, 134.9, 134.8, 134.3, 133.5
(2C), 133.3, 129.7, 128.4, 127.7 (2C); MS (EI), m/z 236 (M⁺, 100), 237 (75), 235 (90), 207 (38).

**Benzyl bromides HMAQ-b and 2.1b**

A mixture of HMAQ-a (2 g, 8 mmol), NBS (1.8 g, 10 mmol) and benzoyl peroxide (0.2 g, 0.8 mmol) in 100 mL of benzene was refluxed overnight. After reaction, the mixture was washed with distilled water (2 x 50 mL) and the collected organic solution was dried over anhydrous MgSO₄. After the solvent was removed, the brown crude product was purified by column chromatography with silica gel using CH₂Cl₂ as an eluent, to give HMAQ-b (yellow powder, 2.3 g) in 92% yield. ¹H NMR (CDCl₃, 300 MHz) δ 8.33-8.22 (m, 4H), 7.84-7.71 (m, 3H), 4.57 (s, 1H).

Compound 2.1b (yellow powder, 2.1 g, 90% yield) was prepared by bromination of 2.1a following the same procedure as that described for HMAQ-b. ¹H NMR (CDCl₃, 300 MHz) δ 8.32-8.13 (m, 3H), 8.03 (d, 1H, J = 8.1 Hz), 7.78 (d, 1H, J = 8.1 Hz), 7.75-7.67 (m, 2H), 5.20 (q, 1H, J = 6.6 Hz), 2.03 (d, 3H, J = 6.6 Hz).

**2-(1-Hydroxyethyl)-9,10-anthraquinone (2.1)**

A mixture of 2.1b (2.0 g, 6.3 mmol) and CaCO₃ (4.5 g, 4.5 mmol) in 50 mL of 1:1 water and dioxane was refluxed for 2 days. After the reaction, 5 mL of H₂SO₄ (0.5 M) was added to the mixture to neutralize the excess CaCO₃ and extracted with 2 x 50 mL CH₂Cl₂. The collected extractions were dried over anhydrous MgSO₄ and solvent was removed. The crude material was purified by column chromatography with silica gel using a mixture of hexane and EtOAc as eluent, to give 2.1 (yellow powder, 1.2 g, m.p. 101-103°C) in 75% yield, ¹H NMR (300 MHz, CDCl₃) δ 8.35-8.24 (m, 4H), 7.87-7.74 (m, 2H), 7.50 (d, 1H, J = 8.6 Hz).  

* The compound has been previously synthesized. (G. Manecke, and W. Storck, The Vinyl-9,10-anthraquinone, *Chemische Berichte*, 1961, 94, 3239-3250)
3H), 5.08 (q, 1H, J = 6.6 Hz), 2.0 (s, broad OH peak), 1.56 (d, 3H, J = 6.6 Hz); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) 183.3, 183.1, 152.9 (2C), 134.4, 134.3, 133.7, 133.6, 132.7, 131.3, 127.9, 127.4, 127.3, 124.2; MS (EI), m/z 252 (M\(^+\), 3), 237 (75), 210 (100); HRMS calculated for C\(_{16}\)H\(_{12}\)O\(_3\) 252.0786; observed 252.0776; IR (KBr, cm\(^{-1}\)) 3418, 3069, 2973, 1675, 1591.

2-(Ethoxymethyl)-9,10-anthraquinone (2.2)*

A mixture of HMAQ-b (0.37 g, 1.2 mmol) and CaCO\(_3\) (0.31 g, 6 mmol) in 20 mL of CH\(_3\)CH\(_2\)OH was refluxed overnight. After the reaction, 6 mL of H\(_2\)SO\(_4\) (0.5 M) was added to neutralize the excess CaCO\(_3\) and extracted by 2 × 50 mL CH\(_2\)Cl\(_2\). The collected extracts were dried over anhydrous MgSO\(_4\) and solvent was removed to give a brown crude material which was purified by column chromatography with silica gel using CH\(_2\)Cl\(_2\) as an eluent, to give 2.2 (pale yellow powder, 0.18 g, 115-117\(^\circ\)C) in 56% yield. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.33-8.25 (m, 3H), 8.23 (s, 1H), 7.82-7.74 (m, 2H), 4.65 (s, 2H), 3.61 (q, 2H, J = 7.4 Hz), 1.28 (t, 3H, J = 7.4 Hz); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz) 183.3, 183.1, 152.9 (2C), 134.4, 134.3, 133.7, 133.6, 132.7, 131.3, 127.9, 127.4, 127.3, 124.2; MS (EI), m/z 266 (M\(^+\), 10), 237 (75), 210 (100); HRMS calculated for C\(_{17}\)H\(_{14}\)O\(_3\) 266.0943; observed 266.0945; IR (KBr, cm\(^{-1}\)) 3068, 2974, 2867, 1677, 1590.

2-(1-Methoxyethyl)-9,10-anthraquinone (2.3)

A mixture of 2.1b (0.27 g, 0.86 mmol) and CaCO\(_3\) (0.43 g, 4.3 mmol) in 30 mL of CH\(_3\)OH was refluxed for 3 days. After the reaction, 9 mL of H\(_2\)SO\(_4\) (0.5 M) was added to neutralize excess CaCO\(_3\). This was followed by the addition of 200 mL of water to the mixture to give a yellow precipitate. After suction filtration, the yellow precipitate

(powder) was recrystallized from CH₃CH₂OH to give 2.3 (yellow crystalline plates, 0.17g, m.p. 95-96ºC) in 74% yield. ¹H NMR (CDCl₃, 300 MHz) δ 8.34-8.26 (m, 3H), 8.22 (s, 1H), 7.82-7.73 (m, 3H), 4.47(q, 1H, J = 6.6 Hz), 3.28 (s, 3H), 1.47 (d, 3H, J = 6.6 Hz); ¹³C NMR (CDCl₃, 75 MHz) 183.4, 183.1, 150.9 (2C), 134.4, 134.3, 133.9, 133.7, 133.0, 131.8, 128.0, 127.4 (2C), 125.1, 79.3, 57.1, 23.8; MS (EI), m/z 266 (M⁺, 10), 251 (100), 235 (20); HRMS calculated for C₁₇H₁₄O₃ 266.0943; observed 266.0941; IR (KBr, cm⁻¹) 3064, 2974, 2823, 1677, 1590.

2-(Acetoxyethyl)-9,10-anthraquinone (2.4)*

A mixture of HMAQ (0.20 g, 0.8 mmol) and CH₃COCl (0.12 g, 1.6 mmol) was refluxed in 10 mL of THF for 12 h in the presence of pyridine (0.3 mL). After the reaction, the solution was poured into 50 mL of ice-cold water and stirred to give a yellow precipitate. The precipitate was isolated by suction filtration and purified by column chromatography with silica gel using 20% EtOAc-CH₂Cl₂ as an eluent, to give 2.4 in 70% yield (pale yellow powder, 0.14 g, m.p. 149-150ºC); ¹H NMR (CDCl₃, 300 MHz) δ 8.35-8.25 (m, 4H), 7.85-7.72 (m, 3H), 5.25 (s, 2H), 2.16 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) 183.1, 182.9, 170.8, 142.9 (2C), 134.5, 134.4, 133.9, 133.7, 133.3, 133.1, 127.9, 127.5 (2C), 126.3, 65.3, 21.1; MS (EI), m/z 280 (M⁺, 3), 238 (100), 221 (10), 209 (25); HRMS calculated for C₁₇H₁₂O₄ 280.0736; observed 280.0740; IR (KBr, cm⁻¹) 3068, 2945, 1741, 1677, 1590.

9-Phenyl-7,11-dihydro-8,10-dioxacyclohepta [b]anthracene-5,13-dione (2.5)

A solution of 2.7 (0.2 g, 0.74 mmol) and benzoic acid (0.4 mL, 3.0 mmol) in 10 mL of toluene along with one drop of con. H₂SO₄ was refluxed for 0.5 h in a Dean-Stark

apparatus, to give a brown solution. After the reaction, the solution was neutralized with 5% NaHSO₃ to give a brown precipitate. The brown precipitate was isolated by suction filtration and purified by column chromatography with silica gel using CH₂Cl₂ as eluent, to give 2.5 (pale yellow powder, 0.13 g, m.p. 223-225°C) in 49% yield. ¹H NMR (CDCl₃, 300 MHz) δ 8.35-8.24 (m, 2H), 8.06 (s, 2H), 7.84-7.75 (m, 2H), 7.60-7.52 (m, 2H), 7.44-7.33 (m, 3H), 6.00 (s, 1H), 5.12 (d, 2H, J = 14.7 Hz), 5.02 (d, 2H, J = 14.7 Hz); ¹³C NMR (CDCl₃, 75 MHz) 183.0 (2C), 145.6 (2C), 138.0, 134.4 (2C), 133.7 (2C), 132.5 (2C), 129.1, 128.6 (2C), 127.5 (2C), 126.7 (2C), 125.8 (2C), 103.6, 68.4 (2C); MS (EI), m/z 356 (M⁺, 2), 250 (80), 234 (100); IR (KBr, cm⁻¹) 3057, 2958, 2885, 1671, 1590.

9-Methyl-9-phenyl-7,11-dihydro-8,10-dioxacyclohepta[b]anthracene-5,13-dione (2.6)

Compound 2.6 was prepared from 2.7 (0.1g, 0.37 mmol) and acetophenone (0.18 mL, 1.5 mmol) following the synthetic procedure described for 2.5 in 30% overall yield (2.6, white powder, 0.041 g, m.p. 209-210°C). ¹H NMR (CDCl₃, 300 MHz) δ 8.26-8.18 (m, 2H), 7.92 (s, 2H), 7.76-7.68 (m, 2H), 7.58-7.51 (m, 2H), 7.38-7.24 (m, 3H), 5.02 (d, 2H, J = 15.5 Hz), 4.82 (d, 2H, J = 15.5 Hz), 1.64 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) 183.0 (2C), 145.4 (2C), 142.4, 134.3 (2C), 133.8 (2C), 132.3 (2C), 128.6, 128.4 (2C), 127.4 (2C), 126.2 (2C), 125.3 (2C), 104.7, 65.7 (2C), 26.1; MS (EI), m/z 370 (M⁺, 2), 355 (20), 250 (40), 105 (100); HRMS calculated for C₂₄H₁₈O₄ 370.1205; observed 370.1209; IR (KBr, cm⁻¹) 3050, 2934, 2867, 1675, 1591.

2.3-Di(hydroxymethyl)-9,10-anthraquinone (2.7)

A mixture of 2.7a (Aldrich, 1.0 g, 4.5 mmol), NBS (1.8 g, 10.4 mmol) and benzoyl peroxide (0.10 g, 0.04 mmol) in 50 mL of benzene was refluxed overnight. After the reaction, the mixture was washed with distilled water (2 × 50 mL) and the collected
organic solution was dried over anhydrous MgSO₄. After solvent was removed, a brown residue (2.7b, 1.8g, 90% yield) was obtained. A mixture of 2.7b (1.8 g, 4.6 mmol) and CaCO₃ (4.6g, 46 mmol) was refluxed in 1:1 water and dioxane for 2 days to give a brown solution. After the reaction, 75 mL of H₂SO₄ (0.5 M) was added to neutralized excess CaCO₃. Upon addition of 200 mL water, a brown precipitate was formed which was collected by suction filtration. This crude material was recrystallized from toluene to give 2.7 (yellow brown needles, 0.34 g, m.p. 214-216°C) in 30% yield. ¹H NMR (acetone-d₆, 500 MHz) δ 8.42 (s, 1H), 8.30-8.26 (m, 2H), 7.94-7.90 (m, 2H), 4.88 (d, 2H, J = 5.5 Hz), 4.65 (t, OH, J = 5.5 Hz); ¹³C NMR (acetone-d₆, 125 MHz) 183.6 (2C), 147.3 (2C), 135.1 (2C), 134.7 (2C), 133.2 (2C), 127.7 (2C), 125.8 (2C), 61.7 (2C); MS (EI), m/z 267 (M⁺-1, 3), 264 (70), 248 (65), 235 (100); IR (KBr, cm⁻¹) 3205, 3069, 2932, 1672, 1587.

2-[1,3]Dioxolan-2-yl-9,10-anthraquinone (2.8)

Compound 2.8 was prepared from FAQ (0.3 g, 1.3 mmol) and ethylene glycol (0.08 g, 1.3 mmol) followed the procedure described for 2.5 with 74% overall yield (2.8, pale yellow powder, 0.27 g, m.p. 129-131°C). ¹H NMR (CDCl₃, 300 MHz) δ 8.34 (s, 1H), 8.28-8.19 (m, 3H), 7.84 (d, 1H, J = 8.1 Hz), 7.78-7.70 (m, 2H), 5.89 (s, 1H), 4.16-4.00 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) 183.1 (2C), 144.7 (2C), 134.4, 134.1, 133.8, 133.7, 133.6, 132.2, 127.8, 127.5, 127.4, 125.7, 102.8, 65.8 (2C); MS (EI), m/z 280 (M⁺, 75), 279 (100); HRMS calculated for C₁₇H₁₂O₄ 280.0736; observed 280.0728; IR (KBr, cm⁻¹) 3069, 2956, 2889, 1724, 1676, 1592.

1,2-Dibenzoyl-4-methylbenzene (2.9)
Compound 2.9 was prepared from 2.9a (0.8 g, 2.7 mmol) following the synthetic procedure described for 2.7. Column chromatography with silica gel by using CH$_2$Cl$_2$ was employed to give pure 2.9 in an overall yield of 65% (2.9, pale yellow oil, 0.55 g). $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.70-7.61 (m, 4H), 7.57 (s, 1H), 7.56 (d, 2H, $J = 5.9$ Hz), 7.53-7.44 (tt, 2H, $J = 8.1$ Hz), 7.53-7.43 (tt, 4H, $J = 8.1$ Hz), 4.79 (s, 2H), 2.0 (s, broad OH peak); $^{13}$C NMR (CDCl$_3$, 75 MHz) 197.1, 196.6, 144.3, 140.7, 138.9, 137.4, 137.3, 133.3, 133.2, 130.4, 130.0 (2C), 129.9 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.7, 64.4; IR (KBr, cm$^{-1}$) 3448, 3059, 2870, 1655, 1596; MS (EI), m/z 316 (M$^+$, 10), 314 (M$^+$-2, 60), 237 (55), 105 (100).

Compound 2.9a was in turn prepared following a literature procedure with 30% overall yield (2.9a, pale yellow oil, 1.2 g). $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.65-7.54 (m, 4H), 7.49-7.35 (m, 3H), 7.35-7.22 (m, 6H), 2.38 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) 197.2, 196.5, 141.7, 140.8, 137.7, 137.6, 137.0, 133.2, 133.0, 131.0, 130.4, 130.3, 130.0 (2C), 129.9 (2C), 128.6 (2C), 128.5 (2C), 21.7; MS (EI), m/z 300 (M$^+$, 60), 223 (100).

2.6.7 Photolysis Procedures for HMAQ-$\alpha$D, 2.1-2.9 and Characterization of Products

Photolysis of HMAQ-$\alpha$D

Compound HMAQ-$\alpha$D (6 mg in 50 mL CH$_3$CN and 50 mL H$_2$O, pH 7) was irradiated for 1 min, 2 min and 4 min at 300 nm (2 lamps) under argon, to give a yellow brown solution. After work-up in air, the brown residue was characterized by $^1$H NMR to give a mixture of FAQ (8-28%) and FAQ-D (17-57%). Further purification was obtained by prep. TLC (silica gel, CH$_2$Cl$_2$) to give a mixture of FAQ and FAQ-D (yellow powder, 5 mg), $^1$H NMR (CDCl$_3$, 300 MHz) δ 10.2 (s, 1H), 8.77 (s, 3.1 H), 8.45 (d, 3.1 H, $J = 8.1$ Hz).
Hz), 8.40-8.23 (m, 8.8 H), 7.91-7.76 (m, 6.2 H); MS (EI), m/z 237 (M⁺, 80), 236 (60), 235 (100).

Photolysis of 2.1 and 2.3

Photolysis of compound 2.1 (10 mg, 1:1 H₂O-CH₃CN, 350 nm, 16 lamps, 1 min, argon purged) gave a yellow brown solution. After work-up in air, the brown residue was characterized by ¹H NMR to give 2.11 (70% conversion). Further purification was obtained by prep. TLC (silica gel, CH₂Cl₂), to give 2.11 (yellowish powder, 6 mg, 60% yield). Following the same photolysis procedure of 2.1, photolysis of 2.3 also gave product 2.11 (60% yield). ¹H NMR (CDCl₃, 300 MHz) δ 8.79 (s, 1H), 8.41-8.23 (m, 4H), 7.86-7.75 (m, 2H), 2.73 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) 196.97, 182.7, 182.6, 141.3, 136.3, 134.7 (2C), 134.0, 133.7, 133.6, 133.1, 128.1, 127.69, 127.67, 127.6, 22.3; MS (EI), m/z 322 (M⁺, 3), 280 (10), 238 (100); HRMS calculated for C₁₉H₁₄O₅ 250.0630; observed 250.0630; IR (KBr, cm⁻¹) 3065, 1693, 1673, 1589.

Photolysis of 2.2

Following the same photolysis procedure as for 2.1, photolysis of 2.2 gave product FAQ (yellow powder, 60% yield).

Photolysis of 2.5 and 2.6

Photolysis of 2.5 (5 mg, 1:3 H₂O-CH₃CN, pH 7, 300 nm, 16 lamps, 5 min, argon purged) gave a yellow brown solution. After work-up in air, the brown residue was characterized by ¹H NMR to give 2.16 (30% conversion). Further purification was obtained by TLC (silica gel, CH₂Cl₂) to give 2.16 (white powder, 1 mg, 25% yield). Photolysis of 2.6 also gave 2.16 by following the same photolysis procedure of 2.5. ¹H NMR (Acetone-d₆, 500 MHz) δ 8.66 (s, 1H), 8.59 (s, 1H), 8.37-8.33 (m, 2H), 8.03-7.98
(m, 2H), 5.67 (s, 2H); MS (EI), m/z 264 (M+, 60), 248(5), 235 (100); HRMS calculated for C₁₆H₈O₄ 264.0432; observed 2264.0420; IR (KBr, cm⁻¹) 3076, 2932, 1764, 1673, 1586, 1332, 1303.

**Photolysis of 2.7**

Photolysis of 2.7 (5 mg, 1:3 H₂O-CH₃CN, pH 7, 300 nm, 16 lamps, 1 min, argon purged) gave a brown solution. After work-up in air, the brown residue was characterized by ¹H NMR to give 2.14 (50% conversion). Further purification was obtained by prep. TLC (silica gel, 20% EtOAc-CH₂Cl₂) to give 2.14 (brown yellow powder, 2 mg, 40%). ¹H NMR (Acetone-d₆, 300 MHz) δ 8.40 (s, 1H), 8.36-8.28 (m, 2H), 8.23 (s, 1H), 7.85-7.77 (m, 2H), 6.63 (d, 1H, J = 7.3 Hz), 5.38 (d, 1H, J = 14.0 Hz), 5.17 (d, 1H, J = 14.0 Hz), 3.08 (d, OH, J = 7.3 Hz); MS (EI), m/z 266 (M⁺, 60), 248(100), 235 (45); HRMS calculated for C₁₆H₁₀O₄ 266.0579; observed 266.0572; IR (KBr, cm⁻¹) 3368, 3067, 2916, 2866, 1675 1590, 1327, 1300.

**Photolysis of 2.8**

Photolysis of 2.8 (10 mg, 1:1 H₂O-CH₃CN, pH 7, 300 nm, 16 lamps, 1 min, argon purged) gave a yellow solution. After work-up in air, the yellow residue was characterized by ¹H NMR to give 2.18 in 40% yield. Separation and purification was achieved by prep. TLC (silica gel, CH₂Cl₂) to give 2.18 (yellow powder, 3.5 mg, 30%). ¹H NMR (CD₃Cl, 500 MHz) δ 8.94 (d, 1H, J = 1.8), 8.44 (dd, 1H, J = 1.8, J = 8.1.), 8.38 (d, 1H, J = 8.1), 8.35-8.30 (m, 2H), 7.85-7.80 (m, 2H), 4.54 (t, 2H, J = 4.6 Hz), 4.02 (t, 2H, J = 4.6 Hz); ¹³C NMR (CD₃Cl, 500 MHz) 182.4, 182.2, 165.2, 136.1, 134.8, 134.6, 134.44, 134.38, 133.5, 133.33, 133.3, 128.6, 127.5 127.4, 127.3, 67.3, 61.1; MS (EI), m/z
295 (M⁺-1, 1), 253 (M⁺-C₂H₃O, 70), 235(100), 207 (25); IR (KBr, cm⁻¹) 3358, 3056, 2956, 2884, 1726, 1680, 1591, 1273, 1247.

Photolysis of 2.9

Photolysis of 2.9 (20 mg, 1:1 H₂O-CH₃CN, pH ~ 0 (5% H₂SO₄), 300 nm, 16 lamps, 1.5 h, argon purged) gave a yellow solution. After work-up in air, the yellow powder was characterized by ¹H NMR and assigned to be a mixture of product 2.29 (30% conversion) and 2.30 (14% conversion). The mixture was separated by prep. TLC (silica gel, 20% EtOAc-CH₂Cl₂) to give pure 2.30 (colourless oil, 2 mg, 10% yield) and 2.29 (yellow-orange powder, 5 mg) contaminated with 10% of 2.30 since 2.29 was found to be sensitive to oxygen and light, being readily converted to 2.30 under such conditions.

Characterization of 2.29: ¹H NMR (CD₃Cl, 300 MHz) δ 9.95 (s, 1H), 8.35 (s, 1H), 8.03-7.83 (m, 5H), 7.59-7.44 (m, 5H), 7.44-7.29 (m, 2H); MS (EI), m/z 298 (M⁺, 100), 269(15); HRMS calculated for C₂₁H₁₄O₂ 298.0994; observed 298.0995. Characterization of 2.30: ¹H NMR (CD₃Cl, 300 MHz) δ 10.12 (s, 1H), 8.12 (d, 1H, J = 8.8 Hz), 8.10 (s, 1H), 7.75 (d, 1H, J = 8.8 Hz), 7.70 (d, 4H, J = 7.3 Hz), 7.59-7.50 (m, 2H), 7.45-7.35 (tt, 4H, 1H, J = 7.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) 196.0, 195.5, 190.9, 145.7, 140.8, 137.1, 136.7 (2C), 133.8, 133.7, 131.5, 130.7, 130.2 (2C), 130.0 (2C), 128.8 (4C); MS (EI), m/z 314 (M⁺, 80), 237 (70), 105 (100); HRMS calculated for C₂₁H₁₄O₃ 314.0943; observed 314.0937; IR (neat film, cm⁻¹) 3061, 1703, 1664, 1597.

2.6.8 Trapping of Photolysis Product of HMAQ

Compound HMAQ (20 mg in 50mL of CH₃CN and 50 mL of H₂O, pH 7) was irradiated for 1 min at 300 nm (16 lamps) under argon to give a yellow brown solution. Sufficient solid NaOH was added to change the solution colour to blue. This was
followed by the addition of 1 mL of Ac₂O, which turned the solution to a bright yellow. After work-up in air, the material was characterized by ¹H NMR showing formation of 2.34 (50% conversion). Separation and purification was achieved by prep. TLC (silica gel, CH₂Cl₂) to give 2.34 in 40% yield (yellow powder, 11 mg, m.p. 175-177°C). ¹H NMR (CDCl₃, 300 MHz) δ 10.16 (s, 1H), 8.43 (s, 1H), 8.05-7.91 (m, 4H), 7.66-7.05 (m, 2H), 2.69 (s, 3H), 2.65 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) 191.8, 169.5 (2C), 142.6, 140.8, 134.5 (2C), 130.4, 128.2, 127.5, 126.7, 125.7, 125.1, 123.5, 122.4 (2C), 122.2, 21.0, 20.9; MS (EI), m/z 322 (M⁺, 3), 280 (10), 238 (100); HRMS calculated for C₁₉H₁₄O₅ 322.0841; observed 322.0845; IR (KBr, cm⁻¹) 3067, 2918, 2849, 1757, 1689, 1626.

Following with the above procedure, photolysis of compound HMAQ (20 mg, 350 nm, 16 lamps, 20 min) in neat CH₃CH₂OH gave 2.35 (75% conversion). Further purification was obtained by prep. TLC (silica gel, CH₂Cl₂) to give 2.35 in 60% yield (pale yellow powder, 16 mg, m.p. 194-196°C). ¹H NMR (CDCl₃, 300 MHz) δ 7.97-7.89 (m, 3H), 7.87 (s, 1H), 7.56-7.45 (m, 3H), 4.87 (s, 2H), 2.63 (s, 3H), 2.62 (s, 3H); MS (EI), m/z 324 (M⁺, 10), 282 (15), 240 (100); HRMS calculated for C₁₉H₁₆O₅ 324.0998; observed 324.1000; IR (KBr, cm⁻¹) 3449, 1751.

2.6.9 pH Effects on Photolysis Efficiency of HMAQ
Solutions of HMAQ (10⁻⁴ M, 1:1 H₂O-CH₃CN, pH from 1 to 13) in 100 mL quartz vessels were purged with Ar for 15 minutes prior to photolysis and were irradiated (300 nm, 2 lamps for 1 min. Irradiated solutions were neutralized by 5% NaHCO₃ solution and were extracted by 3 × 50 mL CH₂Cl₂ in air. Collected organic extracts was dried over anhydrous MgSO₄. Removal of solvent was carried out under reduced pressure.
Photolysis yields (%) were determined with proton NMR. Conversion yields (%) were calculated based on the integration of the aldehyde proton of FAQ vs. the total integration of the aldehyde proton of FAQ and one methylene proton of HMAQ.

2.6.10 Quenching of Triplet HMAQ

A mixture of HMAQ \((10^{-4} \text{ M})\) and sorbic acid \((0.001 \text{ M})\) in 1:1 H\(_2\)O-CH\(_3\)CN (pH 7) in a 100 mL large quartz tube was purged with Ar for 15 minutes prior to photolysis and were irradiated (300 nm, 2 lamps) for 1 min. After work-up in air (followed the same procedure as shown in Section 2.6.3), a brown residue was characterized by \(^{1}\text{H}\) NMR to give FAQ in 24 % conversion yield. Following the above procedure, photolysis of HMAQ \((10^{-4} \text{ M})\) and sorbic acid \((0-0.02 \text{ M})\) in 1:1 H\(_2\)O-CH\(_3\)CN (pH 7) were carried out to give FAQ in 5-34% yield.

Following the above irradiation procedure and the work-up procedure as shown in Section 2.6.3, photolysis of HMAQ in oxygen saturated solution (1:1 H\(_2\)O-CH\(_3\)CN, pH 7) gave FAQ in 28% yield.
3. Long-Range Intramolecular Photoredox Reaction of Biphenyl Anthraquinones Mediated by Water*

3.1 Introduction

Previous studies of HMAQ (Chapter 2) supported a mechanism involving a highly polarized triplet excited state in which electron density of the “distal” phenyl moiety is transferred to the central anthraquinone ring via a conjugated π system (Sections 2.4.6 and 2.4.7), which is subsequently trapped adiabatically by protonation at the anthraquinone carbonyl oxygen and deprotonation at the benzyl C–H. This eventually results in an overall photoredox reaction. We wondered whether or not the photoredox reaction observed for HMAQ could occur for substrates in which the benzyl alcohol moiety is much further away from the anthraquinone ketone.

Since the electronic communication for the above reaction relies on π system conjugation, a good way of separating the above reactive moieties (CH₂OH and carbonyl group) is to insert phenyl ring “spacers” that will still allow for potential electronic communication through the π system (in the excited state) but clearly lack substantial ground state electronic communication (due to the twisted nature of biphenyls and biaryls in general). Wan and coworkers have reported the photochemistry of twisted ground state biaryls,⁹² that it is possible to induce photochemistry (e.g., photosolvolyisis) at one end, by a “reactive” chromophore at the other end in a number of biphenyl and terphenyl systems. Exploring the photoredox chemistry of the proposed new types of anthraquinones could give new insights into the photoactivation of distal functional groups mediated by

---

* [Y. Hou, L. A. Huck, and P. Wan, Long-Range Intramolecular Photoredox Reaction via Coupled Charge and Proton Transfer of Triplet Excited Anthraquinones Mediated by Water, Photochem. Photobiol. Sci., 2009, 8, 1408-1415.]-Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association, and RSC.
phenylene (aromatic) spacers. Thus, we synthesized new anthraquinones 3.1-3.4 with phenyl and biphenyl “spacers” between two potentially reactive functional groups (Chart 3.1).

![Chart 3.1]

3.2 Syntheses

3.2.1 Synthesis of 3.1-3.3
Phenyl-substituted anthraquinones are relatively rare compounds. Additionally, we were unable to locate general procedures for Suzuki-type couplings in which one of the coupling partners was an anthraquinone. However, we were eventually successful in using a general Suzuki-type coupling for the synthesis for all of 3.1-3.3. Thus, the synthesis of 3.1-3.3 employed the palladium-catalyzed Suzuki coupling reaction which in this case involved the required phenylboronic acids and the key anthraquinone triflate 3.5 (Scheme 3.1). Initial Pd(PPh₃)₄ catalyzed coupling gave the corresponding methylphenyl compounds (3.1a-3.3a) which were readily transformed to 3.1-3.3 via 3.1b-3.3b using standard functional group manipulation. The overall yields of 3.1-3.3 are 50-60%.
Scheme 3.1 Syntheses of phenyl-substituted anthraquinones 3.1-3.3

3.2.1 Synthesis of 3.4
The synthesis of 3.4 also utilized the key anthraquinone triflate 3.5 (Scheme 3.2). The required bromobiphenyl 3.6 was synthesized from an initial Suzuki coupling of \( p \)-methylphenylboronic acid with \( p \)-iodobromobenzene. Transformation of 3.6 to the corresponding boronic acid 3.7 was followed by Suzuki coupling with 3.5, to give initially 3.4a, which was transformed to 3.4b, and then ultimately to the required 3.4 in 20% overall yield.
Scheme 3.2 Synthesis of biphenyl anthraquinone 3.4

3.3 Product Studies

3.3.1 Photoredox Chemistry of 3.1-3.3

We anticipated that the 3.1-3.3 could undergo intramolecular photoredox reaction in the manner observed for the parent compound HMAQ. Thus, initial studies of the photochemistry of 3.1-3.3 were carried out using semi-preparative scales in 1:1 H₂O-CH₃CN in 100 mL quartz vessels (10⁻⁴ M, pH 7, λₑₓ = 300 nm, argon purged) and worked up in air. After irradiation in argon saturated solution, all compounds gave rise to a light
yellow color. When the solutions were exposed to air, the color was bleached quickly. On work-up, these runs gave cleanly the fully oxidized anthraquinone-aldehyde products 3.8-3.10 but in low yield (<10%) (eqn. 3.1). However, photolyses at pH 1 resulted in much higher yields, up to almost quantitative conversion. This is the first observation of acid catalysis of the photoredox reaction of anthraquinones. For these compounds, the catalytic effect is observable below ca. pH 3. No reaction was observed on photolysis in neat CH₃CN or when the above solutions were left in the dark. Moreover, photolysis of the corresponding methylphenyl compounds 3.1a-3.3a did not give any reaction under similar photolysis times and solvent conditions, showing the need for the readily oxidizable benzyl alcohol moiety.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{H₂O-CH₃CN, pH 1} & \quad \text{O₂} \\
\text{3.1 o-CH₂OH} & \quad \text{3.8 o-CHO} \\
\text{3.2 m-CH₂OH} & \quad \text{3.9 m-CHO} \\
\text{3.3 p-CH₂OH} & \quad \text{3.10 p-CHO}
\end{align*}
\]

(3.1)

To further explore the nature of the coloured species formed initially in the photolysis (before the addition of oxygen on work-up), the photochemical reactions of 3.1-3.3 were studied by UV-Vis spectroscopy. UV-Vis traces of photolysis of 3.1 (10⁻⁵ M, 1:1 H₂O-CH₃CN, pH 1, argon purged, λₑₓ = 300 nm) showed formation of two new bands at 270 and 395 nm, the latter being a completely new long wavelength band (Figure 3.1). The presence of several isosbestic points indicate all these new bands belong to the same product(s) and no secondary reactions occur. These new bands are bleached within 40 min after aeration, to give rise to a spectrum identical to that of anthraquinone aldehyde.
3.8. Visually, the almost colorless solution turned to medium yellow on exposure to light, and then back to colorless on aeration.

![Graph showing absorbance vs wavelength](image)

**Figure 3.1** UV-Vis traces for photolysis of 3.1 in 1:1 H₂O-CH₃CN, pH 1 (λₑₓ = 300 nm; argon purged). Each trace represents 5 s of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 3.1) at 266 and 338 nm and formation of new absorption bands at 270 and 395 nm. Inset: ten-fold expansion of the long wavelength region.

To further exemplify the observed clean photochemical reaction of 3.1, NMR studies of 3.1 were carried out in NMR tubes (10⁻³ M, 10% D₂O-CD₃CN, pD 1, argon purged). Photolysis (5 min) of 3.1 gave a yellow species that is consistent with 3.11-OD (100% conversion since the benzylic proton (δ 4.49) of 3.1 was fully consumed, and all of the aromatic protons assignable to 3.11-OD), with a distinctive aldehyde peak at δ 10.05. After aeration, the yellow color disappeared. The NMR spectrum is now entirely consistent with the quantitative formation of 3.8, with an aldehyde peak shifted upfield to δ 9.95 (Figure 3.2) (Scheme 3.3). All of these observations indicate that 3.1 undergoes a
clean photoredox reaction in aqueous solution catalyzed by acid. The need for water was further illustrated by a photolysis in neat CD$_3$OD (NMR tube) which resulted in only photodecomposition with little if any photoredox reaction.

![Figure 3.2](image)

**Figure 3.2** Proton NMR studies of photolysis of 3.1 in 10% D$_2$O-CD$_3$CN (pD 1, argon saturated). Bottom spectrum for 3.1 prior to photolysis, middle spectrum shows formation of 3.11-OD, and the top spectrum is that of 3.8 (formed upon aeration of 3.11-OD).

Although the initially formed photoredox product 3.11 could be observed by proton NMR on photolysis *in situ* in an NMR tube (the direct product is 3.11-OD), it could not be isolated in preparatory runs; only the oxidized product 3.8 could be characterized in these experiments (eqn. 3.1). However, we have successfully trapped 3.11 as follows. Photolysis of 3.1 ($10^{-4}$ M, argon saturated 1:1 H$_2$O-CH$_3$CN) was carried out in a large 100
mL quartz tube to give a yellow species assignable to 3.11. This was deprotonated by addition of excess NaOH pellets, to give a dark red solution (assigned to the dianion of the dihydroxyanthracene 3.11). The red solution was bleached by the addition of excess Ac₂O. Upon work-up, diacetate 3.11-OAc was isolated in 90% yield (Scheme 3.3), thus confirming the formation of 3.11. In the absence of Ac₂O and NaOH, only the oxidized product 3.8 (90% conversion) was isolated.

Scheme 3.3 Photolysis of 3.1 and trapping of the photoredox product 3.11 of 3.1

UV-Vis studies of 3.2 also showed the clean photoredox reaction, to generate an initial photoredox product which has absorption bands at 288 nm and 399 nm. These two absorption bands were bleached to give the spectrum identical to that of anthraquinone aldehyde 3.9 within 20 min after aeration (Figure 3.3). Similar results were observed for 3.3.
**Figure 3.3** UV-Vis traces of photolysis of 3.2 in 1:1 H$_2$O-CH$_3$CN, pH 1 ($\lambda_{ex}$ = 300 nm; argon purged). Each trace represents 5 s of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 3.2) at 267 and 341 nm with formation of 3.12 (288 and 399 nm). Inset: eightfold expansion of the long wavelength region.

Product studies of 3.2 in NMR tubes also confirmed the formation of an initial photoredox product. Photolysis (5 min) of 3.2 (10% D$_2$O-CD$_3$CN, pD 1, argon purged) gave a yellow species that is consistent with 3.12-OD (100% conversion since the benzylic proton (δ 4.68) of 3.2 is fully consumed, and all the aromatic protons assignable to 3.12-OD) with a distinctive aldehyde peak at δ 10.13 (Figure 3.4) (eqn. 3.2). After aeration, the yellow color disappeared. The NMR spectrum is now entirely consistent with quantitative formation of 3.9, with an aldehyde peak shifted upfield to δ 10.12. Anthraquinone 3.3 also underwent clean photoreaction to generate the corresponding initial photoredox product 3.13-OD which were observed by proton NMR.
Figure 3.4 Proton NMR studies of photolysis of 3.2 in 10% D$_2$O-CD$_3$CN (pD 1, argon saturated). Bottom spectrum is 3.2 prior to photolysis, middle spectrum is 3.12-OD, and top spectrum is that of 3.9 (formed upon aeration of 3.12-OD).
As noted above, the efficiency of the photoredox reaction of 3.1-3.3 was rather low at pH 7. This was confirmed by quantum yield measurements which were measured by the formation of oxidized products (3.8-3.10) with $^1$H NMR (Table 3.1). Indeed, when compared to the parent compound HMAQ ($\Phi \sim 0.8$; pH 7), this was rather disappointing. However, they have substantially high quantum yields at pH 1, which is a redeeming feature (eqn. 3.2). The parent compound HMAQ does not exhibit acid catalysis of reaction in the pH range of 7-1 (Section 2.4.2 in Chapter 2), which is not surprising since its quantum yield of reaction is already quite high in neutral solution.

**Table 3.1 Quantum yields for the formation of photoredox products of biphenyl anthraquinones 3.1-3.3 in 1:1 H$_2$O-CH$_3$CN**

<table>
<thead>
<tr>
<th>Biphenyl anthraquinones</th>
<th>Photoredox products</th>
<th>pH</th>
<th>Quantum yield ($\Phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>3.11</td>
<td>7</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>0.05</td>
</tr>
<tr>
<td>3.2</td>
<td>3.12</td>
<td>1</td>
<td>0.3</td>
</tr>
</tbody>
</table>
3.3.2 Photoredox Chemistry of 3.4

We finally turned our attention to terphenyl system 3.4, which has the longest separation of the two reactive functional groups in our studied anthraquinones. Photolysis of 3.4 \( (10^{-4} \text{ M, 1:3 H}_2\text{O-CH}_3\text{CN, pH 7}) \) in 100 mL quartz vessels gave only a trace yield of 3.14 after work-up in air. However, when the photolysis was carried out in acidic solution (pH 1), a much more intense yellow solution was generated, which was oxygen sensitive. Work-up gave the expected oxidized product 3.14 in good yields (up to 80%; \( \Phi \sim 0.1 \)) (eqn. 3.3).

![Chemical structures](image)

UV-Vis studies were carried out for 3.4 \( (10^{-5} \text{ M}) \) in 1:3 H\(_2\)O-CH\(_3\)CN (pH 1). Exposure to 300 nm resulted in the formation of an intense band at 312 nm and a less intense band at 399 nm. These two bands are bleached within 20 min after aeration, to give rise to a spectrum identical to that of anthraquinone aldehyde 3.14 (Figure 3.5) (eqn. 3.3).
Figure 3.5 UV-Vis traces of photolysis of 3.4 (10^{-5} M, 1:1 H_2O-CH_3CN, pH 1, argon purged, \lambda_{\text{ex}} = 300 \text{ nm}). Each trace represents 1 min of photolysis. Photolysis resulted in loss of absorption (due to photoreaction of 3.4) at 292 and 381 nm with formation of 3.15 (312 and 399 nm). Inset: four-fold expansion of the long wavelength region.

Proton NMR studies of 3.4 also confirmed formation of 3.15 (characteristic aromatic and aldehyde peaks). Finally, semi-preparative photolysis of 3.4 (10^{-4} M, 1:3 H_2O-CH_3CN, pH 1, argon saturated) was carried out in 100 mL quartz vessels and worked up in air, to give the oxidized product 3.14 (eqn. 3.4). Although the insertion of an additional phenyl group spacer in 3.4 has modulated the reaction efficiency, the clean photoredox reaction that was still observed indicates that the inherent driving force of this reaction is still apparent and substantial.
3.4 Mechanistic Studies

3.4.1 pH Effects on Photolysis Efficiency of 3.1-3.4

As noted above, the photoredox reactions of 3.1-3.3 exhibited acid catalysis. To explore the effect of pH on the efficiency of the intramolecular photoredox reaction of 3.1-3.3, photolyses of 3.1-3.3 (10^{-4} M, 1:3 H_{2}O-CH_{3}CN, argon purged, \lambda_{ex} = 300 \text{ nm}, \text{pH } 7-0) were carried out in 100 mL quartz vessels. After irradiation, all solutions were worked up in air. Conversion yields (%) of the photoredox product were determined with proton NMR. The results are plotted as a function of pH as shown in Figure 3.6. The photoredox reaction of 3.1-3.3 displayed acid catalysis above pH 3. These observations strongly suggest that the possible mechanistic step of the photoredox reaction of 3.1-3.3 involves protonation of carbonyl oxygen on the anthraquinone moiety. A similar result was observed for 3.4.
Figure 3.6 pH Dependence of intramolecular photoredox efficiency for 3.1 (Δ), 3.2 (○) and 3.3 (×) (~ 10^{-4} M, 1:3 H_2O-CH_3CN, argon saturated) (pH refers to the aqueous portion). Measurement error is about ± 5%.

3.4.2 Evidence for Unimolecular Reaction in Anthraquinone

Prior studies\textsuperscript{62} provided evidence that the photoredox reaction of HMAQ is unimolecular in anthraquinone molecule. In this work, additional supporting kinetic evidence is provided. In a reaction mechanism that is unimolecular in anthraquinone molecule, due to the large excess of water, the reaction rate will be directly proportional to the concentration of anthraquinone (pseudo first order reaction). The kinetics for photoredox reaction of 3.1 (10^{-7} - 10^{-5} M, 1:1 H_2O-CH_3CN, pH 1, argon saturated) were studied by monitoring the absorption intensity of product 3.11 at 387 nm with UV-Vis spectroscopy, to generate observed reaction rates at different substrate concentrations. The plot of observed rate vs. concentration of 3.1 clearly showed a linear relationship.
with respect to 3.1 in the $10^{-7}$-$10^{-5}$ M range, with an apparent rate constant of $1.6 \times 10^{-3}$ L·mol$^{-1}$·s$^{-1}$ (Figure 3.7).

![Graph showing observed rate vs. concentration of 3.1](image)

**Figure 3.7** Effect of concentration of 3.1 (1:1 H$_2$O-CH$_3$CN, pH 1, argon purged) on the observed reaction rate of photoredox reaction. Measurement error is about ±5%.

Additionally, if the mechanism of reaction proceeded via a bimolecular interaction of an excited anthraquinone with a ground state partner, one would expect the initial formation of equal amounts of "half-oxidized" (e.g., 3.8) and "half-reduced" (i.e., 3.11 but with the aldehyde replaced by CH$_2$OH) products. Such types of mixtures were never observed at any conversion. Moreover, bimolecular-type coupling products that might be anticipated on bimolecular reaction were never observed. All of these observations are consistent with an intramolecular redox reaction that is unimolecular in substrate and may be regarded as "single molecule" reaction catalyzed by water or acid.
3.4.3 Solvent isotope Effect on Photoredox Reaction

The proposed mechanism (Scheme 2.8) of the intramolecular photoredox reaction of anthraquinone HMAQ involves two key proton transfer steps. One is protonation of the carbonyl oxygen on the anthraquinone moiety and the other is deprotonation of the C-H bond on the benzyl CH₂OH moiety. A kinetic isotope effect of 2.1 ± 0.1 for C-H bond breaking was also presented in Section 2.4.1. In addition, the effect of H₂O vs. D₂O on photoredox reaction of HMAQ was also explored in which lower quantum yields (ca. 20%) were observed in D₂O compared to H₂O. All these results are consistent with the required proton transfers in the proposed mechanism (Scheme 2.8).

To explore the effect of H₂O vs. D₂O in the present study, photolysis of 3.1 was carried out in a 50 mL quartz tube (deaerated by argon purge) as a function of water (H₂O or D₂O) content in CH₃CN (pH or pD 1) and worked up in air. The yield of the photoredox product 3.8 were determined by proton NMR and plotted as a function of H₂O/D₂O content (Figure 3.8). The results show a reaction that is highly sensitive to water content in CH₃CN but no reaction in neat CH₃CN. The efficiency of reaction is always lower in D₂O compared to H₂O, by as much as 10% at 10% (v/v) H₂O(D₂O). These results are consistent with a mechanism that requires protonation of the carbonyl oxygen (by H₂O or H₃O⁺) in the rate limiting step.
Figure 3.8 Solvent isotope effect (H$_2$O (●) and D$_2$O (●) (pH or pD = 1, 50% CH$_3$CN as cosolvent) on the photoredox efficiency of 3.1 as determined by $^1$H NMR (% yield is for the formation of 3.8). Measurement error is about ±5%.

3.4.4 Nanosecond Laser Flash Photolysis (LFP) of 3.1

LFP of HMAQ in Section 2.4.4 showed a triplet excited state transient at 390 nm. We expect compounds 3.1-3.4 would have a triplet excited transient state due to the same anthraquinone chromophore, which could be observed on LFP. Compound 3.1 was chosen for study since it has the highest quantum yield of reaction of all the compounds. LFP of 3.1 (10$^{-5}$ M, in neat CH$_3$CN, argon saturated) showed a weak absorption band at 380 nm and an intense broad band at 600 nm (within the laser pulse) (Figure 3.9). Both signals decayed with the first order kinetics ($1.4 \pm 0.1 \times 10^5$ s$^{-1}$; $\tau \sim 7.0$ μs). The intensity and lifetime of this transient was significantly reduced in the presence of oxygen ($\tau \sim 0.14$ μs).
Figure 3.9 Triplet-triplet absorption spectra of 3.1 in neat CH$_3$CN (nitrogen-saturated) after the 266 nm pulse, 1.8 μs (○), 7.9 μs (□), 21 μs (Δ), 78 μs (×). Inset: triplet decay at 600 nm. Measurement error is about ±10%.

It is not possible to assign the above bands from previous literature since no prior articles about photochemical and photophysical studies of 3.1 have been reported. A survey of the literature shows that photochemical and photophysical studies of 3.16 were reported only by Shigorin et al.$^{93}$ Compound 3.16 undergoes a photoreduction reaction in CH$_3$CH$_2$OH as for 9,10-anthraquinone. The authors suggested that the reaction proceeds via a lowest π,π* triplet. However, no details of the excited transients such as a triplet-triplet absorption spectrum were reported.
Photochemical and photophysical studies of 9,10-anthraquinone are well-known. Triplet 9,10-anthraquinone has an intense 380 nm absorption ($\tau \sim 6$ \(\mu\)s in argon saturated solution), and is quenched by oxygen ($\tau \sim 10$ ns).\(^{59a}\) Similar observations were obtained for HMAQ in neat CH\(_3\)CN or aqueous solution (Chapter 2). Triplet excited HMAQ has an intense 380 nm absorption ($\tau \sim 6$ \(\mu\)s) in argon saturated CH\(_3\)CN and has an intense 390 nm absorption ($\tau < 0.1$ \(\mu\)s) in argon saturated H\(_2\)O-CH\(_3\)CN. Although there is a big difference between absorption bands of 3.1 (380/600 nm) and 9,10-anthraquinone or HMAQ (380 nm), it can be rationalized by the differences of their chromophores. Since 3.1 with an attached phenyl ring is more planar on the electronically excited state than on the ground state, electronically excited 3.1 has a longer conjugated system (details are presented in Section 3.4.6) and is expected to have a longer wavelength absorption band than excited HMAQ. Based on these facts, we tentatively assigned the 380/600 nm transient observed for 3.1 to the triplet state. The assignment was also confirmed by LFP studies of methyl compound 3.1a in neat CH\(_3\)CN, which showed only formation of the triplet excited state (380/600 nm, $\tau \sim 15$ \(\mu\)s, quenched by oxgen, $\tau_{\text{ox}} \sim 0.18$ \(\mu\)s).

In the presence of water, LFP of 3.1 (1:1 H\(_2\)O-CH\(_3\)CN, pH 7, N\(_2\) purged) also showed the formation of the triplet state but at 620 nm (red shifted) with significantly shorter lifetime ($\tau \sim 0.74$ \(\mu\)s) compared to neat CH\(_3\)CN, consistent with photochemical reactivity in aqueous solution. With decaying of the triplet excited transient, a new long lived transient ($\tau \sim 2.4$ ms) was observed at 520 nm (Figure 3.10). Its yield was reduced greatly by the presence of oxygen, but its decay rate was not affected. These observations are consistent with the 520 nm being a ground state species and generated from the triplet excited state. This assignment is also consistent with the observation that LFP studies of
the methyl compound 3.1a in 1:1 H₂O-CH₃CN (pH 7) showed only formation of the
triplet excited state (620 nm, τ ~2.5 μs, quenched by oxygen, τ ox ~ 0.27 μs) without the
formation of the 520 nm species.

![Graph](image)

**Figure 3.10** Triplet-triplet absorption spectra of 3.1 in 1:1 H₂O-CH₃CN (pH 7, nitrogen-
saturated) after the 266 nm pulse, 0.23 μs (○), 0.60 μs (□), 1.7 μs (Δ), 6.3 μs (×). Inset: triplet
decay at 620 nm. Measurement error is about ±10%.

The effect of pH on the decays of the above transients offered a critical clue for
assigning the 520 nm transient to an intermediate. In pH 1 the triplet signal at 620 nm
was shorter lived (τ ~ 0.39 μs, compared to 0.74 μs at pH 7), consistent with acid
catalysis of the reaction. In addition, the observed decay rate of the 520 nm transient was
strongly dependent on pH (kₚH₇:kₚH₁ ~ 40:1), consistent with ketonation of the enol
generated from p-benzoylephosphylacetic acid (kₚH₇:kₚH₁ ~ 100:1). The faster decay at pH 7
is associated with base catalysis of ketonization. Thus, we tentatively assign the 520 nm
transient to an enol intermediate. Indeed, the decay of this species ultimately leads to a weak broad absorption in the 400 nm region that is assignable to the photoredox product 3.11 which was observed by LFP (100 ms time scale) (Figure 3.11). LFP studies of the methyl compound 3.1a at pH 1 also supported the assignment.

![Graph](image)

**Figure 3.11** Triplet-triplet absorption spectra of 3.1 in 1:1 H$_2$O-CH$_3$CN (pH 1, nitrogen-saturated) after the 266 nm pulse, 31 ms (○), 122 ms (□), 405 ms (△), 686 ms (×). Inset: intermediate decay at 520 nm. Measurement error is about ±10%.

### 3.4.5 Quenching of Triplet 3.1

To explore the reactivity of the triplet 3.1, photolyses of 3.1 (10$^{-4}$ M, 1:1 H$_2$O-CH$_3$CN, pH 1, argon purged, λ$_{ex}$ 350 nm) were carried out in 100 mL solution in a quartz tube with a triplet quencher, sorbic acid (0 ~ 0.01 M). After work-up in air, the photolysis conversion yields (the formation of 3.8, 10%~ 40%) were determined with NMR. A Stern-Volmer plot for the photolysis of 3.1 was made (Φ$_0$/Φ vs. the concentration of
sorbic acid). The biphasic plot (Figure 3.12) showed initial linear quenching at low concentrations of sorbic acid (< 0.004 M) and a plateau region with $\Phi_0/\Phi \sim 3$ at the high concentrations of sorbic acid (0.004-0.01 M).

![Graph showing Stern-Volmer plots](image)

**Figure 3.12** Stern-Volmer plots of quenching of photoredox reactions for 3.1 (○), 3.2 (△) and 3.3 (■) in the presence of sorbic acid. $\Phi_0/\Phi$ refer to the yields in the absence and presence of quencher. Measurement error is about ± 5%.

These values can be interpreted to mean that with the respect of the photoredox reaction, about 33% of the photoredox reaction of 3.1 cannot be quenched by sorbic acid. This means that about 67% of the photoredox reaction of 3.1 is via the triplet excited state. The remaining “unquenchable” fraction (the flat region) is most likely due to the singlet excited state reaction although one cannot rule out the possibility of reaction via another short-lived triplet state. From the initial linear region of the plot, the slope ($k_\tau$) was determined to be 458 M$^{-1}$. Assuming that the bimolecular triplet quenching rate
constant is diffusion-controlled in water \((5 \times 10^9 \text{ M}^{-1}\text{s}^{-1})\),\(^{88}\) it was estimated that the reactive triplet lifetime of \(3.1\) was 90 ns. This result is consistent with the observations from LFP studies that indicates that the reactive triplet \(3.1\) was short-lived in acidic aqueous solution. Similar results were observed for \(3.2\) and \(3.3\). About 85% and 80% of the photoredox reaction for \(3.2\) and \(3.3\) are via the triplet excited state. Estimated reactive triplet lifetimes of \(3.2\) and \(3.3\) are 1.0 \(\mu\)s and 0.23 \(\mu\)s, respectively.

Oxygen quenching for the triplet \(3.1\)-\(3.3\) were also carried out in large quartz vessels with oxygen saturated solution (1:1 H\(_2\)O-CH\(_3\)CN, pH 1). After work-up in air, conversion yield of \(3.8\)-\(3.10\) in the absence and presence of oxygen was \(\Phi_0/\Phi \sim 1.38\), 5.0 and 4.7. Thus, it was concluded that the triplet state is reactive, which is consistent with much of the known photochemistry of anthraquinones.\(^{56,59}\)

**3.4.6 HOMO/LUMO Calculations**

We have shown that a variety of “extended” anthraquinones \(3.1\)-\(3.4\) undergo a clean intramolecular photoredox reaction, to generate the corresponding initially formed dihydroxyanthracenes \(3.11\)-\(3.13\) with high quantum yields in acid. Based on examinations of calculated HOMOs and LUMOs (AM1, Chem 3D, MOPAC) (Figure. 3.13 and 3.14), one can readily see that electronic excitation would give rise to excited states that would be highly polarized. For example, in the case of \(3.2\) (Fig. 3.13), electron density would be transferred from the benzene ring with the CH\(_2\)OH substituent (and the anthraquinone carbons closest to this ring) to the central anthraquinone ring including the carbonyl oxygens. For \(3.4\) (Figure 3.14), electron density would be transferred from *both* of the attached biphenyl rings to the central anthraquinone ring system. Such excited states would exhibit high basicity at the
anthraquinone carbonyl oxygen. Note also that the AM1 calculations show the biphenyl and terphenyl rings to be twisted (dihedral angle ~ 30-40°). There is tendency for these rings to be more planar on electronic excitation that would facilitate the charge transfer.$^{92a}$

![Figure 3.13](image1.png)  
**Figure 3.13** Calculated (AM1) HOMO (left) and LUMO (right) for 3.2

![Figure 3.14](image2.png)  
**Figure 3.14** Calculated (AM1) HOMO (top) and LUMO (bottom) for 3.4

### 3.4.7 Proposed Mechanism

The intramolecular photoredox reactions of phenyl and biphenyl anthraquinones are proposed to proceed via a mechanism similar to that of **HMAQ** presented in Section 2.4.7. Like **HMAQ** in Chapter 2 and phenyl anthraquinone 3.16,$^{93}$ the lowest triplet states for 3.1-3.3 should also be $\pi,\pi^*$ states since these photoredox reactions occur in the
presence of a highly polar solvent such as water (even acidic solution), which is essential to stabilize the initial excited states (the lowest triplet).

In the proposed mechanism (Scheme 3.4), the carbonyl oxygen of the highly polarized triplet 3.1 is protonated by solvent water (or proton, depending on pH), to give 3.17a. This results in a net positive charge on the benzene ring with the attached hydroxymethyl group (3.17b). Deprotonation of 3.17b gives (after ISC) a double enol intermediate 3.18. This is followed by ketonization/enolization to give the final product 3.11.

\[
\text{Scheme 3.4 Proposed mechanism for the intramolecular photoredox reaction of 3.1}
\]
3.5 Summary

The photoredox reaction of HMAQ has been successfully extended to phenyl anthraquinone derivatives. We have shown that suitably designed triplet excited anthraquinones with distal benzyl alcohol moieties possess high degrees of electronic communication through the aromatic π system that can lead to clean intramolecular photoredox electron in aqueous solution. Electronic communication in the excited state is apparently a key step for the reaction. Just as noted in the introduction, since excited phenyl and biphenyl anthraquinones tend to a planar structure, electronic communication between the anthraquinone carbonyl and the benzylic alcohol occurs through the extended π system, and result in formation of the highly polarized excited state. This leads to protonation of the ketone on the anthraquinone moiety and deprotonation of the benzylic C-H to give photoredox products. Different quantum yields of studied compounds also suggest the different efficiency of electronic communication in these molecules. The longer the distance between the carbonyl group and the benzylic alcohol, the lower the efficiency of reaction.

3.6 Experimental

3.6.1 General

EI mass spectra were obtained using a double focusing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system. All of these data were taken at the University of British Columbia. The other details are reported in 2.6.1.

3.6.2 UV-Vis Studies

UV-Vis studies (≈10⁻⁵ M in H₂O-CH₃CN, pH 7 and pH1) were carried out in 3.0 mL quartz cuvette. Details are reported in Section 2.6.2.
3.6.3 Product Studies
Compounds were photolyzed in 100 mL quartz tubes using a Rayonet RPR 100 photochemical reactor equipped with 300 nm or 350 nm lamps. Typically, a solution of the compound ($10^{-4} - 10^{-5}$ M, H$_2$O-CH$_3$CN (1:1 or 1:3), pH7 or 1) was bubbled with argon for 15 min and then irradiated under argon purge. The irradiated solution was extracted by 3 $\times$ 50 mL CH$_2$Cl$_2$ in air and the collected organic extracts was dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and the photolysate analyzed by NMR, MS and IR.

In order to monitor the initially formed redox product, photolyses were carried out in NMR tubes which allowed characterization of the first formed redox products. NMR tubes were filled with 1 mL of the appropriate solution ($10^{-3}$ M, 10% D$_2$O-CD$_3$CN). Solutions were bubbled using a fine needle through rubber stoppers with argon for 15 min before irradiation then irradiated with 300 nm or 350 nm lamps.

3.6.4 Quantum Yield Measurements
Quantum yields were measured using NMR and the reaction of 2-(hydroxymethyl)anthraquinone (HMAQ) as a secondary actinometer ($\Phi = 0.8$). A solution of the compound (3.1-3.4, $10^{-4}$ M, in H$_2$O-CH$_3$CN (1:1 or 1:3), pH 7 or 1) was purged with argon for 15 min and irradiated for 1 min at 300 nm (2 lamps) under argon purge. After irradiation, the conversion to product was determined by $^1$H NMR and compared to an identical run using HMAQ. All conversions were kept below 30% and repeated twice.

3.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ
LFP studies were conducted at the University of Victoria LFP facility employing a Spectra Physics Quanta-Ray YAG laser, model GSR-11, with a pulse width of $\sim$ 10 ns
and excitation wavelength 266 nm. Quartz flow cells were used and solutions were
purged with nitrogen or oxygen for 20 min prior to measurement. Optical densities at 266
nm were ~ 0.6.

3.6.6 Syntheses of 3.1-3.4
Methylphenyl boronic acids

\[
\text{Bromotoluene (ortho, meta and para) (0.3, 1.8mmol) in 20 mL of THF was added}
\]
dropwise into THF solution with Mg under N₂ at room temperature and the mixture was
stirred for 2 hours. After the reaction, the Grignard solution under N₂ was transferred into
a solution of B(OCH₃)₃ at -30°C in 0.5 hour. After the addition, the solution was warmed
up and stirred overnight at room temperature to give a white paste. The solution was
washed with conc. HCl to give white precipitates. The precipitates were recrystallized by
water to give methyl phenyl boronic acid (white needle crystals, 70-80% yield). ¹H NMR
(CDCl₃, 300 MHz) (o-methylphenyl)boronic acid: δ 8.20 (d, H, J = 8.1 Hz), 7.42-7.30
(m, H), 7.35-7.25 (m, 2H), 2.81 (s, 3H); (m-methylphenyl)boronic acid: δ 8.06-8.01 (m,
2H), 7.42-7.38 (m, 2H), 2.47 (s, 3H); (p-methylphenyl)boronic acid: δ 8.11 (d, 2H, J =
8.1 Hz), 7.30 (d, 2H, J = 8.1 Hz), 2.43 (s, 3H).

Preparation of 3.5

\[
\text{Conc. H₂SO₄, NaNO₂, CH₂Cl₂, Tf₂O, pyridine}
\]
NaNO₂ (0.56 g, 8.1 mmol) was added in three portions into a solution of 3.5a (1.5 g, 6.8 mmol) in conc. H₂SO₄ (15 mL) cooled in an ice bath. After the addition, the mixture was stirred in the ice bath for 10 min and warmed up to room temperature and stirred for 4 hours. The mixture was poured onto 100 mL of ice and transferred to 500 mL flask and refluxed for 45 min. After cooling, the brown solid was filtered, washed with water and dissolved in 10 mL of 1 M NaOH. The dark red solution was washed 3 × 25mL CH₂Cl₂. The combined aqueous layers was acidified with conc. HCl and extracted with 5 × 25 mL EtOAc, dried over anhydrous MgSO₄. A yellow brown powder 3.5b (1.1 g, 70% yield) was obtained after removal of solvent. ¹H NMR (CDCl₃, 300 MHz) δ 8.30-8.24 (m, 2H), 8.21 (d, 1H, J = 8.5 Hz), 7.94-7.88 (m, 2 H), 7.67 (d, 1H, J = 2.6 Hz), 7.34 (dd, 1H, J = 2.6 Hz, 8.5 Hz).

A solution of 3.5b (0.90, 4.0 mmol) in 50 mL of CH₂Cl₂ in a cold water bath was flushed with N₂. Pyridine (1.95 mL, 24.1 mmol) was added dropwise into the above solution, then Tf₂O (2.0 mL, 12 mmol) was added. After the addition, the mixture was warmed up to room temperature and stirred for overnight. After the reaction, the solvent was removed and the residue was washed with 2 × 25 mL water. The combined aqueous solutions were extracted with 2 × 25 mL EtOAc. The collected organic layers were dried over anhydrous MgSO₄. After removal of solvent, a brown powder was purified by column chromatography with silica gel using CH₂Cl₂ as an eluent, to give 3.5 (white powder, 1.4 g) in 98% yield. ¹H NMR (CDCl₃, 300 MHz) δ 8.44 (d, 1H, J = 8.8 Hz), 8.36-8.29 (m, 2H), 8.18 (d, 1H, J = 2.2 Hz), 7.87-7.80 (m, 2H), 7.67 (dd, 1H, J = 8.8, 2.2 Hz).

2-(o-Hydroxymethylphenyl)-9,10-anthraquinone (3.1)
A mixture of (o-methylphenyl)boronic acid (0.50 g, 2.4 mmol), 3.5 (0.27 g, 2 mmol), anhydrous K$_2$CO$_3$ (1.93 g, 14 mmol) and Pd(PPh$_3$)$_4$ (100 mg) was added into a 100 mL flask contained 60 mL of DME saturated with N$_2$. The mixture was refluxed for 3 days under N$_2$. After the reaction, solvent was removed and the residue was dissolved in 100 mL CH$_2$Cl$_2$ and washed with 2 × 25 mL of 1 M NaOH. The solution was dried over anhydrous MgSO$_4$. After removal of solvent, a brown powder was purified by column chromatography with silica gel using CH$_2$Cl$_2$ as an eluent, to give 2-(o-methylphenyl)-9,10-anthraquinone (3.1a) (yellow powder, 0.41 g, mp. 160-161°C) in 70% yield. $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.39-8.24 (m, 4H), 7.84-7.71 (m, 3H), 7.34-7.25 (m, 4H), 2.31 (s, 3H); $^{13}$C (CDCl$_3$, 75 MHz) 183.44, 183.20, 148.41, 140.11, 135.38, 135.12, 134.38, 134.31, 133.84 (2C), 133.55, 132.19, 130.96, 129.73, 128.64, 128.08, 127.52, 127.46, 127.44, 126.38, 20.64; IR (neat from CH$_2$Cl$_2$ solution, NaCl plates) ν 3054, 1673, 1588, 1327, 1289, 930, 707 cm$^{-1}$.

A mixture of 3.1a (0.30 g, 1.0 mmol) and NBS (0.21 g, 1.2 mmol) in benzene (30 mL) was refluxed for overnight under N$_2$. After the reaction, the solution was washed with 2 × 25 mL water and the collected organic layer was dried over anhydrous MgSO$_4$. After the removal of solvent, a brown residue (3.1b) was obtained. The brown residue and Na$_2$CO$_3$ (0.42 g, 5.0 mmol) in 1:1 H$_2$O-dioxane were refluxed for overnight under N$_2$. After the reaction, the mixture was acidized by 10 mL of 1 M HCl and extracted with 2 × 25 mL CH$_2$Cl$_2$. The collected extracts were dried over anhydrous MgSO$_4$ and evaporated to give brown powders. The crude product was purified by column chromatography with silica gel using 20% EtOAc-CH$_2$Cl$_2$ as an eluent to give yellow powder. The yellow powder was further purified with recrystallization from CH$_3$CH$_2$OH to give 2-(o-
hydroxymethylphenyl)-9,10-antraquinone (3.1) (yellow needle crystals, 0.22 g, m.p. 184-185°C) in 70% yield. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 8.36 (d, 1H, \(J = 7.7\) Hz), 8.34-8.30 (m, 3H), 7.85 (dd, 1H, \(J = 7.7, 1.8\) Hz), 7.83-7.78 (m, 2H), 7.60 (d, 1H, \(J = 7.0\) Hz), 7.46 (td, 1H, \(J = 7.5, 1.5\) Hz), 7.41 (td, 1H, \(J = 7.5, 1.5\) Hz), 7.34 (dd, 1H, \(J = 7.5, 1.5\) Hz), 4.63 (s, 2H), 1.63 (s, broad OH peak); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) 183.39, 183.16, 147.16, 139.74, 138.08, 135.12, 134.45, 134.38, 133.84 (2C), 133.63, 132.53, 130.11, 129.22, 129.10, 128.35, 128.05, 127.63, 127.52, 127.50, 63.24; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) \(v\) 3384, 3060, 2884, 1673, 1588, 1330, 1294, 707 cm\(^{-1}\); MS (EI) \(m/z\) 314 (M\(^+\), 100), 297 (28), 283 (19); HRMS, calculated for C\(_{21}\)H\(_{14}\)O\(_3\) 314.09429; observed 314.09436.

2-(\(m\)-Hydroxymethylphenyl)-9,10-antraquinone (3.2)

By following the same synthetic procedure of 3.1, 2-(\(m\)-methylphenyl)-9,10-antraquinone (3.2a) (yellow powder, 0.30 g, m.p. 137-138°C) in 70% yield was obtained. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 8.47 (d, 1H, \(J = 1.5\) Hz), 8.34-8.25 (m, 3H), 7.97 (dd, 1H, \(J = 8.1, 1.5\) Hz), 7.81-7.73 (m, 2H), 7.49 (d, 2H, \(J = 8.1\) Hz), 7.36 (t, 1H, \(J = 8.1\) Hz), 7.22 (d, 1H, \(J = 8.1\) Hz), 2.43 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) 183.43, 183.06, 147.15, 139.05 (2C), 134.35, 134.22, 134.02, 133.84, 133.80, 132.54, 132.25, 129.84, 129.24, 128.25, 128.18, 127.47, 127.40, 125.72, 124.62, 21.74; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) \(v\) 3060, 3027, 2912, 1670, 1588, 1330, 1278, 932, 770, 707 cm\(^{-1}\).

2-(\(m\)-Hydroxymethylphenyl)-9,10-antraquinone (3.2) (yellow plate, 0.20 g, m.p. 158-161°C) in 80% yield was obtained via bromination of 3.2a followed with hydrolysis of 3.2b. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 8.53 (d, 1H, \(J = 2.0\) Hz), 8.37 (d, 1H, \(J = 8.1\) Hz), 8.34-8.31 (m, 2H), 8.01 (dd, 1H, \(J = 8.1, 2.0\) Hz), 7.83-7.79 (m, 2H), 7.73 (t, 1H, \(J = 1.8\) Hz).
Hz), 7.65 (dt, 1H, J = 7.7, 1.8 Hz), 7.50 (t, 1H, J = 7.7 Hz), 7.44 (d, 1H, J = 7.7 Hz), 4.81 (s, 1H), 1.59 (s, broad OH peak); $^{13}$C NMR (CDCl$_3$, 125 MHz) 183.46, 183.12, 146.90, 142.12, 139.53, 134.44, 134.31, 134.16, 133.90, 133.86, 132.64, 132.49, 129.62, 128.31, 127.59, 127.54, 127.47, 126.83, 126.07, 125.84, 65.37; IR (neat from CH$_2$Cl$_2$

solution, NaCl plates) v 3307, 3017, 2912, 2862, 1670, 1588, 1333, 1281, 707 cm$^{-1}$; MS

(El) m/z 314 (M$^+$, 100), 285 (67), 283 (18), 208 (11); HRMS, calculated for C$_{21}$H$_{14}$O$_3$

314.09429; observed 314.09421.

2-(p-Hydroxymethylphenyl)anthraquinone (3.3)

By following the same synthetic procedure of 3.1, 2-(p-methylphenyl)-9,10-
anthaquinone (3.3a) (yellow powder, 0.50g, m.p. 166-167°C) in 75% yield was obtained.

$^1$H NMR (CDCl$_3$, 300 MHz) δ 8.47 (d, 1H, J = 1.5 Hz), 8.34-8.25 (m, 3H), 7.97 (dd, 1H, J = 8.1, 1.5 Hz), 7.81-7.73 (m, 2H), 7.59 (d, 2H, J = 8.1 Hz), 7.28 (d, 1H, J = 8.1 Hz), 2.40 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) 183.47, 183.06, 146.95, 139.21, 136.18, 134.34, 134.20, 133.85, 133.82, 132.26, 132.08, 130.07 (2C), 128.22, 127.46, 127.39, 127.35 (2C), 125.42, 21.45; IR (neat from CH$_2$Cl$_2$ solution, NaCl plates) v 3021, 2917, 1673, 1588, 1330, 1275, 812, 707 cm$^{-1}$.

2-(p-hydroxymethylphenyl)-9,10-anthaquinone (3.3) (yellow needle, 0.30 g, mp.199-201°C) in 70% yield was obtained via bromination of 3.3a followed with hydrolysis of

3.3b. $^1$H NMR (300MHz, CDCl$_3$) δ 8.54 (d, 1H, J = 2.0 Hz), 8.37 (d, 1H, J = 8.1 Hz), 8.35-8.31 (m, 2H), 8.01 (dd, 1H, J = 8.1, 2.0 Hz), 7.83-7.79 (m, 2H), 7.73 (d, 2H, J = 8.1 Hz), 7.51 (d, 2H, J = 8.1 Hz), 4.78 (s, 1H), 1.72 (s, broad OH peak); $^{13}$C NMR (CDCl$_3$, 125 MHz) 183.48, 183.12, 146.74, 141.90, 138.52, 134.44, 134.31, 134.18, 133.91, 133.87, 132.53, 132.43, 128.33, 127.86 (2C), 127.76 (2C), 127.54, 127.48, 125.73, 65.13; IR (neat from CH$_2$Cl$_2$ solution, NaCl plates) v 3247, 3057, 2906, 2846, 1673, 1591, 1330,
1303, 820, 707 cm\(^{-1}\); MS (EI) \(m/z\) 314 (M\(^+\), 100), 318 (M\(^+\), 60), 298 (16), 285 (79), 283 (16); HRMS, calculated for 314.09429; observed 314.09441.

**Bromobiphenyl 3.6**

A mixture of (p-methylphenyl)boronic acid (0.80 g, 5.9 mmol), p-bromoiodobenzene (8.4 g, 30 mmol), anhydrous K\(_2\)CO\(_3\) (1.64g, 11.9 mmol) and Pd(PPh\(_3\))\(_4\) (0.69 g, 0.59 mmol) in 50 mL of DME was refluxed for 20 h under N\(_2\). After the reaction, black solids were removed by filtration through Celite and rinsed by CH\(_2\)Cl\(_2\). After removal of solvent, white plate crystals were obtained and purified by column chromatography with silica gel using neat hexane as an eluent to give 3.6 (white powder, 0.62 g) in 42 % yield.

\(^1\)H-NMR (300MHz, CDCl\(_3\)) \(\delta\) 7.53 (d, 2H, \(J = 8.5\) Hz), 48-7.38 (m, 4H), 7.24 (d, 2H, \(J = 8.0\) Hz).

**Boronic acid 3.7**

A solution of 3.6 (0.50 g, 2.0 mmol) in 10 mL of THF (water and oxygen free) was added dropwise into the solution of THF with Mg under N\(_2\). The mixture was refluxed for 1 h. After cooling, the Gringard reagent under N\(_2\) was transferred into the solution of trimethyl borate in 10 mL of THF at -78°C. After the addition, the mixture was warmed up to room temperature and stirred for overnight to give a white paste. The white paste was poured into 20 mL of cold water and acidified to pH 2 with 0.1 M H\(_2\)SO\(_4\). The solution was extracted by \(2 \times 30\) mL of ethyl ether and collected organic solution was dried over MgSO\(_4\). After the removal of solvent, a white powder was obtained. Further purification was operated with column chromotagrapy on silica gel using 20% EtOAc-CH\(_2\)Cl\(_2\) to give a white powder (3.7, 0.20 g, 47% yield). \(^1\)H-NMR (250 MHz, CDCl\(_3\)) \(\delta\)
8.31 (d, 2H, \(J = 8.0\) Hz), 7.73 (d, 2H, \(J = 8.0\) Hz), 7.58 (d, 2H, \(J = 8.0\) Hz), 7.29 (d, 2H, \(J = 8.0\) Hz).

2-(\(p\)-Methylbiphenyl)-9,10-anthraquinone (3.4a)

By following the same synthetic procedure of 3.1a, 2-(\(p\)-methylbiphenyl)-9,10-anthraquinone (3.4a) (0.12 g, 83%, yellow powder, mp. 235~236°C) was obtained. \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.58 (d, 1H, \(J = 1.8\) Hz), 8.38 (d, 1H, \(J = 8.0\) Hz), 8.35-8.31 (m, 2H), 8.05 (dd, 1H, \(J = 1.8, 8.0\) Hz), 7.82-7.78 (m, 4H), 7.72 (td, 2H, \(J = 1.8, 8.5\) Hz), 7.50 (td, 2H, \(J = 1.8, 8.0\) Hz), 7.27 (d, 2H, \(J = 8.0\) Hz), 2.40 (s, 3H); \(^{13}\)C-NMR (CDCl\(_3\), 125 MHz) 183.49, 183.10, 146.65, 141.94, 137.86, 137.65, 137.54, 134.41, 134.27, 134.19, 133.92, 133.87, 132.36 (2C), 129.87 (2C), 128.33, 127.90 (2C), 127.83 (2C), 127.52, 127.46, 127.15 (2C), 125.58, 21.37; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) ν 3025, 2915, 1668, 1588, 806, 705 cm\(^{-1}\).

2- (\(p\)-Hydroxymethylbiphenyl)-9,10-anthraquinone (3.4)

2- (\(p\)-Hydroxymethylbiphenyl)-9,10-anthraquinone (3.4) was obtained by bromination of 3.4a followed by the hydrolysis of 3.4b in 74% yield (3.4, 0.10 g, yellow powder, decomposed at 224°C) \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.54 (d, 1H, \(J = 1.8\) Hz), 8.34 (d, 1H, \(J = 8.1\) Hz), 8.32-8.26 (m, 2H), 8.01 (dd, 1H, \(J = 1.8, 8.1\) Hz), 7.80-7.73 (m, 4H), 7.68 (td, 2H, \(J = 1.8, 8.5\) Hz), 7.61 (td, 2H, \(J = 1.8, 8.2\) Hz), 7.42 (d, 2H, \(J = 8.2\) Hz), 4.71 (s, 2H); \(^{13}\)C-NMR (CDCl\(_3\), 125 MHz) 183.50, 183.11, 146.56, 141.60, 140.66, 139.86, 138.06, 134.45, 134.31, 134.22, 133.93, 133.87, 132.44, 132.41, 128.37, 128.00 (2C), 128.99 (2C), 127.80 (2C), 127.54, 127.52, 127.48 (2C), 125.64, 65.31; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) ν 3164, 2917, 2851, 1670, 1588, 1327, 1303, 803,
707 cm\(^{-1}\); MS (EI) \(m/z\) 390 (M\(^+\), 100), 374 (M\(^+\), 25), 273 (12), 361 (25); HRMS, calculated for 390.12339; observed 390.12528.

### 3.6.7 Photolysis Procedures for 3.1-3.4 and Characterization of Products

All photolyses were carried out in H\(_2\)O-CH\(_3\)CN (pH 1) under argon purged. After the photolysis, solutions were neutralized by 5% NaHCO\(_3\) solution and were extracted by \(3 \times 25\) mL CH\(_2\)Cl\(_2\) in air. The combined organic solutions were dried over anhydrous MgSO\(_4\) and solvent was removed by reduced evaporation. Crude products were purified by prep. TLC (silica gel).

#### Photolysis of 3.1

Compound 3.1 (5 mg in 50 mL CH\(_3\)CN and 50 mL H\(_2\)O, pH 1) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by \(^1\)H NMR to give 3.8 (45% yield). Further purification was obtained by prep. TLC (silica gel, CH\(_2\)Cl\(_2\)) to give 3.8 (yellow powder, 2 mg), \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 9.94 (s, 1H), 8.36 (d, 1H, \(J = 7.9\) Hz), 8.32-8.26 (m, 3H), 8.02 (dd, 1H, \(J = 1.5, 7.6\) Hz), 7.80-7.71 (m, 3H), 7.66 (dt, 1H, \(J = 1.5, 7.6\) Hz), 7.54 (mt, 1H, \(J = 7.6\) Hz), 7.44 (dd, 1H, \(J = 1.1, 7.6\) Hz); \(^{13}\)C-NMR (CDCl\(_3\), 125 MHz) 191.14, 182.76, 182.61, 144.08, 143.28, 135.32, 134.36, 133.37, 133.36, 133.27, 132.65, 130.68, 128.94, 128.68, 128.19, 127.34, 127.17, 127.15, 116.55; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) \(\nu\) 3053, 1690, 1676, 1591, 1330, 1292, 705 cm\(^{-1}\); MS (EI) \(m/z\) 312 (M\(^+\), 100), 283 (23); HRMS, calculated for C\(_{21}\)H\(_{12}\)O\(_3\) 312.07864; observed 312.07874.

#### Photolysis of 3.2

Compound 3.2 (6 mg in 50 mL of CH\(_3\)CN and 50 mL of H\(_2\)O, pH 1) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air,
the brown residue was characterized by \(^1\)H NMR to give \textbf{3.9} (22\% yield). Further purification was obtained by prep. TLC (silica gel, CH\(_2\)Cl\(_2\)) to give \textbf{3.9} (yellow powder, 1 mg). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 10.07 (s, 1H), 8.52 (d, 1H, \(J = 1.8\) Hz), 8.37 (d, 1H, \(J = 8.2\) Hz), 8.33-8.25 (m, 2H), 8.18 (t, 1H, \(J = 1.8\) Hz), 8.00 (dd, 1H, \(J = 2.0, 8.2\) Hz), 7.97-7.88 (m, 2H), 7.81-7.73 (m, 2H), 7.64 (t, 1H, \(J = 7.6\) Hz); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz) 191.79, 182.88, 182.71, 145.25, 139.98, 137.17, 134.30, 134.18, 134.04, 133.57, 133.52, 133.06, 132.69, 132.36, 130.02, 129.92, 128.26 (2C), 127.35, 127.29, 125.65; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) \(\nu\) 3060, 1700, 1673, 1591, 1327, 705 cm\(^{-1}\); MS (EI) \(m/z\) 312 (M\(^+\), 100), 283 (18); HRMS, calculated for C\(_{21}\)H\(_{12}\)O\(_3\) 312.07864; observed 312.07866.

\textbf{Photolysis of 3.3}

Compound \textbf{3.3} (5 mg in 50 mL CH\(_3\)CN and 50 mL H\(_2\)O, pH 1) was irradiated for 1 min at 300 nm (2 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by \(^1\)H NMR to give \textbf{3.10} (45\% yield). Further purification was obtained by prep. TLC (silica gel, CH\(_2\)Cl\(_2\)) to give \textbf{3.10} (yellow powder, 2 mg). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 10.04 (s, 1H), 8.52 (d, 1H, \(J = 1.8\) Hz), 8.37 (d, 1H, \(J = 8.2\) Hz), 8.32-8.25 (m, 2H), 8.03-7.94 (m, 3H), 7.83 (td, 2H, \(J = 1.8, 8.2\) Hz), 7.80-7.73 (m, 2H); \(^{13}\)C-NMR (CDCl\(_3\), 75 MHz) 191.60, 182.92, 182.68, 145.24, 144.70, 136.26, 134.34, 134.23, 134.00, 133.55, 133.50, 132.92, 132.55, 130.43 (2C), 128.22, 128.00 (2C), 127.35, 127.30, 125.96; IR (neat from CH\(_2\)Cl\(_2\) solution, NaCl plates) \(\nu\) 3049, 1700, 1673, 1591, 1333, 1278, 707 cm\(^{-1}\); MS (EI) \(m/z\) 312 (M\(^+\), 100), 283 (28); HRMS, calculated for C\(_{21}\)H\(_{12}\)O\(_3\) 312.07864; observed 312.07854.

\textbf{Photolysis of 3.4}
Compound 3.4 (6 mg in 50 mL CH$_3$CN and 50 mL H$_2$O, pH 1) was irradiated for 1 min at 300 nm (16 lamps) under argon, to give a yellow solution. After work-up in air, the brown residue was characterized by $^1$H NMR to give 3.14 (23% yield). Further purification was obtained by prep. TLC (silica gel, CH$_2$Cl$_2$) to give 3.14 (yellow powder, 1 mg), $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 10.06 (s, 1H), 8.59 (d, 1H, $J$ = 1.8 Hz), 8.40 (d, 1H, $J$ = 8.1 Hz), 8.36-8.32 (m, 2H), 8.07 (dd, 1H, $J$ = 1.8, 8.1 Hz), 7.98 (td, 2H, $J$ = 1.8, 8.4 Hz), 7.85 (td, 2H, $J$ = 1.8, 8.4 Hz), 7.83-7.80 (m, 4H), 7.79 (td, 2H, $J$ = 1.8, 8.4 Hz); $^{13}$C-NMR (CDCl$_3$, 125 MHz) 192.05, 183.44, 183.06, 146.39, 146.18, 140.39, 139.22, 135.75, 134.51, 134.37, 134.24, 133.88, 133.83, 132.64, 132.47, 130.61, 128.42, 128.33, 128.19, 127.90, 127.56, 127.51, 125.75; IR (neat from CH$_2$Cl$_2$ solution, NaCl plates) ν 3023, 1673, 1591, 1330, 809, 705 cm$^{-1}$; MS (EI) m/z 388 (M$^+$, 100), 359 (9); HRMS, calculated for C$_{27}$H$_{16}$O$_3$ 388.10994; observed 388.11046.

3.6.8 Trapping of Photolysis Product of 3.1

Photolysis of 3.1 (20 mg, 1:1 H$_2$O-CH$_3$CN, pH 1) was carried out in a 100 mL quartz tube under argon to give a yellow photoredox product 3.11. Under Ar, NaOH (solid, 2 g) were added into the above solution to give a dark red solution which was converted to yellow solution with the addition of Ac$_2$O (2 mL). After the addition, the solution was extracted with 2 × 25 mL CH$_2$Cl$_2$ and the collected organic layer was dried over anhydrous MgSO$_4$. After the removal of solvent, a brown residue was obtained. The brown residue was purified by prep. TLC by neat CH$_2$Cl$_2$ as an eluent to give 3.11-OAc (10 mg, light red) $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 9.98 (s, 1H), 8.02 (dd, 1H, $J$ = 1.5, 8.0Hz), 7.99 (d, 1H, $J$ = 0.5, 9.0 Hz), 7.96-7.87 (m, 2H), 7.80 (s, 1H), 7.93 (td, 1H, $J$ = 1.5, 8.0 Hz), 7.55-7.46 (m, 5H), 2.60 (s, 3H), 2.53 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 125 MHz)
192.31, 169.65 (2C), 145.35, 140.97, 140.69, 135.88, 134.35, 133.89, 131.19, 128.55, 128.50, 128.18, 127.09 (2C), 125.06, 124.89, 123.87, 123.53, 123.43, 122.60, 122.05 (2C), 21.00, 20.95; MS (EI) *m/z* 398 (M⁺, 7), 356 (27), 314 (100); HRMS, calculated for C₂₅H₁₈O₅ 398.11542; observed 398.11570.

3.6.9 Concentration Effects on Photolysis Conversions of 3.1

Photolysis of 3.1 (10⁻⁷~10⁻⁵ M, 1:1 H₂O-CH₃CN, pH 1, argon saturated) was carried out in a 3 mL quartz cuvette and the absorption intensity of product 3.11 at 387 nm was determined with UV-Vis spectroscopy. The rates at different concentrations were determined by taking the slope of the plot of absorbance vs time (0~20s). The rate constant was obtained by taking the slope of the plot of rates vs concentration. The experimental results showed the rates were reasonably linear with respect to concentrations of 3.1 and the rate constant 1.6 × 10⁻³ L·mol⁻¹·s⁻¹.

3.6.10 pH Effects on Photolysis Efficiency of 3.1-3.4

Solutions of 3.1-3.4 (1 mg 1:1 H₂O-CH₃CN, pH from 0 to 7) in a 100 mL large quartz tube were purged with Ar for 15 minutes prior to photolysis and were irradiated (300 nm, 2 lamps for 1 min (3.1-3.3) and 8 lamp(s) for 1 min (3.4). After work-up (followed the same procedure as shown in Section 3.6.7), the photolysis yields (%) were determined with proton NMR.

3.6.11 Quenching of Triplet 3.1-3.3

A mixture of 3.1 (10⁻⁴ M) and sorbic acid (0.001 M) in 1:1 H₂O-CH₃CN (pH 1) in a 100 mL large quartz tube was purged with Ar for 15 minutes prior to photolysis and were irradiated (300 nm, 2 lamps) for 1 min. After work-up in air (followed the same procedure as shown in Section 3.6.7), a brown residue was characterized by ¹H NMR to
give 3.8 in 22% conversion yield. Following the above procedure, photolysis of 3.1 (10^{-4} M) and sorbic acid (0-0.01 M) in 1:1 H₂O-CH₃CN (pH 1) were carried out to give 3.8 in 12-36% yield. The same procedure was employed for 3.2 and 3.3.

Following the above irradiation procedure and the work-up procedure as shown in Section 3.6.7, photolysis of 3.1 in oxygen saturated solution (1:1 H₂O-CH₃CN, pH 1) gave 3.8 in 26% yield. The same procedure was employed for 3.2 and 3.3.
4. A Pentacene Intermediate via Intramolecular Photoredox of a 6,13-Pentacenequinone in Aqueous Solution*

4.1 Introduction

Pentacene is a promising candidate for application as a novel organic semiconductor. However, it is highly sensitive to both oxygen and light, and has low solubility. To overcome these disadvantages, considerable efforts have been directed at synthesizing new pentacene derivatives. Among them, pentacenequinone derivatives have been employed as synthetic precursors due to their stability and ready accessibility. Recently, photochemical methods based on extrusion of molecular fragments for the synthesis of pentacenes have also been reported.

Chapter 2 has shown that anthraquinone derivatives undergo a very efficient intramolecular photoredox in neutral aqueous solution to give the corresponding photoredox products with high quantum yields. Chapter 3 showed that phenyl or biphenyl anthraquinones in which the benzyl alcohol moiety is much further away from the carbonyl group also undergo the same photoredox reaction, but require pH < 3. We anticipated that 2-(hydroxymethyl)-6,13-pentacenequinone (4.1) might undergo the photoredox reaction as well, which would give rise to the corresponding dihydroxypentacene aldehyde. Thus, we might have a new photochemical method involving an intramolecular redox process to prepare a pentacene intermediate from 4.1.

In addition, both Chapter 2 and Chapter 3 presented photoredox reactions that involve electronic communication between the benzyl alcohol moiety and the anthraquinone carbonyl group in the excited state via the \( \pi \) conjugated system. In particular, the

tendency for electronically excited phenyl and biphenyl anthraquinones (Chapter 3) to be more planar results in strong electronic communication. The same reaction would not occur in the corresponding ground state. Note that the anthraquinone moiety of \textbf{HMAQ} has one benzene ring on each side of the central quinone. The structure is symmetric. Thus, we would not know whether or not the benzene ring on the side without the attached hydroxymethyl group would have any effect on the electronic communication. In order to further study the electronic communication via $\pi$ conjugation, a good way of increasing or decreasing $\pi$ system conjugation is to add or remove benzene rings to the anthraquinone moiety. Thus, pentacenequinone \textbf{4.1} and associated acenequinones \textbf{4.2-4.4} were synthesized (Chart 4.1) and their potential photoredox chemistry explored in this chapter.

\begin{center}
\textbf{4.2 Synthesis}
\end{center}

Acenequinones \textbf{4.1} and \textbf{4.4} were readily prepared via the condensation (\textit{in situ} Diels-Alder reaction) of the corresponding acenequinones \textbf{4.3} and \textbf{4.2}, respectively, with $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-$o$-xylene (Scheme 4.1). The reaction proceeds via initial
debromination of the tetrabromide, to generate the diene, which reacts with 4.2 and 4.3 via Diels-Alder reaction. This is subsequently followed by another debromination step to regenerate the aromatic system, and hence 4.1 or 4.4. Acenequinones 4.2 and 4.3 are known compounds and were prepared by following or adapting the corresponding literature methods.\textsuperscript{99,100} Methylpentacenequinone 4.1a was also studied to test the requirement of a hydroxymethyl (alcohol) moiety in the anticipated photoredox chemistry. It was made using the same reaction shown in Scheme 4.1, starting with methylnaphthoquinone 4.3a.

![Scheme 4.1 Syntheses of acenequinones 4.1 and 4.4](image-url)
4.3 Product Studies

4.3.1 Photoredox Chemistry of 4.1

Pentacenequinone 4.1 was the first compound studied in this chapter not only because it is the synthetic precursor of pentacene introduced in Section 4.1, but also because it has a unique structure. Pentacenequinone 4.1 has one more benzene ring on the each side of the central quinone than HMAQ. This keeps the same symmetric structure on the acenequinone moiety as for HMAQ. However, this increases the distance between the benzyl alcohol moiety and the quinone carbonyl group. This might have an effect on electronic communication on the excited state of 4.1 and hence photoredox efficiency.

As already shown for reactions of many anthraquinone derivatives (Chapters 2 and 3), UV-Vis studies were particular informative of reaction since the photochemical transformation involves a substantial change in chromophore, going from an aromatic ketone/quinone to a dihydroxy-substituted polycyclic aromatic compound (anthracene). In the case of HMAQ, the initial photochemical product DHA is coloured orange. We anticipated that similar UV-Vis changes will take place on photoredox reaction of 4.1.

UV-Vis studies of 4.1 (10⁻⁶ to 10⁻⁵ M, 25% H₂O-CH₂CN, pH 1 and 7 (water portion), argon purged, 300 or 350 nm lamps, 3.0 mL quartz cuvette) were initially carried out. No changes were observed in neat CH₂CN or in pH 7, but dramatic changes were observed at pH 1 (Figure 4.1). Photolysis at this pH resulted in formation of an intense new absorption band at 318 nm and two additional (less intense) visible bands at 470 and 660 nm, the latter a very broad band covering 550-780 nm.
Figure 4.1 UV-Vis traces observed on photolysis of pentacenequinone 4.1 (25% H$_2$O-CH$_3$CN, pH 1, $\lambda_{ex}$ 350 nm, argon purged). Each trace represents 10-20 s of photolysis except for the final trace (2 min). Photolysis resulted in the loss of absorption (due to photoreaction of 4.1) at 302 and 407 nm with the formation of 4.5 (318, 473 and 657 nm). Inset: ten-fold expansion of the long wavelength region.

Based on what is known for HMAQ, the same reaction for 4.1 would give rise to 6,13-dihydroxypentacene 4.5 (eqn. 4.1). Pentacenes are known to absorb strongly in the visible region, with longest wavelength band in the 500-700 nm, depending on substituents.$^{98a,100}$ The broad absorption at 660 nm is consistent with formation of a pentacene. These new absorption bands disappeared within 1 min of opening the cuvette to air or oxygen (Figure 4.2), and within 1 h when the cuvette was unopened. The resulting UV-Vis spectrum was identical to an authentic sample of pentacenequinone aldehyde 4.6, which has a UV-Vis spectrum similar to that of 4.1. This is consistent with a highly reactive dihydroxypentacene derivative that is readily air-oxidized to give 4.6. 2-
Methyl-6,13-pentacenequinone (4.1a) was also studied, to test the requirement of a hydroxymethyl (alcohol) moiety in the anticipated photoredox chemistry. Notably, 4.1a, although structurally very similar to 4.1, did not show a reaction under the above conditions.

Figure 4.2 Decay of photogenerated dihydroxypentacene 4.5 (from pentacenequinone 4.1 in 25% H₂O-CH₃CN, pH 1) on exposure to air upon opening cuvette (time “0”) monitored at 473 nm.

Semi-preparative photolysis of 4.1 (pale yellow) in 25% H₂O-CH₃CN (pH 1) gave a green to dark green solution depending on irradiation time indicative of photoredox chemistry. When left standing in the photolysis tube after irradiation with no precautions to prevent entry of air, the colour changed to a pale yellow within one hour, indicative of a reactive initial photoproduction. When the photolyzed solution was exposed to air after photolysis (pouring the solution into a flask exposed to air), the green colour disappeared immediately. In view of the reactive nature of the initially formed photoprocess no
attempts were made to isolate it in these runs. Instead, the solutions were exposed to air after photolysis and extracted with CH$_2$Cl$_2$. Work-up using this method gave exclusively 2-formyl-6,13-pentacenequinone (4.6) (yields 20-70 % by NMR, depending on photolysis time) (eqn. 4.1). No reaction was observed when photolyzed in pH 7 or in neat CH$_3$CN, consistent with the UV-Vis studies reported above. In addition, no reactions were observed without photolysis (in the presence or absence of oxygen). Using the photoredox reaction reported for HMAQ as a secondary actinometer (Φ = 0.8, pH 1), we estimated a quantum yield of photoredox for 4.1 (25% H$_2$O-CH$_3$CN, pH 1) to be about 0.2. Although pentacenequinone 4.1 is not as reactive as the parent anthraquinone system HMAQ, it nevertheless has substantial quantum yields of reaction at a suitable pH.

\[ \text{4.1} \xrightarrow{\text{hv}} \text{4.6} \]
\[ \text{H}_2\text{O-CH}_3\text{CN} \quad (\text{pH} < 3) \]

Photolysis of the closely related methylpentacenequinone 4.1a under similar conditions as for 4.1 or even on extended photolysis did not give any reaction. The photolyzed solution did not develop any colour and upon work-up, the starting material was recovered unchanged. Thus, the photoredox reaction requires an α-hydroxy moiety at the carbon directly attached to the aromatic ring for the reaction to proceed.

Attempts were made to characterize the initially formed (green) dihydroxyanthracene intermediate 4.5. Initial experiments were carried out by photolyzing samples of 4.1 in
an NMR tube so the formation of 4.5 could be observed directly by NMR without work-up or exposure to air. However, due to the very low solubility of 4.1 in aqueous CH$_3$CN these photolyses proved to be impractical. Attempts were also made to trap 4.5 using acetic anhydride (as the ester) and methyl iodide (as the methyl ether) \emph{in situ} (Scheme 4.2) but in all experiments attempted, only 4.6 was isolated, consistent with the highly reactive nature of the initially formed product 4.5.

![Scheme 4.2 Attempts to trap the photoredox product 4.5](image)

4.3.2 Photoredox Chemistry of 4.2

Naphthoquinone 4.2 has one less benzene ring on the side of the central quinone without the attached hydroxymethyl group than HMAQ. UV-Vis studies of 4.2 (pH 7) gave rise to two new strongly absorbing bands at 268 and 392 nm which were assignable to dihydroxynaphthalene 4.7 (Figure 4.3, Scheme 4.3). For this compound, acid was not required for the photoredox reaction, contrary to what was observed for 4.1. Indeed, use of acid did not result in any enhancement of the photoredox reaction. Photolysis in neat CH$_3$CN gave no observable changes. The photoredox product in this case (dihydroxynaphthalene 4.7) was more stable to air or oxygen as the coloured intermediate remained for at least 1 day in the sealed cuvette.
Figure 4.3 UV-Vis traces observed on photolysis of naphthoquinone 4.2 (50% H$_2$O-CH$_3$CN, pH 7, $\lambda_{ex}$ 350 nm, argon purged). Photolysis times were 2-20 s. Growth of absorption bands at 268 and 392 nm is consistent with formation of dihydroxynaphthalene 4.7.

Shown in Figure 4.4 are solutions of photolyzed acenequinones HMAQ, 4.1 and 4.2 illustrating the varied colours observable in this family of photoredox reactions in aqueous solution.
Figure 4.4 Dramatic differences in observed colors in the photolysis of 4.2 (pH 7), HMAQ (pH 7), and 4.1 (pH 1) (L to R) in 1:1 H₂O-CH₃CN (λₑₐ, 350 nm; 15 min; argon purged). The color remained unchanged for at least a day for 4.2 and HMAQ and a few hours for 4.1.

Photolysis of 4.2 (50% H₂O-CH₃CN, pH 7) resulted in a yellow solution which slowly (several days) faded when left in the vessel and which turned to pale yellow within a few hours when exposed to air. On work-up in air, naphthoquinone aldehyde 4.8 was formed exclusively (> 60 %; Φ ~ 0.4). In order to provide further evidence for the reaction scheme shown in Scheme 4.3, trapping of 4.7 was attempted. Thus, after photolysis under an argon purge, sufficient solid NaOH was added to the photolysate to basicify the solution. This resulted in the solution turning from yellow to red consistent with formation of a naphtholate chromophore (via deprotonation of 4.7). Excess Ac₂O was then added under argon, which quenched the red colour. Upon work-up, the only product isolable was diacetoxyanthracene aldehyde 4.7-OAc thus confirming the reaction sequence shown in Scheme 4.3.
Scheme 4.3 Photolysis of 4.2 and trapping of the photoredox product 4.7 of 4.2

As further evidence for formation of 4.7 as the primary photochemical product from 4.2, photolyses were also carried out in NMR tubes (10^{-3} M, 10% D₂O-CD₃CN, pD 7, λₑ 350 nm, argon purged, 10 min). Photolysis gave a dark yellow solution with reduction of the signals at δ 4.80 (s) and 8.07 (s) assigned to the methylene and aromatic Hₐ protons of 4.2, respectively (Scheme 4.2), with concomitant growth of the aldehyde (CHO; δ 10.07) and Hₐ (δ 8.65) protons assignable to the initial photoredox product 4.7. Based on NMR integration, the yield of 4.7 was estimated to be about 14%. Upon introduction of oxygen via a syringe needle, the dark yellow colour was bleached. In the NMR, the peaks assignable to 4.7 disappeared. In particular, a new aldehyde peak at δ 10.13 and an aromatic singlet (Hₐ) at δ 8.55 are assignable to oxidized product 4.8.

4.3.4 Photoredox Chemistry of 4.3 and 4.4
Anthraquinone 4.3 has one more benzene ring between benzyl alcohol and quinone moiety than 4.2. Based on studies of 4.1 and 4.2, we expected that 4.3 would also undergo the same photoredox reaction. UV-Vis studies of 4.3 (pH 1 and 7) gave only
small incremental changes even on prolonged photolysis, indicative of a much less reactive chromophore. Semi-preparative studies of 4.3 in 100 mL quartz vessels showed that although acenequinone 4.3 underwent the photoredox reaction, it exhibited low reactivity in neutral or acidic solution ($\Phi \sim 0.01$). This compound required photolysis times that were about an order of magnitude longer for similar conversion. Due to its much lower reactivity, no attempts were made to characterize the initially formed photoredox product and only the final air-oxidized product 4.9 was isolated (eqn. 4.2). No reaction was observed without irradiation (in the presence or absence of oxygen).

Naphthacenequinone 4.4 has one more benzene rings on the side of the central quinone with the attached hydroxymethyl group than HMAQ. Thus, we also expected that 4.4 would undergo photoredox reaction efficiently. However, UV-Vis studies of 4.4 gave no observable changes in the UV-Vis spectrum (pH 1 or 7) even on prolonged irradiation time indicative of an essentially unreactive acenequinone. Of all the acenequinones studied in this work, compound 4.4 proved to be the only one that was photochemically inert. Semi-preparative photolysis of this compound (pH 1, 7) gave no reaction and the compound could be recovered unchanged. Initially we were puzzled by this result although one could imagine a number of photophysical reasons to explain the lack of reaction. However, the lack of reactivity of this compound as well as the reactivity of the other systems can be partly rationalized by resorting to examination of HOMO/LUMO characteristics (presented in Section 4.4.3).
4.4 Mechanistic Studies of Photoredox Reaction of Pentacenequinone 4.1

4.4.1 pH Effects on the Photoredox Reaction

The effect of pH on the relative quantum efficiency of the photoredox reaction of 4.1 is examined in this chapter. As noted, in pH 7, no reaction was observed. (Section 4.3.1) Using the UV-Vis method, the relative quantum efficiency for formation of 4.5 was followed at different pH’s (25% H₂O-CH₃CN, pH of the water portion varied). The results are shown in Figure 4.5 and show a strong dependence of photoredox efficiency on solution pH. The photoredox reaction was not observable above pH 3 and reaches maximum efficiency at about pH ≈ 0, although higher acidities were not employed in this study. The observations strongly suggest that the possible mechanistic step of the photoredox reaction of 4.1 might involve the protonation of the carbonyl oxygen on the anthraquinone moiety.

![Graph showing pH vs. ΔA](image)

**Figure 4.5** Effect of pH on the efficiency of photoredox reaction of pentacenequinone 4.1 monitored at 318 nm (formation of dihydroxypentacene 4.5; λₑₓ 350 nm; 25% H₂O-CH₃CN (pH
1\), argon purged). \(\Delta A\) is the difference of the absorbance before and after irradiation. Measurement error is about ± 5%.

**4.4.2 Nanosecond laser flash photolysis (LFP) of 4.1**

LFP studies of 4.1 (10^{-5} M, in neat CH\(_3\)CN, argon saturated) showed a sharp absorption band at 430 nm and an intense broad band at 570 nm (within the laser pulse). Both signals decayed with the first order kinetics (\(1.1 \pm 0.1 \times 10^5\) s\(^{-1}\); \(\tau \sim 9.0\) \(\mu\)s) (Figure 4.6). The intensity and lifetime of this transient were significantly reduced in the presence of oxygen (\(\tau \sim 0.09\) us). Triplet excited 6,13-pentencenquinone has been reported by G\(^{-}\)mer.\(^{61a}\) It has two absorption band at 430 nm and 590 nm in neat CH\(_3\)CN (\(\tau \sim 9\) \(\mu\)s in argon saturated solution) and is quenched by oxygen (\(\tau \sim 10\) ns). Based on these facts, we assign the 430/580 nm transient observed for 4.1 to the triplet state.

![Graph showing absorption spectra](image)

**Figure 4.6** Transient absorption spectra of 4.1 in neat CH\(_3\)CN (1.1 \(\pm\) 0.1 \(\times\) 10\(^5\) s\(^{-1}\); \(\tau \sim 9.0\) \(\mu\)s) (nitrogen-saturated) after the 266 nm pulse, 3.2 \(\mu\)s (\(\varnothing\)), 9.6 \(\mu\)s (\(\square\)), 21 \(\mu\)s (\(\triangle\)), 66 \(\mu\)s (\(\times\)). Measurement error is about ± 10%.
In the presence of water, LFP of 4.1 (1:1 H₂O-CH₃CN, pH 7, N₂ purged) also showed formation of the triplet state with a lifetime (τ ~ 10 μs) similar to that in neat CH₃CN. With decaying of the triplet excited transient, a new and weak signal (τ ~ 10 μs) was observed at 450 nm. In the presence of oxygen, with fast decaying of the triplet state (τ ~ 0.33 μs), no new band at 450 nm was observed. These observations suggest that the transient at 450 nm might be an intermediate generated from the triplet excited state. Due to the fast quenching of the triplet state to the ground state, no transient at 450 nm could be observed, consistent with very low photochemical reactivity in neutral aqueous solution. This assignment is also supported by with the observation that LFP studies of the methyl compound 4.1a (does not undergo the photoredox reaction) in 1:1 H₂O-CH₃CN (pH7) which showed only formation of the triplet excited state (430/570nm, τ ~5.0 μs, quenched by oxygen, τox ~ 0.35 μs) without formation of the 450 nm species.

In pH 1, the triplet signals at 430 and 570 nm were shorter lived (τ ~ 5.4 μs, compared to 10 μs at pH 7), consistent with acid catalysis of reaction. With decaying of the triplet state, a more intense new band (twice stronger than at pH 7) at 450 nm was observed with a long lifetime (τ ~ 60 μs). Its yield was reduced greatly by the presence of oxygen, but its decay rate was not affected (Figure 4.7). In addition, the observed decay rate of the 450 nm transient was dependent on pH (kₚH7:kₚH1 ~ 6:1), consistent with ketonation of enols generated from p-benzoylphenylacetic acid (kₚH7:kₚH1 ~ 100:1). The faster decay at pH 7 is associated with base catalysis of ketonization. Thus we tentatively assign the 450 nm transient to an enol intermediate. LFP studies of the methyl compound 4.1a also supported the assignment. LFP studies of 4.1a in 1:1 H₂O-CH₃CN (pH1) showed only the
formation of the triplet excited state (430 and 570 nm, \( \tau \sim 0.8 \mu s \), quenched by oxygen, \( \tau_{\text{ox}} \sim 0.18 \mu s \)) without observation of the 450 nm species.

**Figure 4.7** Transient absorption spectra of 4.1 in 1:9 H₂O-CH₃CN (pH 1, nitrogen-saturated) after the 266 nm pulse, 2.04 \( \mu s (\circ) \), 5.5 \( \mu s (\square) \), 12.2 \( \mu s (\triangle) \), 72.5 \( \mu s (\times) \). Inset: triplet decay at 550 nm. (5.4 \( \mu s \)). Measurement error is about ± 10%.

### 4.4.3 HOMO/LUMO Calculations

We have carried out calculations of HOMO's and LUMO's (Chem 3D, AM1) for all of the compounds studied in this chapter in an attempt to predict reactivity on excitation. For all the reactive acenequinones (HMAQ, 4.1-4.3), examination of HOMO and LUMO coefficients (some of which are shown in Figure 4.8) show that there is significant to substantial migration of charge from at least the ring with \( \text{CH}_2\text{OH} \) substituent to the carbonyl and to the other ring(s) in the compound. This charge transfer (migration) would make the carbonyl oxygen more basic. On trapping of this charge transfer state with a proton (protonation of the carbonyl oxygen), one can assume that
some of the residual positive charge (sites of electron deficiency) will be localized on the ring with the CH₂OH substituent, making the CH proton on the CH₂OH more acidic. At this level of calculation, there is also evidence to suggest that the C-H bond (of the CH₂OH) moiety also donates electron density for compounds \textbf{HMAQ} and \textbf{4.2}. This would have the added effect of making this proton even more acidic. Indeed, \textbf{HMAQ} and \textbf{4.2} were the most reactive compounds and reacted without the need for acid. For pentacenequinone \textbf{4.1}, the HOMO/LUMO characteristics do not display this effect: for this compound, the reaction was only observable below pH 3. The presence of the OH group is also particularly crucial: it provides a further inductive acidifying effect and also makes the whole group readily oxidizable (to the aldehyde). For the unreactive compound \textbf{4.4} (Figure 4.8), the same calculations show that the charge transfer is in the \textit{opposite direction}, that is, from the rings without the CH₂OH group (the “naphthalene” ring) to the carbonyl and to the ring containing the CH₂OH group. Although this charge transfer will still make the carbonyl oxygen more basic in the excited state and hence undergo protonation, one would not anticipate the same reactivity of the CH₂OH group since the ring in which it is attached is now more electron rich than in the ground state. Indeed, this compound proved to be photochemically inert! Thus simple semi-empirical MO calculations at the AM1 level are useful for the prediction of qualitative reactivity patterns for these compounds.
Figure 4.8 Calculated (Chem 3D, AM1) HOMOs (left) and LUMOs (right) for Acenequinones (top to bottom) HMAQ (reactive), 4.1 (reactive), 4.2 (reactive) and 4.4 (unreactive).

4.4.4 Proposed Mechanism

We believe that the observed formal intramolecular photoredox reactions of the present acenequinones, including the “parent” anthraquinone and “simple” benzophenone systems, are closely related to the acid-catalyzed photohydration of benzophenone (1.47) reported by Wirz and coworkers (Scheme 1.8). They discovered that protonation (at the carbonyl) of triplet benzophenone results in an overall photohydration reaction, to give water-adducts 1.49 and 1.50 with a preference for 1.49, i.e., hydration at the meta position. This reaction was unexpected and has missed detection in the past due to the
instability of the hydration products (1.49 and 1.50), which readily revert back to 1.47. Wirz and coworkers\textsuperscript{41} assigned a pK\textsubscript{a} of -0.4 for the protonated triplet excited state. The mechanism\textsuperscript{41} of photohydration presumably involves initiation protonation of the carbonyl oxygen of triplet excited benzophenone, to generate an excited triplet state conjugate acid 1.48 that has its positive charge significantly delocalized to the ortho and meta positions of the benzene ring (Scheme 1.8), as would be anticipated based on the Zimmerman "ortho-meta" effect for benzene ring site activation in photochemical reactions\textsuperscript{43}. Attack by water at these sites of positive charge would lead to the observed hydration products which upon deactivation to their ground states would not be expected to be long-lived and readily returns to benzophenone (1.47) by dehydration (with re-aromatization). Although the above acid-catalyzed photohydration of benzophenone reported by Wirz and coworkers\textsuperscript{41} gave no isolable stable product, it seemed reasonable to assume that the protonation of triplet excited benzophenone and aromatic ketones and related compounds such as acenequinones might lead to other types of acid-catalyzed chemistry, a prime example of which was the photoredox reaction of benzophenone 1.51 to give 1.52 in acidic aqueous solution reported by Wan and coworkers\textsuperscript{49} (eqn. 1.11).

In view of this background and the fact that acenequinones also tend to react via triplet excited state with photochemical behaviour\textsuperscript{59a} that is closely allied to what is known for benzophenones and our LFP studies of 4.1, we believed that the photoredox reaction of the acenequinones involves a triplet excited state. In addition, photoredox reactions of acenequinones 4.1-4.3 only occur in the presence of water and 4.1 requires acid. Thus, we proposed that the mechanism of photoredox reaction of the acenequinones reported in this work also start with lowest $\pi,\pi^*$ as for HMAQ (presented in Section 2.4.7). The
lowest $\pi,\pi^*$ reactive state is sufficiently basic to be protonated at pH 7 or at pH < 3, depending on the substrate. Intramolecular photoredox reaction requires protonation of the ketone (by acid or by water) and deprotonation of the C-H proton at the CH$_2$OH moiety. This is a unique mechanism in photochemistry in that two very different types of excited state proton transfers are required (simultaneously or sequentially).

Scheme 4.4 Proposed mechanism for the intramolecular photoredox reaction of 4.1

A working mechanism is shown for pentacenequinone 4.1 (Scheme 4.4). A highly polarized triplet excited state 4.1$^*$ undergoes protonation to give 4.10a. This results in a net positive charge on the benzene ring with the attached hydroxymethyl group (4.10b).
Subsequent deprotonation of the C-H proton in the CH₂OH moiety gives the double enol 4.11 which upon ketonization/enolization would give the redox product 4.5.

4.5 Summary
The photoredox reaction of HMAQ (Chapter 2) has been extended to acenequinones 4.1-4.4. Design of these compounds concerns not only the effect of electronic communication as for phenyl anthraquinone 3.1-3.4 (Chapter 3), but also the effect of a benzannelation (adding or removing a benzene ring to the anthraquinone moiety) on the efficiency of photoredox reactions of 4.1-4.4. Results show that acenequinone 4.1-4.3 undergo the photoredox reaction and 4.4 is photoinert. Table 4.1 lists the experimental conditions and quantum yields of HMAQ and 4.1-4.4. The photoredox reaction of HMAQ is the most efficient among these compounds and 4.2 is the second efficient.

Table 4.1 Comparison of efficiency of photoredox reactions of HMAQ and 4.1-4.4

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solvent</th>
<th>pH</th>
<th>Quantum Yield (Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMAQ</td>
<td>1:1 H₂O-CH₃CN</td>
<td>7</td>
<td>0.8</td>
</tr>
<tr>
<td>4.1</td>
<td>1:3 H₂O-CH₃CN</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>4.2</td>
<td>1:1 H₂O-CH₃CN</td>
<td>7</td>
<td>0.4</td>
</tr>
<tr>
<td>4.3</td>
<td>1:1 H₂O-CH₃CN</td>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>4.4</td>
<td>1:1 H₂O-CH₃CN</td>
<td>7 or 1</td>
<td>0</td>
</tr>
</tbody>
</table>

All of these results suggest that a highly polarized triplet excited state leads to the intramolecular redox reaction in highly benzannelated systems. Adding or removing a benzene ring to the anthraquinone moiety affects the degree and orientation of electronic distribution on both the ground and electronically excited states. This explains why compound 4.4 is photoinert while 4.1-4.3 are photoreactive. All of these results confirm
that charge polarization of the \( \pi \) system plays an important role in the photoredox reaction.

4.6 Experimental

4.6.1 General
Details are the same as those shown in Section 2.6.1.

4.6.2 UV-Vis Studies
UV-Vis studies (\( \sim 10^{-5} \) M in H\(_2\)O-CH\(_3\)CN, pH 7 or pH 1) were carried out in 3.0 mL quartz cuvette. Details are reported in Section 2.6.2.

4.6.3 Product Studies
Compounds were photolyzed in 100 mL quartz tubes using a Rayonet RPR 100 photochemical reactor equipped with 300 nm or 350 nm lamps. Typically, a solution of the compound (\( 10^{-4}-10^{-5} \) M, H\(_2\)O-CH\(_3\)CN (1:1 or 1:3), pH7 or 1) was bubbled with argon for 15 min and then irradiated under argon purge. The irradiated solution was extracted by 3 \( \times \) 50 mL CH\(_2\)Cl\(_2\) in air and the collected organic extracts was dried over anhydrous MgSO\(_4\). The solvent was removed under reduced pressure and the photolysate analyzed by NMR, MS and IR.

In order to monitor the initially formed redox product, photolyzes were carried out in NMR tubes which allowed characterization of the first formed redox products. NMR tubes were filled with 1 mL of the appropriate solution (\( 10^{-3} \) M, 10\% D\(_2\)O-CD\(_3\)CN). Solutions were bubbled using a fine needle through rubber stoppers with argon for 15 min before irradiation then irradiated with 300 nm or 350 nm lamps.
4.6.4 Quantum Yield Measurements
Quantum yields were measured using NMR and the reaction of 2-(hydroxymethyl)anthraquinone (HMAQ) as a secondary actinometer ($\Phi = 0.8$). A solution of the compound (4.1-4.3, $10^{-4}$ M, in H$_2$O-CH$_3$CN (1:1 or 1:3), pH 7 or 1) was purged with argon for 15 min and irradiated for 1 min at 300 nm (2 lamps) under argon purge. After irradiation, the conversion to product was determined by $^1$H NMR and compared to an identical run using HMAQ. All conversions were kept below 30% and repeated twice.

4.6.5 Nanosecond Laser Flash Photolysis Studies of HMAQ
LFP studies were conducted at the University of Victoria LFP facility employing a Spectra Physics Quanta-Ray YAG laser, model GSR-11, with a pulse width of $\sim$ 10 ns and excitation wavelength 266 nm. Quartz flow cells were used and solutions were purged with nitrogen or oxygen for 20 min prior to measurement. Optical densities at 266 nm were $\sim$ 0.6.

4.6.6 Syntheses of 4.1-4.4
Preparation of 6-(hydroxymethyl)-1,4-anthraquinone 4.3)\textsuperscript{99}

2-(Bromomethyl)-1,4-anthraquinone was obtained in 50 % yield via the literature procedure\textsuperscript{99} and hydroxylated by silver trifluoroacetate in 4:1 dioxane and water at room temperature to give 4.3 in 90% yield (yellow powder, m.p. 180-182 °C, lit.\textsuperscript{99} 178-179°C). $^1$H-NMR (300MHz, CDCl$_3$) δ: 8.59 (s, 2H), 8.05 (d, 1H, $J$ = 8.80 Hz), 8.03 (s, 1H), 7.68 (d, 1H, $J$ = 8.80 Hz), 6.05 (s, 2H), 4.92 (s, 2H); $^{13}$C NMR (DMSO-$d_6$, 75 MHz) 184.4, 184.3, 144.6, 134.0, 139.9, 134.3, 133.4, 130.0, 128.8, 128.2, 127.9, 127.7 (2C), 126.3, 62.7; MS (EI), $m/z$ 239 (M$^+$, 15), 238 (M$^+$, 100), 221 (10); IR (KBr) 3498, 3070, 2817, 1670, 1650 cm$^{-1}$.
Preparation 2-(hydroxymethyl)-6, 13-pentacenequinone (4.1)

A mixture of 4.3 (0.43 g, 1.8 mmol), \(\alpha,\alpha,\alpha',\alpha'\)-tetrabromo-o-xylene (1.14 g, 2.7 mmol) and NaI (2.70 g, 18 mmol) were heated in 5 mL DMF for 3 h at 80 °C to give a dark brown mixture. After cooling, 50 mL of cold water was added followed by the addition of 10 mL 10 % NaHSO₃ dropwise until the dark brown colour was bleached. The mixture was extracted with 3 x 25 mL CH₂Cl₂ and dried over anhydrous MgSO₄. Removal of the solvent gave a brown solid, which upon separation by column chromatography (silica gel; CH₂Cl₂ and ethyl acetate as eluents) gave 0.13 g of 4.1 (21 %, yellow powder), m.p. (decomp) 286 °C; \(^1\)H NMR (DMSO-\(d_6\), 500 MHz) \(\delta\) 8.95 (s, 1H), 8.94 (s, 1H), 8.93 (s, 1H), 8.89 (s, 1H), 8.38-8.33 (m, 2H), 8.31 (d, 1H, \(J = 8.54\) Hz), 8.23 (s, 1H), 7.84-7.79 (m, 2H), 7.75 (d, 1H, \(J = 8.54\) Hz), 5.54 (t, OH, \(J = 5.56\) Hz), 4.75 (d, 2H, \(J = 5.56\) Hz); \(^{13}\)C NMR (DMSO-\(d_6\), 125 MHz) 182.2, 182.1, 144.7, 134.8 (2C), 134.74, 134.72, 133.9, 130.4, 130.3, 130.1 (2C), 129.9 (2C), 129.8 (2C), 129.1 (2C), 129.0, 128.9, 128.8, 126.2, 62.7; MS (EI), m/z 338 (M⁺, 100), 321 (5); HRMS calculated for C₂₃H₁₄O₃ 338.0943; observed 338.0928; IR (KBr) 3403, 3054, 2924, 2854, 1691, 1676 cm⁻¹.

Preparation 2-methy-6,13-pentacenequinone (4.1a)

Following the method described for the synthesis of 4.1, use of 6-methyl-1,4-anthraquinone (4.3a, from ref. 135) (0.12 g, 0.54 mmol), \(\alpha,\alpha,\alpha',\alpha'\)-tetrabromo-o-xylene (0.32 g, 0.81 mmol), NaI (0.81 g, 5.4 mmol) gave 60 mg (35%, yellow powder), m.p. (decomp) 307 °C; \(^1\)H NMR (CDCl₃, 500 MHz) \(\delta\) 8.92 (s, 2H), 8.89 (s, 1H), 8.83 (s, 1H), 8.13-8.09 (m, 2H), 8.01 (d, 1H, \(J = 8.44\) Hz), 7.87 (s, 1H), 7.71-7.67 (m, 2H), 7.53 (d, 1H, \(J = 8.44\) Hz), 2.58 (s, 3H); \(^{13}\)C (CDCl₃, 125 MHz) 183.4, 183.3, 140.2, 135.8 (2C), 135.52, 135.49, 133.8, 132.1, 130.98, 130.94, 130.3 (2C), 130.2, 130.1, 129.96, 129.94, 129.8, 129.6
(2C), 129.3 (2C), 22.2; MS (EI), m/z 322 (M\(^+\), 100); HRMS calculated for C\(_{23}\)H\(_{14}\)O\(_2\) 322.0994; observed 322.0993 IR (KBr) 3051, 2920, 1676, 1615 cm\(^{-1}\).

**Preparation 6-(hydroxymethyl)-1,4-naphthoquinone (4.2)**

This compound was synthesized according to the published procedure\(^{100}\), except for the last hydrolysis step involving 6-(bromomethyl)-1,4-naphthoquinone, in which 1.5 equiv of silver trifluoroacetate was used instead of 5 equiv of CaCO\(_3\). Upon column chromatography (silica gel; CH\(_2\)Cl\(_2\)), 0.2 g (70 %, yellow powder) was obtained, m.p. 80-82\(^\circ\)C, lit.\(^{100}\) 81-82\(^\circ\)C; \(^1\)H-NMR (300MHz, CDCl\(_3\)) \(\delta\): 8.07 (d, 1H, \(J = 8.07\) Hz), 8.05 (s, 1H), 7.76 (d, 1H, \(J = 8.07\) Hz), 6.96 (s, 2H), 4.85 (s, 2H); \(^{13}\)C (75 MHz, CDCl\(_3\)) 185.3, 185.1, 147.7, 139.0, 138.8, 132.2, 131.9, 131.3, 127.1, 124.4, 64.5; MS (EI), m/z 189 (M\(^+\), 10), 188 (M\(^+\), 100), 160 (90); IR (KBr) 3447, 3064, 2864, 1662, 1598 cm\(^{-1}\).

**Preparation 2-(hydroxymethyl)-5,12-naphthacenequinone (4.4)**

A mixture 4.2 (0.22 g, 1.2 mmol), NaI (1.76 g, 11.7 mmol) and \(\alpha,\alpha,\alpha',\alpha'\)-tetrabromo-o-xylene (0.74 g, 1.76 mmol) in 4 mL DMF was heated to 80 °C overnight. After work-up and purification (as described for 4.1), 0.29 g (85%) of a yellow powder was obtained, m.p. (decomp) 190 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 8.84 (s, 2H), 8.40 (d, 1H, \(J = 8.08\) Hz), 8.38 (s, 1H), 8.13-8.05 (m, 2H), 7.83 (d, 1H, \(J = 8.08\) Hz), 7.73-7.64 (m, 2H), 4.91 (s, 2H); \(^{13}\)C NMR (DMSO-\(d_6\), 75 MHz) 182.2, 181.9, 149.8, 134.5 (2C), 133.7, 132.5, 131.9, 130.0 (2C), 129.6 (2C), 129.3, 128.9, 128.8 (2C), 127.0, 124.1, 62.2; MS (EI), m/z 288 (M\(^+\), 100), 259 (50); HRMS calculated for C\(_{19}\)H\(_{12}\)O\(_3\) 288.0786; observed 288.0792; IR (KBr) 3327, 3052, 2926, 1675, 1621, 1603 cm\(^{-1}\).

**4.6.7 Photolysis Procedures for 4.1-4.4 and Characterization of Products**

**Photolysis of (4.1)**
Compound 4.1 (3 mg in 75 mL CH₃CN and 25 mL H₂O, pH 1) was irradiated (350 nm, 16 lamps) for 1 minute to give 18% yield of 4.6 (2-formyl-6,13-pentacenequinone) which was subsequently isolated in pure form, ¹H-NMR (300MHz, CDCl₃) δ 10.2 (s, 1H), 9.10 (s, 1H), 8.97 (s, 1H), 8.95 (s, 2H), 8.93 (d, 1H, J = 8.6 Hz), 8.58 (s, 1H), 8.23 (d, 1H, J = 8.6 Hz), 8.19-8.05 (m, 2H), 7.78-7.64 (m, 2H); m/z 336 (M⁺, 100), 307 (10); HRMS calculated for C₂₃H₁₂O₃ 336.0786; observed 336.0787; IR (KBr) 3054, 1698, 1675 cm⁻¹

Photolysis of (4.1a)

Photolysis of 4.1a as for 4.1 gave no reaction. The NMR of the isolated material was identical to starting material.

Photolysis of (4.2)

Photolysis of 4.2 (5 mg in 50 mL CH₃CN and 50 mL H₂O, pH 7; 4 lamps, 1 minute) gave 4.8 (6-formyl-1,4-naphthoquinone, 44% yield by NMR), which was subsequently isolated in pure form, ¹H-NMR (300MHz, CDCl₃) δ: 10.17 (s, 1H), 8.57 (s, 1H), 8.25 (s, 2H), 7.07 (ss, 2H); ¹³C NMR (CD₃Cl, 75 MHz) 190.8, 184.4, 184.1, 139.9, 139.2, 139.1, 135.4, 133.4, 132.8, 128.7, 127.6; MS (EI), m/z 186 (M⁺, 100), 157 (40); HRMS calculated for C₁₁H₆O₃ 186.0317; observed 186.0322; IR 3051, 1697, 1664, 1597 cm⁻¹.

Photolysis of (4.3)

A solution of 5 (3 mg in 50 mL CH₃CN and 50 mL H₂O, pH 7, 16 lamps) was irradiated for 1 minute which gave an aldehyde product in < 2% conversion. Upon photolysis for 30 min, 30% conversion to 6-formyl-1,4-anthraquinone (4.9) could be achieved; ¹H-NMR (300MHz, CDCl₃) δ 10.22 (s, 1H), 8.78 (s, 1H), 8.67 (s, 1H), 8.54 (s, 1H), 8.16 (dd, 2H, J = 8.10 Hz), 7.11 (s, 2H); ¹³C-NMR (CDCl₃, 75 MHz) 191.5, 184.5, 184.3, 140.3 (2C), 137.9, 136.7, 135.7, 134.5, 131.5, 130.6, 130.3, 129.5, 128.8, 126.5.
MS (EI), m/z 236 (M⁺, 100), 207 (20); HRMS calculated for C₁₅H₆O₃ 236.0473; observed 236.0466; IR (KBr, cm⁻¹) 3071, 1706, 1668, 1589 cm⁻¹.

Photolysis of (4.4)

Photolysis of 4.3 (3 mg in 50 mL CH₃CN and 50 mL H₂O, pH 7 and pH 7, up to 30 min irradiation) gave no reaction. The NMR of the isolated material was identical to starting material 4.3.

4.6.8 Trapping the Photoredox Product of 4.2

Photolysis of 4.2 was also carried out in which the initially formed photoredox product 4.7 was trapped with Ac₂O, to give 4.7-OAc, as follows (all carried out under argon): A solution of 4.2 (10 mg in 50 mL CH₃CN and 50 mL pH 7 H₂O) was irradiated for 5 min. Upon photolysis, sufficient solid NaOH was added to turn the yellow brown solution to red. This was followed by the addition of 1 mL of Ac₂O, which turned the solution to a brown colour. After work-up in air, the crude material was characterized with ¹H NMR which was consistent with 50% conversion to 4.7-OAc (6-formyl-1,4-diacetoxynaphthalene). Further separation and purification was achieved by prep. TLC (silica gel, CH₂Cl₂), ¹H-NMR (300MHz, CDCl₃) δ 10.15 (s, 1H), 8.38 (s, 1H), 7.99 (s, 2H), 7.39 (dd, 2H, J = 8.08 Hz, J = 8.08 Hz), 2.50 (s, 3H), 2.47 (s, 3H), ¹³C-NMR (CDCl₃, 75 MHz) 191.9, 169.4 (2C), 145.5, 144.4, 134.8, 130.5, 127.9, 127.4, 124.3, 123.2, 121.4, 119.3, 21.4, 21.2; m/z 272 (M⁺, 5), 230 (15), 188 (100), 43 (40); HRMS calculated for C₁₅H₁₂O₃ 272.0685; observed 272.0687; IR (KBr, cm⁻¹) 3070, 2942, 2817, 1754, 1699 cm⁻¹.
4.6.9 pH Effects of Photolysis of 4.1

A solution of 4.1 (2.5 mg in 10 mL CH$_3$CN, diluted 20-fold with 25% H$_2$O / CH$_3$CN, pH from 1 to 7, respectively) in a 3 mL quartz cuvette was purged with argon for 2 minutes prior to photolysis and the cuvette was covered by a cap and sealed with parafilm after the argon purge. The deoxygenated solutions were irradiated with UV light (350 nm, 16 lamps, 50s) for 4.1 to give photoredox products 4.5, which was recorded by UV-Vis spectroscopy.
5. Summary

5.1 Intramolecular Photoredox Reaction of Anthraquinones

Results presented in this Thesis showed that the intramolecular photoredox reaction originally reported for HMAQ is a general reaction for a variety of anthraquinone derivatives in aqueous solution. Suitably designed anthraquinones with distal benzyl alcohol moieties and related acenequinones undergo an efficient and clean intramolecular redox reaction in acidic aqueous solution. Based on all of these studies, a better understanding of the intramolecular photoredox reaction of anthraquinone derivatives has been achieved. The photoredox reaction of anthraquinon-2-yl system possesses the following properties:

- Dramatical visible colours changes in this family of the photoredox reaction
- Unimolecular reaction in the anthraquinone molecule
- Water is an essential medium for reaction
- Product forming step probably involves C-H bond breaking at the CH₂OH moiety
- Competes effectively with simple photoreduction
- Highly polarized and photoreactive triplet excited state (lowest π,π* configuration)
- Unusual dienol intermediate generated from the excited state

5.2 Potential Applications of the Intramolecular Photoredox Reaction of Anthraquinones

5.2.1 Photodeprotecting group

Based on the above studies, the anthraquinon-2-yl chromophore can be used for photocaging of alcohols, aldehydes and ketones. It has the following advantages:

- Photoprotected compounds are readily synthesized
- High yields of photorelease (90% conversion in one hour) upon irradiation.
- The photorelease reaction works in water with excitation wavelengths above 300 nm

- Clean photoreaction and with photoinert products

### 5.2.2 Oxygen Sensor

The photoredox reaction of anthraquinons generally exhibits a dramatical visible colour change. For example, photolysis of HMAQ undergoes a series of colour changes from yellowish (starting material) to orange (photoredox product) to yellowish (oxidized product). These colour changes can be used for oxygen sensing. Indeed, such an application has been reported by Scaiano and his coworkers using HMAQ. The oxygen sensor was designed based on the intramolecular photoredox reaction of HMAQ adsorbed within zeolite cavities.

### 5.2.3 Manufacture of H$_2$O$_2$

In the Introduction, it was noted that in the manufacture industry of H$_2$O$_2$, anthraquinones are used, based on an initial thermal autoxidation. The intramolecular photoredox reaction of anthraquinones can open up a photochemical way to produce H$_2$O$_2$. The photoredox products of anthraquinones are oxidized by O$_2$ to produce H$_2$O$_2$ (eqn. 5.1). In order to make this a process useful, a selective reductant that will reduce the aldehyde back to the alcohol is required without reacting with the anthraquinone. This ultimately will be challenging.
5.2.3 Solar Energy Storage

The overall photoredox reaction requires the formal movement of π electrons from one end (CH₂OH) of the molecule to the other (C=O). Since some of the studied compounds absorb visible light, such as 4.1 (up to 450 nm), the photochemical transformation could be a way of storing solar energy, in the form of the high energy dihydroxyacenes, which are compounds capable of reducing other molecules. Activation of O₂ has already been discussed above, but other activation can be envisaged, such as readily reducible quinones, etc.
Bibliography


Excited Azoalkanes and Ketones. In V. Ramamurthy and K. S. Schanze (eds),
2006, 75–129; (c) J. Mattay, and A. G. Griesbeck (eds), Carbonyl Compounds. In

22. (a) M. A. Garcia-Garibay, and L. M. Campos, Photochemical Decarbonylation of
Ketones: Recent Advances and Reactions in Crystalline Solids. In W. M. Horspool
and F. Lenci (eds), CRC Handbook of Organic Photochemistry and Photobiology,
Song (eds), CRC Handbook of Organic Photochemistry and Photobiology, CRC

23. (a) P. J. Wagner, and P. Klán, Norrish Type II Photoelimination of Ketones: Cleavage
of 1,4-Biradicals Formed by a-Hydrogen Abstraction. In W. M. Horspool, and F.
Lenci (eds), CRC Handbook of Organic Photochemistry and Photobiology, 2nd edn,
CRC Press LLC, Boca Raton, FL, 2004, Chapter 52, 1–31; (b) R. G. Weiss, Norrish
Type II Processes of Ketones: Influence of Environment. In W. M. Horspool and P.-S.
Song (eds), CRC Handbook of Organic Photochemistry and Photobiology, CRC
Press, Boca Raton, FL, 1995, 471–483; (c) J. C. Scala, Laser Flash-photolysis
258.

24. (a) P. J. Wagner, Yang Photocyclization: Coupling of Biradicals Formed by
Intramolecular Hydrogen Abstraction of Ketones. In W. M. Horspool and F. Lenci
(eds), CRC Handbook of Organic Photochemistry and Photobiology, 2nd edn, CRC
Press LLC, Boca Raton, FL, 2004, Chapter 58, 1–70; (b) P. Wessig, and O. Mühl, Abstraction of (γ ± n)-Hydrogen by Excited Carbonyls. In A. G. Griesbeck and J.
Mattay (eds), Synthetic Organic Photochemistry, Vol. 12, Marcel Dekker, New York,

25. (a) F. Muller, and J. Mattay, Photocycloadditions – Control by Energy and Electron
Transfer, Chem. Rev., 1993, 93, 99–117; (b) A.G. Griesbeck, Photocycloadditions of
Alkenes to Excited Carbonyls. In A.G. Griesbeck and J. Mattay (eds), Synthetic
Organic Photochemistry, Marcel Dekker, New York, 2005, 89–139; (c) S. C. Freilich,
and K. S. Peters, Observation of the 1,4-Biradical in the Paternò–Buchi Reaction,
J. Am. Chem. Soc., 1981, 103, 6255–6257; (d) S. C. Freilich, and K. S. Peters,
Picosecond Dynamics of the Paternò–Buchi Reaction, J. Am. Chem. Soc., 1985, 107,
3819–3822.

26. J. A. Barltrop, and J. D. Coyle, Excited States in Organic Chemistry, Jone Wiley &

27. (a) N. C. Yang, and C. J. Rivas, A New Photochemical Primary Process, The
Photochemical Enolization of o-Substituted Benzophenones, J. Am. Chem. Soc.,


39. (a) P. Wan, E. Krogh, and B. Chak, Enhanced formation of 8.pi.(4n) conjugated cyclic carbonanions in the excited state: first example of photochemical C-H bond


89. (a) I. Loeff, A. Treinin, and H. Linschitz, Photochemistry of 9,10-Anthraquinone-2-Sulfonate in Solution. 1. Intermediates and Mechanism, J. Phys. Chem., 1983, 87, 2536-2544; (b) S. A. Carlson, and D. M. Hercules, Studies of Some Intermediates and Products of the Photoreduction of 9,10-Anthraquinone, Photochem. Photobiol., 1973, 17, 123-131; (c) H. Gan, and D. G. Whitten, A Sterically Controlled Recyclable


Figure A - 1 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(1-hydroxyethyl)-9,10-anthraquinone (2.1) in CDCl$_3$ at 300 K
Figure A - 2 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(ethoxymethyl)-9,10-anthraquinone (2.2) in CDCl$_3$ at 300 K
Figure A - 3 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(1-methoxyethyl)-9,10-anthraquinone (2.3) in CDCl$_3$ at 300 K
Figure A - 4 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(acetoxymethyl)-9,10-anthraquinone (2.4) in CDCl$_3$ at 300 K
Figure A - 5 $^1$H (top) and $^{13}$C NMR (bottom) for 9-phenyl-7,11-dihydro-8,10-dioxacyclohepta [b]anthracene-5,13-dione (2.5) in CDCl$_3$ at 300 K.
Figure A - 6 $^1$H (top) and $^{13}$C NMR (bottom) for 9-methyl-9-phenyl-7,11-dihydro-8,10-dioxa-cyclohepta [b]anthracene-5,13-dione (2.6) in CDCl$_3$ at 300 K.
Figure A - 7 $^1$H (top) and $^{13}$C NMR (bottom) for 2,3-di(hydroxymethyl)-9,10-anthraquinone (2.7) in Acetone-$d_6$ at 300 K.
Figure A - 8 $^1$H (top) and $^{13}$C NMR (bottom) for 2-[1,3]dioxolan-2-yl-9,10-anthraquinone (2.8) in CDCl$_3$ at 300 K
Figure A - 9 $^1$H (top) and $^{13}$C NMR (bottom) for 1,2-dibenzoyl-4-methylbenzene (2.9) in CDCl$_3$ at 300 K.
Figure A - 10 $^1$H for 2-acetyl-9,10-anthraquinone (2.11) in CDCl$_3$ at 300 K.

Figure A - 11 $^1$H for 1-hydroxy-1,3-dihydro-anthra[2,3-c]furan-5,10-dione (2.14) in CDCl$_3$ at 300 K.
Figure A-12 $^1$H for 3H-anthra[2,3-c]furan-1,5,10-trione (2.16) in CDCl$_3$ at 300 K.

Figure A-13 $^1$H for 9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid 2-hydroxy-ethyl ester (2.18) in CDCl$_3$ at 300 K.
Figure A - 14 $^1$H for 1,3-diphenyl-isobenzofuran-5-carbaldehyde (2.29) in CDCl$_3$ at 300 K.

Figure A - 15 $^1$H for 1,2-dibenzoyl-4-formylbenzene (2.30) in CDCl$_3$ at 300 K.
Figure A - 16 $^1$H for 2-formyl-9,10-diacetoxyanthracene (2.34) in CDCl$_3$ at 300 K.

Figure A - 17 $^1$H for 2-(hydroxymethyl)-9,10-diacetoxyanthracene (2.35) in Acetone-$d_6$ at 300 K.
Figure A - 18 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(o-hydroxymethylphenyl)-9,10-anthraquinone (3.1) in CDCl$_3$ at 300 K.
Figure A - 19 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(o-methylphenyl)-9,10-anthraquinone (3.1a) in CDCl$_3$ at 300 K
Figure A - 20 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(m-hydroxymethylphenyl)-9,10-anthraquinone (3.2) in CDCl$_3$ at 300 K.
Figure A - 21 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(m-methylphenyl)-9,10-anthraquinone (3.2a) in CDCl$_3$ at 300 K.
Figure A - 22 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(p-hydroxymethylphenyl)-9,10-anthraquinone (3.3) in CDCl$_3$ at 300 K.
Figure A - 23 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(p-methylphenyl)-9,10-anthraquinone (3.3a) in CDCl$_3$ at 300 K
**Figure A - 24** $^1$H (top) and $^{13}$C NMR (bottom) for 2-(p-hydroxymethylbiphenyl)-9,10-anthraquinone (3,4) in CDCl$_3$ at 300 K.
Figure A - 25 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(p-methylbiphenyl)-9,10-antraquinone (3.4a) in CDCl$_3$ at 300 K.
Figure A - 26 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(o-formylphenyl)-9,10-anthraquinone (3.8) in CDCl$_3$ at 300 K.
Figure A - 27 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(m-formylphenyl)-9,10-anthraquinone (3.9) in CDCl$_3$ at 300 K.
Figure A - 28 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(p-formylphenyl)-9,10-anthraquinone (3.10) in CDCl$_3$ at 300 K.
Figure A - 29 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(o-formylphenyl)-9,10-diacetoxyanthracene (3.11-OAC) in CDCl$_3$ at 300 K.
Figure A - 30 $^1$H (top) and $^{13}$C NMR (bottom) for 2-($p$-formylbiphenyl)-9,10-anthraquinone (3.14) in CDCl$_3$ at 300 K.
Figure A - 31 $^1$H (top) and $^{13}$C NMR (bottom) for 2-(hydroxymethyl)-6,13-pentacenequinone (4.1) in DMSO-$d_6$ at 300 K.
Figure A - 32 $^1$H (top) and $^{13}$C NMR (bottom) for 2-methyl-6,13-pentacenequinone (4.1a) in CDCl$_3$ at 300 K.
Figure A - 33 $^1$H (top) and $^{13}$C NMR (bottom) for 6-(hydroxymethyl)-1,4-naphthoquinone (4.2) in CDCl$_3$ at 300 K.
Figure A - 34 $^1$H (top) and $^{13}$C NMR (bottom) for 6-(hydroxymethyl)-1,4-anthraquinone (4.3) in CDCl$_3$ at 300 K.
Figure A - 35 $^1$H (in CDCl$_3$, top) and $^{13}$C NMR (in DMSO-$d_6$, bottom) for 2-(hydroxymethyl)-5,12-naphthacenequinone (4.4) at 300 K.
**Figure A - 36** \(^1^H\) (top) and \(^1^C\) NMR (bottom) for 6-methyl-1,4-naphthoquinone (4.2a) in CDCl\(_3\) at 300 K.

**Figure A - 37** \(^1^H\) (top) and \(^1^C\) NMR (bottom) for 6-methyl-1,4-anthraquinone (4.3a) in CDCl\(_3\) at 300 K.
Figure A - 38 $^1$H (top) and $^{13}$C NMR (bottom) for 6-formyl-1,4-diaceoxynaphthalene (4,7-OAc) in CDCl$_3$ at 300 K.
Figure A - 39 \textsuperscript{1}H (top) and \textsuperscript{13}C NMR (bottom) for 6-formyl-1,4-naphthoquinone (4.8) in CDCl\textsubscript{3} at 300 K.
Figure A - 40  $^1$H (top) and $^{13}$C NMR (bottom) for 6-formyl-1,4-anthraquinone (4.9) in CDCl$_3$ at 300 K.
Figure A - 41 $^1$H (top) and $^{13}$C NMR (bottom) for 2-formyl-6,13-pentacenequinone (4.6) in CDCl$_3$ at 300 K.
Figure B-1  UV-Vis traces of the photoredox reaction of 2.3 in 1:1 H₂O-CH₃CN (λₑₓ = 300 nm). Each trace represents 10 s of photolysis. Early photolysis resulted in loss of absorption (due to photoreaction of 2.3) at 256 and 328 nm with formation of an observable intermediate (269 and 398 nm). This is subsequently transformed to DHA (over a 10 min period; loss of 269 nm band, formation of 280, 400 and 456 nm bands). Insert: six-fold expansion of the long wavelength region.
**Figure B - 2** UV-Vis traces of the photoredox reaction of 2.6 in 1:1 H₂O-CH₃CN (λₑₓ = 300 nm). Each trace represents 20 s of photolysis. Photolysis resulted in the loss of absorption (due to photoreaction of 2.3) at 264 and 324 nm with formation of 2.13 (270 nm, 391 nm and 448 nm). Insert: ten-fold expansion of the long wavelength region.
**Figure B - 3** Decay of the photolysis product of diketone, diphenylisofuran 2.29 (1: 1 H₂O-CH₂CN, pH 0, 0-15min, 2 lamps, 300 nm in the presence of air). Each trace represents 1 min of photolysis. Photolysis resulted in the loss of absorption (due to the photoreaction of 2.29) at 331 nm and 441 nm with formation of the photoredox product 2.30 (259 nm). Insert: five-fold expansion of the long wavelength region.
Figure B - 4 UV-Vis traces of photolysis of 3.3 in 1:1 H₂O-CH₃CN, pH 1 (λₑₓ = 300 nm; argon purged). Each trace represents 5 s of photolysis. Photolysis resulted in the loss of absorption (due to the photoreaction of 3.3) at 275 nm and 359 nm with formation of the photoredox product 3.10 (297, 408 and 457 nm). Inset: five-fold expansion of the long wavelength region.
Figure C - 1  Excitation spectrum (left, $\lambda_{em} = 550$ nm) and fluorescence spectrum (right, $\lambda_{ex} = 440$ nm) of 2.29 (15 $\mu$mol/L in neat CH$_3$CN) before photolysis (top) and after photolysis in the presence of air (bottom).
Figure C - 2  Excitation (left) and fluorescence spectrum (right) of 2.34 (23 μmol/L in neat CH$_3$CN). Emission wavelength: 430 nm and excitation wavelength: 390 nm.
Appendix D: Others

Figure D - 1 Solvent effect on the competition between intramolecular photoredox (formation of DHA) and simple photoreduction (formation of 2.33) on photolysis of HMAQ in H$_2$O-CH$_3$CH$_2$OH mixtures; ■ absorption due to DHA at 280 nm; ▲ absorption due to 2.33 at 267 nm. Measurement error is about ± 5%.
**Figure D-2** Yield of benzaldehyde (▲) and acetophenone (■) from photolysis of 2.5 and 2.6, respectively, in 10% D$_2$O-CD$_3$CN ($\lambda_{ex}$ 300 nm), as determined by $^1$H NMR (relative to starting material). Measurement error is about ± 5%
Figure D-3 Proton NMR studies of photolysis of 3.3 in 10% D$_2$O-CD$_3$CN (pD 1, argon saturated). Bottom spectrum is 3.3 prior to photolysis, middle spectrum is 3.13-OD, and top spectrum is that of 3.10 (formed upon aeration of 3.13-OD).
Figure D - 4 Proton NMR studies of photolysis of 3.4 in 10% D$_2$O-CD$_3$CN (pD 1, argon saturated). Bottom spectrum is 3.4 prior to photolysis, middle spectrum is 3.15-OD, and top spectrum is that of 3.14 (formed upon aeration of 3.15-OD).
Figure D - 5  pH Dependence of intramolecular photoredox efficiency for 3.4 in 1:3 H₂O-CH₃CN, ≈ 10⁻⁴M, N₂ (pH refers to the aqueous portion). Measurement error is about ± 5%.