CHAPTER 4

PHOTOPHYSICAL AND ELECTRON TRANSFER STUDIES OF A DIAZAOXATRIANGULENIUM CATION

4.1. Abstract

In this Chapter, we report the photophysical and electron transfer properties of the diazaoxatriangulenium derivative, 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}}. Photophysical studies include absorption spectrum, fluorescence spectrum, fluorescence quantum yield and fluorescence lifetime. The singlet energy of 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}} was determined from these studies. Laser flash photolysis resulted in the observation of the triplet state of the molecule. The triplet quantum yield of 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}} was measured using the energy transfer method. 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}} did not exhibit phosphorescence emission and this is attributed to the low triplet quantum yield. Electrochemical studies indicated that 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}} could act as an electron acceptor or electron donor. Our studies have revealed that the fluorescence of 6b\textsuperscript{\textgreek{b}}BF\textsubscript{4}\textsuperscript{\textgreek{b}} is quenched by electron donors such as amines and ethers and also by electron acceptors such as quinones and nitroaromatics. Laser flash photolysis studies have indicated that these quenching reactions are due to electron transfer processes.
4.2. Introduction

The strategy used by Laursen and Krebs for the synthesis of azadioxatriangulenium cation was discussed in Chapter 3 of this thesis.\textsuperscript{12} Their methodology involved the treatment of the tris(2,6-dimethoxyphenyl)carbenium ion, 1 with methylamine at room temperature to get the acridinium derivative 2, which on subsequent demethylation and cyclization with pyridine hydrochloride gave the azadioxatriangulenium derivative 3 (Scheme 4.1). These authors have shown that formation of a second nitrogen bridge is also possible under suitable conditions. In order to accomplish this, the reaction should be carried out at relatively higher temperatures ($\geq 100$ °C) for longer periods of time.\textsuperscript{1} This temperature was not attainable with low-boiling amines such as methylamine or ethylamine. The authors, however, obtained a 77% yield of the doubly nitrogen bridged compound 5a, by heating 1-BF$_4$ with excess of $n$-propylamine in 1-methyl-2-pyrrolidone (NMP) at 100°C for 45 minutes (Scheme 4.1).\textsuperscript{1}

The diazaoxatriangulenium derivative 6a$^{\oplus}$BF$_4^{-}$ is a planar molecule. Since 6 contained two nitrogen atoms, it is expected to be much more stable than the trioxatriangulenium cation 4. For 6a$^{\oplus}$BF$_4^{-}$, Laursen and Krebs obtained a pK$_{R^+}$ value of 19.4.\textsuperscript{1} Thus, the replacement of two oxygen atoms by nitrogen atoms resulted in a remarkable increase in the stability constant by 10 orders of magnitude.
Sa upon heating with pyridine hydrochloride gave an 85% yield of the diazaoxatriangulene salt 6a. The trivial name of 6a is 4,8-Di-n-propyl-4,8-diaza-12-oxatriangulene tetrafluoroborate.

To the best of our knowledge, the chemistry of $6a^{\ominus}BF_4^{\ominus}$ has not been explored. In this Chapter we report the photophysical and electron transfer properties of $6b^{\ominus}BF_4^{\ominus}$. This molecule was prepared by adaptation of the procedure.

Scheme 4.1

5a upon heating with pyridine hydrochloride gave an 85% yield of the diazaoxatriangulene salt 6a. The trivial name of 6a is 4,8-Di-n-propyl-4,8-diaza-12-oxatriangulene tetrafluoroborate.
used for the synthesis of $6a^{\ominus}BF_4^{\ominus}$. Structure of $6b^{\oplus}BF_4^{\ominus}$ was confirmed by spectroscopic methods. Photophysical studies that we carried out include, absorption, emission, fluorescence quenching and laser flash photolysis. Our studies have shown that the fluorescence of $6b^{\oplus}BF_4^{\ominus}$ is quenched by strong electron acceptors and strong electron donors. Laser flash photolysis studies suggested that fluorescence quenching resulted in electron transfer. Thus, in the presence of strong donors $6b^{\oplus}BF_4^{\ominus}$ acts as an acceptor, and in the presence of strong acceptors $6b^{\oplus}BF_4^{\ominus}$ acts an electron donor.

4.3. Results and discussion

As mentioned earlier, diazaoxatriangulnium tetrafluoroborate $6b^{\oplus}BF_4^{\ominus}$ is a stable organic salt. It is only sparingly soluble in water, but highly soluble in polar solvents such as acetonitrile, dichloromethane and methanol. It was insoluble in non-polar solvents such as hexane, benzene and toluene. The photophysical studies carried out on this molecule are described in the following section.
4.3.1. Absorption spectrum

$\text{6b}^{\text{BF}_4^\ominus}$ exhibited several absorption bands in the 250-600 nm region (Figure 4.1). The absorption band in the 260-270 nm region is very intense and sharp, but the other absorption bands are relatively broad and less intense. The low energy absorption bands of $\text{6b}^{\text{BF}_4^\ominus}$ are very much red-shifted compared to the absorption bands of xanthenyl, thioxanthenyl,$^{3,4}$ and trioxatriangulenium cations.$^5$

![Absorption spectrum](image)

Figure 4.1. Absorption spectrum of $\text{6b}^{\text{BF}_4^\ominus}$ in acetonitrile.

Figure 4.2 compares the absorption spectra of trioxatriangulenium cation (4) and the monoaza (3) and diaza (6b) analogs. It can be seen from the figure that
increasing the number of nitrogen atoms leads to a red shift in the absorption spectrum of the cation.

![Absorption spectra](image)

**Figure 4.2. Absorption spectra of 4 (---), 3 (--•--) and 6b\(^\ominus\)BF\(_4\)\(^\ominus\) (—) in acetonitrile.**

In the case of 6b\(^\ominus\)BF\(_4\)\(^\ominus\), the red shift was accompanied by an increase in the extinction coefficient of the absorption. As in the case of 3 and 4, the absorption spectrum of 6b did not exhibit any solvatochromism.

### 4.3.2. Fluorescence properties

6b\(^\ominus\)BF\(_4\)\(^\ominus\) exhibited fluorescence in the 550-700 nm. In Figure 4.3, we have compared the emission spectra of 3, 4 and 6b\(^\ominus\)BF\(_4\)\(^\ominus\). It can be seen from Figure 4.3 that the fluorescence maxima are also progressively red shifted upon increasing the number of skeletal nitrogen atoms. For 6b\(^\ominus\)BF\(_4\)\(^\ominus\) the fluorescence
intensity and maximum did not exhibit any change upon changing the solvent from acetonitrile to dichloromethane.

The fluorescence quantum yield ($\Phi_F$) of $6b^{\Theta}BF_4^\Theta$ was determined in a few solvents by the relative method. The technique is described earlier in Chapter 2 of the thesis. An optically matched solution of Rhodamine 6G ($\Phi_F = 0.90$ in ethanol was used as the reference in these studies.\(^6\)

![Figure 4.3. Fluorescence spectra of 4 (......), 3(---) and 6b$^{\Theta}BF_4^\Theta$ (----) in acetonitrile. Excitation wavelengths were 450, 500 and 523, respectively.](image)

The fluorescence decay of $6b^{\Theta}BF_4^\Theta$ was monoexponential in all the solvents. Figure 4.4 shows the fluorescence decay profile of $6b^{\Theta}BF_4$ in acetonitrile along with the lamp profile. Analysis of the decay using a monoexponential function gave a lifetime of 24.8 ns.
Figure 4.4. Fluorescence decay profile (a) of 6b\textsuperscript{BF\textsubscript{4}} (b) is the lamp profile. Excitation and emission wavelengths were 450 and 590 nm, respectively.

6b\textsuperscript{BF\textsubscript{4}} did not exhibit any phosphorescence emission in ethanol glass at 77 K. This may suggest that the triplet state quantum yield of 6b\textsuperscript{BF\textsubscript{4}} is very low. The photophysical properties of 6b\textsuperscript{BF\textsubscript{4}} in three solvents are summarized in Table 4.1. From the absorption and fluorescence spectra, the singlet energy of 6b\textsuperscript{BF\textsubscript{4}} was calculated and the value obtained was 49.9 kcal M\textsuperscript{-1}. 
Table 2.1. Absorption maxima ($\lambda_{\text{max}}$ (abs)), extinction coefficients ($\varepsilon_{\text{max}}$), emission maxima ($\lambda_{\text{max}}$ (em)), singlet lifetime ($\tau_F$) and singlet quantum yield ($\Phi_F$) of $\text{6b}^{\ominus}\text{BF}_4^{\ominus}$ in acetonitrile, dichloromethane and methanol.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (abs) nm</th>
<th>$\varepsilon_{\text{max}}$, M$^{-1}$cm$^{-1}$</th>
<th>$\lambda_{\text{max}}$ (em) nm</th>
<th>$\tau_F$, ns</th>
<th>$\Phi_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>266</td>
<td>$9.91 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>296</td>
<td>$2.41 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>$0.62 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>$1.05 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>557</td>
<td>$1.63 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>266</td>
<td>$9.91 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>296</td>
<td>$2.41 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>$0.62 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>$1.05 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>557</td>
<td>$1.63 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>266</td>
<td>$9.91 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>296</td>
<td>$2.41 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>$0.62 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>$1.05 \times 10^4$</td>
<td>590</td>
<td>24.8</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>557</td>
<td>$1.63 \times 10^4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.3. Laser flash photolysis studies

In order to gain a better understanding of the excited state properties of $6b^\Theta BF_4^\Theta$, laser flash photolysis experiments were carried out. Excitation of $6b^\Theta BF_4^\Theta$ using 532 nm light from a Nd:YAG laser gave the transient absorption spectrum as shown in Figure 4.5.

![Figure 4.5. Transient absorption spectrum of $6b^\Theta BF_4^\Theta$ (1 x 10^{-4} M) in acetonitrile at 1.4 µs after laser excitation at 532 nm.](image)

The transient exhibited absorption at 390, 480 and 600 nm and bleaching in the 480-570 nm. The bleaching is due to the ground state absorption of $4b^\Theta BF_4^\Theta$. The transient decayed with a lifetime of 4.5 µs and the decay kinetics were the same at all wavelengths. Figure 4.6 shows the kinetic decay trace monitored at 600 nm.
The triplet quantum yield of $6b^{\Theta}BF_4^{\Theta}$ was determined using the energy transfer method. The method was described in Chapter 3 of this thesis. We have used $\beta$-carotene as the triplet energy acceptor and obtained $\Phi_T = 0.14$ for $6b^{\Theta}BF_4^{\Theta}$. The low value of $\Phi_T$ explains the absence of phosphorescence emission from this molecule. Also, notice that the sum of singlet and triplet quantum yields; $\Phi_F + \Phi_T = 0.6$. This indicated that about 40% of the absorbed energy is dissipated by non-radiative pathways.

4.3.4. Electrochemical studies

In order to determine the redox potentials of $6b^{\Theta}BF_4^{\Theta}$, electrochemical experiments were carried out. Cyclic voltammograms obtained showed the presence of irreversible reduction and oxidation potentials for $6b^{\Theta}BF_4^{\Theta}$. In order to get the accurate redox potentials, we have conducted Square Wave Voltammetry (SWV) experiment. Figure 4.7 is the SWV voltammogram of $6b^{\Theta}BF_4^{\Theta}$.
Figure 4.7. Square wave voltammograms of $6b^\oplus BF_4^\ominus$: (a) reduction peak and (b) oxidation peak.

$6b^\oplus BF_4^\ominus$ exhibited a reduction peak at -0.85 V and an oxidation peak at 1.17 V (both vs. SCE). A comparison of the reduction potentials of 4, 3 and 6b indicated that 4 is the better oxidant. Replacement of the skeletal oxygen atoms (in trioxatriangulenium) by nitrogen lowers the oxidizing power. When one oxygen atom is replaced by nitrogen, the reduction potential becomes more negative. When two of the oxygen atoms are replaced, as in $6b^\oplus BF_4^\ominus$, the reduction potential moved to more negative values and an oxidation peak appears on the positive side. This suggests that $6b^\oplus BF_4^\ominus$ may be able to act as an acceptor or a donor (under suitable conditions) in photoinduced electron transfer reactions.$^8,^9$

4.3.5. Electron transfer studies

4.3.5.1. Fluorescence quenching studies

Electrochemical studies have shown that $6b^\oplus BF_4^\ominus$ can be oxidized and reduced under appropriate conditions. In order to look more closely into these
aspects, we have carried out the fluorescence quenching of $6b^{\oplus}BF_4^{\ominus}$ with well-known electron donors and acceptors and the results are reported in this section.

In Figure 4.8, the fluorescence spectra of $6b^{\oplus}BF_4^{\ominus}$ in the presence of millimolar concentrations of N-phenylphenothiazine (NPPT) are presented.

![Figure 4.8. Fluorescence spectra of $6b^{\oplus}BF_4^{\ominus}$ (2 x 10^{-5} M) in the presence of NPPT. [NPPT] were: (a) 0 mM, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM. Quenching patterns similar to this were obtained in the presence of all the donors listed in Table 4.2. In all these cases, plots of the fluorescence intensity ratio ($I_0/I$) against quencher concentrations were linear. Representative examples of the Stern-Völmer plots are given in Figure 4.9.](image-url)
Figure 4.9. Stern-Vöлmer plots for the fluorescence quenching of $6b^{\oplus}BF_4^{\ominus}$. Quenchers were: (O) NPPT, (Δ) N-methylphenothiazine, (■) Diphenylamine and (○) Triphenylamine.

The Stern-Vöлmer quenching constants ($K_{SV}$) were obtained from the slopes of the plots and these are presented in Table 4.2. Using the $K_{SV}$ values, the fluorescence quenching rate constants ($k_q^S$) were calculated and these are also presented in Table 4.2. Notice that $k_q^S$ varied in a relatively wide range of $(0.05 - 13.2) \times 10^9$ M$^{-1}$ s$^{-1}$.

Compared to $6b^{\oplus}BF_4^{\ominus}$, the quencher molecules listed in Table 4.2 absorb at shorter wavelengths. The fluorescence spectrum of $6b^{\oplus}BF_4^{\ominus}$ in the presence of these quenchers did not show any long wavelength bands attributable to exciplexes. Thus, fluorescence quenching in these cases can not be attributed to energy transfer or exciplex formation. In order to attribute the quenching to electron transfer processes, we have calculated the free energies of these electron
transfer reactions using the Weller equation\(^\text{10}\) (see Chapter 2) and the \(\Delta G^0\) values obtained are also given in Table 4.2.

### Table 4.2. List of donors, their oxidation potentials (\(E_{\text{ox}}\) vs. SCE), \(\Delta G^0\) values, Stern-Völmer quenching constants (\(K_{SV}\)) and fluorescence quenching rate constants (\(k_q^S\)) for the electron transfer quenching of \(6b^\oplus\text{BF}_4\Theta\).

<table>
<thead>
<tr>
<th>Quencher</th>
<th>(E_{\text{ox}}, \text{V})</th>
<th>(\Delta G^0, \text{eV})</th>
<th>(K_{SV}, \text{M}^{-1})</th>
<th>(k_q^S, 10^9 \text{M}^{-1}\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)-Mehtylanisole</td>
<td>1.60</td>
<td>0.29</td>
<td>1.28</td>
<td>0.05</td>
</tr>
<tr>
<td>4,4'4&quot;-(trisbromophenyl)amine</td>
<td>1.05</td>
<td>-0.26</td>
<td>62.00</td>
<td>2.50</td>
</tr>
<tr>
<td>Triphenylamine</td>
<td>0.87</td>
<td>-0.44</td>
<td>133.00</td>
<td>5.40</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>0.78</td>
<td>-0.53</td>
<td>165.00</td>
<td>6.70</td>
</tr>
<tr>
<td>(N)-methylphenothiazine</td>
<td>0.69</td>
<td>-0.62</td>
<td>325.00</td>
<td>8.30</td>
</tr>
<tr>
<td>(N)-PhenyIphenothiazine</td>
<td>0.67</td>
<td>-0.64</td>
<td>204.00</td>
<td>13.20</td>
</tr>
</tbody>
</table>

Except for the case of \(m\)-methylanisole, \(\Delta G^0\) values are all negative, indicating that electron transfers from these donors to the singlet excited state of \(6b^\oplus\text{BF}_4\Theta\) are thermodynamically allowed. The reaction can be represented as shown in Equation 4.1. The singlet excited state of \(6b^\oplus\text{BF}_4\Theta\) accepts an electron from the donor and lead to the formation of the radical \(6b^*\) and the radical cation of the donor \(D^{*+}\).

\[
*6b^\oplus + D \quad \text{ET} \quad 6b + D^{*+} \quad (4.1)
\]

We have also observed that the fluorescence of \(6b^\oplus\text{BF}_4\Theta\) is quenched by several electron acceptors. Figure 4.10 shows the fluorescence spectra of \(6b^\oplus\text{BF}_4\Theta\).
in the presence of millimolar concentrations of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

![Fluorescence spectra](image)

**Figure 4.10.** Fluorescence spectra of $6b^\Theta$BF$_4^\Theta$ (2 x 10$^{-5}$ M) in the presence of DDQ. [DDQ] were: (a) 0 mM, (b) 1 mM, (c) 2 mM, (d) 3 mM and (e) 4 mM.

Quenching patterns similar to this were observed in the presence of several electron acceptors (see Table 4.3). For all these acceptors, plots of the fluorescence intensity ratio ($I_0/I$) against acceptor concentration were linear. Representative examples of the Stern-Völmer plots are given in Figure 4.11.
Figure 4.11. Stern-Volmer plots for the fluorescence quenching of \(6b^\ominus\text{BF}_4^\ominus\) by various acceptors.

The Stern-Volmer quenching constants (\(K_{SV}\)) were obtained from the slopes of the \(I_0/I\) vs. [Quencher] plots and these are presented in Table 4.3. Using the \(K_{SV}\) values, the fluorescence quenching rate constants (\(k_q^S\)) were calculated and these are also presented in Table 4.3. Notice that \(k_q^S\) varied in the range of \((1.45 - 12.5) \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1}\).
Table 4.3. List of acceptors, their reduction potentials ($E_{\text{red}}$ vs. SCE), $\Delta G^*$ values, Stern-Volmer quenching constants ($K_{SV}$) and fluorescence quenching rate constants ($k_q$) for the electron transfer quenching of $6b^\Theta \text{BF}_4^\Theta$ with acceptors.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$E_{\text{red}}, \text{V}^a$</th>
<th>$\Delta G^*$, eV</th>
<th>$K_{SV}$, M$^{-1}$</th>
<th>$k_q$, 10$^9$ M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDQ</td>
<td>0.51</td>
<td>1.59</td>
<td>285.00</td>
<td>11.60</td>
</tr>
<tr>
<td>Chloranil</td>
<td>0.02</td>
<td>-1.04</td>
<td>308.00</td>
<td>12.50</td>
</tr>
<tr>
<td>$p$-Benzoquinone</td>
<td>-0.54</td>
<td>-0.48</td>
<td>298.00</td>
<td>12.10</td>
</tr>
<tr>
<td>$m$-Dinitrobenzene</td>
<td>-0.90</td>
<td>-0.12</td>
<td>35.00</td>
<td>1.45</td>
</tr>
</tbody>
</table>

*a* Taken from references 11-13.

Compared to $6b^\Theta \text{BF}_4^\Theta$, the quencher molecules listed in Table 4.3 absorb at shorter wavelengths. The fluorescence spectrum of $6b^\Theta \text{BF}_4^\Theta$ in the presence of these acceptors did not show any long wavelength bands attributable to exciplexes. Thus, fluorescence quenching in these cases can not be attributed to energy transfer reactions or to exciplex formation. These factors suggest that the fluorescence quenching may be due to an electron transfer process, wherein $6b^\Theta \text{BF}_4^\Theta$ plays the role of an electron donor. $6b^\Theta \text{BF}_4^\Theta$ however, is a carbocation. In general, carbocations are electron acceptors (see Chapter 1) and to the best of our knowledge, the possibility of carbocations acting as excited state electron donors has not been examined. Electrochemical studies have revealed the presence of a high lying HOMO for $6b^\Theta \text{BF}_4^\Theta$, and it is quite conceivable that this molecule can participate in a PET reaction as an excited state electron donor. The various stages involved in such a reaction are shown schematically in Figure 4.12.
Figure 4.12. Schematic representation of the mechanistic pathways for the electron transfer reaction, where $6b^\circ BF_4^-$ is the excited-state electron donor and A is the acceptor.

Figure 4.12 shows that $6b^\circ$ goes to the excited state upon irradiation. Diffusive interactions leads to the formation of an encounter complex ($6b^\circ \cdots A$) between $6b^\circ$ and A. Electron transfer takes place in the encounter complex leading to the formation of a contact radical ion pair ($6b^{++} \cdots A^-\cdots$), which undergoes separation to produce the free radical ion pairs. In Figure 4.12, k’s are the rate constants for the various processes. In simple terms, the electron transfer can be represented as given in Equation 4.2.

$$\begin{align*}
*6b^\circ + A & \rightarrow ET \rightarrow 6b^{++} + A^- \\
(4.2)
\end{align*}$$

If the reaction actually involves electron transfer as depicted in Figure 4.12 and Equation 4.2, then the quenching rate constants should show some dependency on the free energy of the reaction. $\Delta G^\circ$ values are usually calculated
using the Weller Equation (Chapter 2, Equation 2.8).\textsuperscript{10} For the electron transfer processes represented by equations 4.1 and 4.2, the coulombic terms in the Weller Equation \( e^2/ed \) have different values. When the carbocation is functioning as an electron acceptor, as in Equation 4.1, electron transfer involves no net change in charge and hence the coulombic term is zero. For the electron transfer described by Equation 4.2, there is net change in charge and hence the coulombic term is not zero. In order to calculate this term, the center-to-center distance ‘d’ is required. \( 6b^{\oplus} \) is an unsymmetrical cation with two flanking alkyl chains. Since these alkyl chains do not participate in the electron transfer process, we considered \( 6b^{\oplus} \) as a symmetrical entity and used a value of 7 Å for d. Using this value, \( \Delta G^\circ \) for electron transfer from \( 6b^{\oplus}BF_4^{\ominus} \) to the various acceptors were calculated and the values obtained are given in Table 4.3.

### 4.3.5.2. Correlation of fluorescence quenching constants with \( \Delta G^\circ \)

We have observed that \( 6b^{\oplus}BF_4^{\ominus} \) can participate as an acceptor or donor in PET reactions. In order to ascertain the electron transfer nature of these reactions, we have attempted to correlate the quenching rate constants obtained, to rate constants calculated using the Rehm-Weller equation, as done previously for the trioxatriangulenium (Chapter 2) and azadioxatriangulenium (Chapter 3) cations. The results are summarized below.

In order to fit the data, electron transfer rate constants were calculated for the cases described by Equations 4.1 and 4.2 using calculated \( \Delta G^\circ \) values (Tables
4.2 and 4.3) and $k_{\text{dif}} = 3.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (see Chapter 2 for details). $\Delta G^\ddagger(0)$ value was varied to get a good fit. The fit obtained, along with the experimental values are shown in Figure 4.13. The triangles are the experimental points from Table 4.2 and circles are from Table 4.3. The fit is reasonably good suggesting that fluorescence quenching reactions described earlier occur by electron transfer mechanisms.

![Figure 4.13. Plot of $\log k_q$ vs. $\Delta G^\ddagger$ for $6b^{\oplus}\text{BF}_4\Theta$/donor ($\Delta$) and $6b^{\oplus}\text{BF}_4\Theta$/acceptor (O) systems. The solid line is a fit using Rehm-Weller equation. See text for fit parameters.](image)

As mentioned earlier, the triangles are for the reduction of $6b^{\oplus}\text{BF}_4\Theta$ and circles are for oxidation of $6b^{\oplus}\text{BF}_4\Theta$. The fact that we have gathered rate constants for two different reactions in one plot may be questioned. In general, the reorganization energies associated with the oxidation and reduction of a given molecule are not the same. The radical anion and the radical cation will have very
different bond lengths and bond angles and hence $\lambda_i$ values (see Chapter 2) associated with these processes may not be the same. $6b^\Theta{BF}_4^\Theta$, however, is a very rigid aromatic molecule. Such molecules resist nuclear reorganization and their oxidation and reduction reactions are associated with very small, nearly identical, $\lambda_i$ values. Because of this factor, we were able to fit data for two different reactions using the same parameters.

4.3.5.3. Laser flash photolysis studies

In order to gain a better understanding of the electron transfer process, laser flash photolysis of $6b^\Theta{BF}_4^\Theta$/donor and $6b^\Theta{BF}_4^\Theta$/acceptor systems were carried out. Figure 4.17 is the transient absorption spectrum obtained upon irradiation of a solution of $6b^\Theta{BF}_4^\Theta$ (6.5 x $10^{-5}$ M) in acetonitrile in the presence of 4,4',4''-tris(bromophenyl)amine (TBPA). Irradiation was carried out using the 532 nm light from a Nd:YAG laser. The fluorescence of $6b^\Theta{BF}_4^\Theta$ was quenched by more than 95% under the experimental conditions, and hence the transient absorption spectrum is expected to exhibit features assignable to the products of reaction 4.1. Transient absorption spectrum obtained is shown in Figure 4.14.
Figure 4.14. Transient absorption spectrum at 1.5 µs for the $6b^6\text{BF}_4^-$ (1 x $10^{-4}$ M)/TBPA (5 x $10^{-3}$ M) system in acetonitrile. 

The transient exhibited very strong absorption at 710 nm. A kinetic trace obtained at this wavelength is shown in Figure 4.15.

Figure 4.15. Kinetic trace at 710 nm for the $6b^6\text{BF}_4^-$ (1 x $10^{-4}$ M)/TBPA (5 x $10^{-3}$ M) system in acetonitrile.
TBPA is the electron donor in this reaction and according to Equation 4.1, the radical cation of TBPA and 6b* should be formed in equal amounts. The pronounced absorption at 710 nm in Figure 4.14 can be assigned to the well known TBPA**. The absorption due to 6b* is not observed in this experiment. This is similar to the case described for the azadioxatriangulenium cation described in Chapter 3 of this thesis. Most probably, the absorption due to 6b* is obscured by the bleaching or it may be occurring below 400 nm. This region could not be probed because of the high absorptions due to 6bBF4 and TBPA.

We have observed that fluorescence of 6bBF4 was quenched by methyl viologen, which is a well-known acceptor. Laser flash photolysis of 6bBF4 was also carried out in the presence of methyl viologen (MV2+). MV2+ was selected for this purpose because the absorption spectrum of its one-electron reduction product (MV**) is very well characterized. Transient absorption spectrum obtained in the flash photolysis of 6bBF4/MV2+ system is given in Figure 4.16.

Since MV2+ is a very good electron acceptor, the reaction should proceed according to Equation 4.2 and lead to the formation of 6b+++ and MV++. The absorption bands at 395 and 610 nm can be attributed to MV++. Since there are no other absorption bands, the absorption due to 6b+++ may be obscured within other absorption bands. It can be noted from Figure 4.16 that the transient absorption spectrum exhibited very little bleaching. MV++ has very little absorption in the 420-500 nm region.
Figure 4.16. Transient absorption spectrum of the $6b^{\Theta}BF_4^{\Theta}$/MV$^{2+}$ system at 1.4 µs following the laser excitation. [6b$^{\Theta}BF_4^{\Theta}$] was 1 x $10^{-4}$ M and MV$^{2+}$ was 5 x $10^{-3}$ M.

Thus, absence of bleaching in this region can most probably be attributed to absorption due to $6b^{+++}$. The extinction coefficient of the absorption due to $6b^{+++}$ may be similar to that of $6b^{\Theta}BF_4^{\Theta}$ in the 420-500 nm region and hence both these are unobservables.

4.4. Summary and conclusions

In this chapter, we have studied the photophysical and electron transfer properties of $6b^{\Theta}BF_4^{\Theta}$. Using absorption and fluorescence spectra, the energy level of the singlet excited state of $6b^{\Theta}BF_4^{\Theta}$ was determined. $6b^{\Theta}BF_4^{\Theta}$ did not exhibit any phosphorescence emission and this indicated low triplet quantum yield. The triplet quantum yield was determined by energy transfer experiments. The
fluorescence of $6b^{\oplus}\text{BF}_4^{-}$ was quenched by several electron donors as well as electron acceptors. In both cases the quenching is due to electron transfer. In the presence of donors, $6b^{\oplus}\text{BF}_4^{-}$ acts as an electron acceptor and in the presence of strong acceptors it acts as an electron donor. Laser flash photolysis experiments are also in accordance with this conclusion.

4.5. Experimental

Diazaoxatriangulenium tetrafluoroborate, $6b^{\oplus}\text{BF}_4^{-}$, was synthesized by adaptation of a reported procedure.\textsuperscript{1} Following spectroscopic data were obtained for $6b^{\oplus}\text{BF}_4^{-}$. Yield 70 %; mp. 230-232 (decomp.); IR ($\nu_{\max}$) = 3494, 2969, 2881, 2382, 1620, 1593, 1465, 1359, 1249, 1161, 1087 c. m.\textsuperscript{1}; $^1\text{HNMR}$ (300 MHz, Acetone $d_6$): δ 8.325-8.3825 (t, 1H), 8.1521-8.8203 (t, 2H), 7.659-7.7822 (m, 4H), 6.477-7.217 (t, 4H), 4.6477-4.701 (t, 4H), 6.550-8.709 (m, 14H); $^{13}\text{C NMR}$ (75 MHz, Acetone $d_6$): δ 153.301, 141.706, 140.823, 140.544, 139. 619, 112.410, 110.253, 109.331, 108.289, 106.893, 48.526, 27.218, 20.438, 14.109; Anal. Calcd: C, 67.23; H, 5.64; N, 5.81. Found. C, 66.97, H, 6.23; N, 5.49.

$N$-methylphenothiazine was prepared by a literature procedure.\textsuperscript{17} $N$-phenylphenothiazine is prepared procedure similar to that of $N$-methylphenothiazine. Methylanisole was prepared as described in Chapter 3. $m$-Dinitrobenzene was prepared by the nitration of nitrobenzene.\textsuperscript{18} Other quenchers were commercial samples and were purified by recrystallization. Solvents used were of spectroscopic grade. Doubly distilled water was used.
Absorption spectra were recorded on a Shimadzu-3101 PC UV-Vis NIR Scanning Spectrophotometer. Fluorescence spectra were recorded on a SPEX fluorolog F-112 X spectrofluorimeter. Fluorescence lifetimes were determined using an Edinburgh FL900CD Single Photon Counting System. Redox potentials were measured using a BAS CV50 W Cyclic voltammetric analyzer. A solution of $6b^{\oplus} \text{BF}_4^{-}$ (1 x 10$^{-3}$ M) in acetonitrile containing 0.1 M tetra-$n$-butylammonium tetrafluoroborate as supporting electrolyte, was thoroughly degassed before use. A glassy carbon electrode was used as the working electrode, platinum gauze was the counter electrode and silver wire was used as the reference electrode. The potential values were corrected by recording the oxidation potential of ferrocene under identical conditions. Laser flash photolysis experiments were carried out using an Applied Photophysics Model LKS-20 Laser Kinetic Spectrometer using a GCR-12 Series Quanta Ray Nd:YAG laser. The excitation wavelength was 532 nm.

4.6. References


9. Fox, M. A.; Chanon, M. Eds.; *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988; Parts A-D.


