

Photoinduced electron transfer in azatriangulenium salts[☆]

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Received 3 February 2003; received in revised form 12 May 2003; accepted 3 July 2003

Abstract

Fluorescence quenching and laser flash photolysis studies of stable azatriangulenium ions 2^{\oplus} – 4^{\oplus} are reported. The fluorescence quenching rate constants were correlated to ΔG_0 values. The results suggest that 2^{\oplus} is an excited state electron acceptor and 4^{\oplus} is an excited state electron donor. 3^{\oplus} , on the other hand, can act as an acceptor or donor in photoinduced electron transfer (PET) reactions. Laser flash photolysis studies also supported these observations. These cations thus present an interesting case, where replacement of oxygen atoms by *N*-alkyl groups leads to a gradual shift of photoinduced electron transfer property from an acceptor to that of a donor.

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Keywords: Photoinduced electron transfer; Azatriangulenium salts; Radical ions; Fluorescence quenching; Laser flash photolysis

1. Introduction

The operation of artificial photosynthetic devices relies mainly on photoinduced electron transfer (PET) processes and hence PET reactions have been the subject of extensive experimental and theoretical research for several years [1–3]. Two general mechanisms can be involved in the electron transfer reaction of an excited molecule: (1) reductive electron transfer quenching of the excited molecule S^* by an electron donor D , leading to the formation of products $S^{\bullet-}$ and $D^{\bullet+}$ and (2) oxidative quenching of the excited molecule by an electron acceptor A , resulting in the formation of products $S^{\bullet+}$ and $A^{\bullet-}$. For the past few years we have been involved in the study of electron transfer reactions of cationic organic molecules [4–7]. Cationic molecules, which are electron deficient to begin with, are expected to be particularly good excited state electron acceptors and one normally expects reductive quenching of the carbocationic excited state in their PET reactions [8–10]. Several examples of this behavior are reported in the literature [4–12]. Since they are very good electron acceptors in the excited state, they can be employed as sensitizers in PET reactions [13]. Besides being good electron acceptors, some of the

cationic molecules have potential uses as sensitizers in electrophotography [14] and also as phototherapeutic agents [15,16].

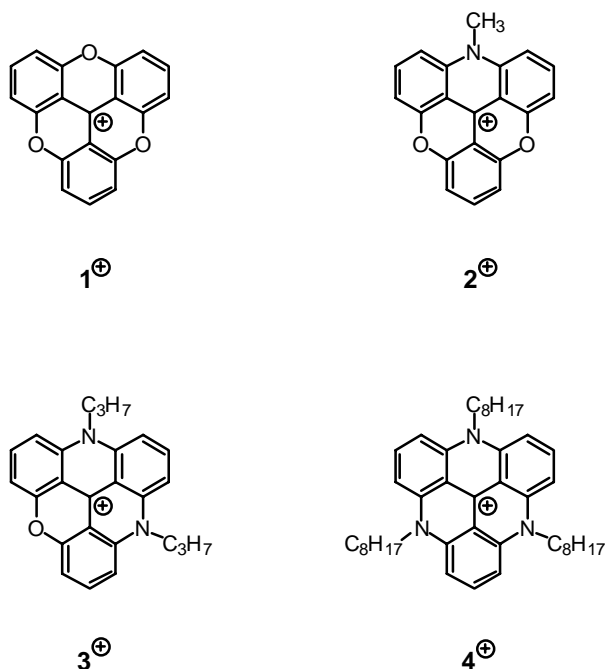
Recently we have reported the photophysical and electron transfer studies of a stable cation, namely, trioxatriangulenium perchlorate $1^{\oplus}ClO_4^{\ominus}$ (Scheme 1) [7]. We have observed that the fluorescence of 1^{\oplus} was quenched efficiently by several electron donors and also by DNA nucleosides. Laser flash photolysis studies of 1^{\oplus} in the presence of the donors confirmed that fluorescence quenching occurred by an electron transfer mechanism [7]. The stability of 1^{\oplus} and its efficiency as an electron acceptor suggested that it should serve as an excellent probe for charge transfer in DNA. Its planar aromatic structure is ideally suited for intercalation into duplex DNA and equilibrium dialysis studies have revealed that 1^{\oplus} binds readily to duplex DNA, with some preference for GC base pairs [17]. These studies have prompted us to investigate the electron transfer properties of structurally similar azatriangulenium ions 2^{\oplus} – 4^{\oplus} (Scheme 1). Azatriangulenium salts 2^{\oplus} – 4^{\oplus} were obtained by replacing one or more of the oxygen bridges in 1^{\oplus} by *N*-alkyl groups [18,19]. Our studies have revealed that, replacing the oxygen atoms by *N*-alkyl groups has the effect of decreasing the electron accepting power and increasing the electron donating ability of the cationic ring system. Thus, upon going from the azadioxo derivative 2^{\oplus} to the triaza derivative 4^{\oplus} , we see a gradual shift of the PET property from an excited state electron acceptor to an excited state electron donor. Details of these studies are presented here.

[☆] This is contribution No. RRLT-PPD 156 from the Regional Research Laboratory, Trivandrum.

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2. Experimental

The azatriangulenium salts were synthesized by a reported procedure [19]. *N*-Methylphenothiazine and *N*-phenylphenothiazine were synthesized by literature procedures [20]. Other quenchers were commercial samples and were purified by recrystallization or distillation. Unless stated otherwise, all studies were carried out in spectroscopic grade acetonitrile.

Absorption spectra were recorded on a Shimadzu 2100 UV-Vis spectrometer. Fluorescence spectra were recorded on a SPEX fluorolog F-112 X spectrofluorometer. Fluorescence quantum yields were measured using the relative method employing optically matched solution of rhodamine-6G in ethanol ($\Phi_F = 0.9$) [21] as standard. Fluorescence lifetimes were measured using a Edinburgh FL900CD single photon counting system. Redox potentials were measured using a BAS CV50W voltammetric analyzer. Laser flash photolysis experiments were carried out using a Applied Photophysics LKS 20 laser kinetic spectrometer using a GCR 12 Series Quanta Ray Nd:YAG laser. The excitation wavelength was 532 nm. Solutions for all experiments were deaerated using argon before the experiments. All the measurements were carried out at 298 K.

3. Results and discussion

Absorption spectra of the azatriangulenium salts 2^{\oplus} – 4^{\oplus} were reported by Laursen and Krebs [19]. Fig. 1 shows the fluorescence spectra of these salts in acetonitrile solution.

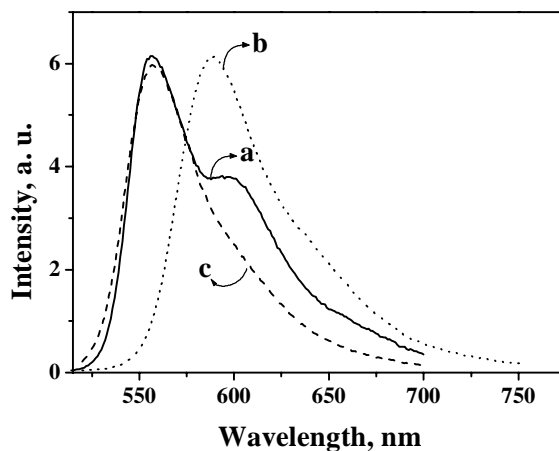


Fig. 1. Normalized fluorescence spectra of (a) $2^{\oplus}\text{BF}_4^{\ominus}$; (b) $3^{\oplus}\text{BF}_4^{\ominus}$; and (c) $4^{\oplus}\text{BF}_4^{\ominus}$ in acetonitrile solution. Excitation wavelengths were 480, 500 and 520 nm, respectively.

Table 1
Photophysical and electrochemical properties of azatriangulenium salts in acetonitrile solution

Property	$2^{\oplus}\text{BF}_4^{\ominus}$	$3^{\oplus}\text{BF}_4^{\ominus}$	$4^{\oplus}\text{BF}_4^{\ominus}$
Absorption maxima (nm)	540	557	525
Fluorescence maxima (nm)	555, 600	590	557
Singlet energy (E_s) (eV)	2.27	2.16	2.29
Fluorescence quantum yield (Φ_F)	0.42	0.46	0.21
Fluorescence lifetime (τ) (ns)	26.8	24.8	9.4
Reduction potential (E_{red}) (V) vs. SCE	−0.50	−0.85	−1.40
Oxidation potential (E_{ox}) (V) vs. SCE	–	+1.40	+1.20

Relevant photophysical and electrochemical properties of 2^{\oplus} – 4^{\oplus} are summarized in Table 1. Singlet energies in Table 1 were calculated from the average value of absorption and fluorescence maxima.

3.1. Fluorescence quenching studies of $2^{\oplus}\text{BF}_4^{\ominus}$

The fluorescence of $2^{\oplus}\text{BF}_4^{\ominus}$ was quenched efficiently by several electron donors (Table 2). These quencher molecules

Table 2
List of electron donors, their oxidation potentials (E_{ox} vs. SCE), ΔG_0 and k_q values for the fluorescence quenching of $2^{\oplus}\text{BF}_4^{\ominus}$

Quencher	E_{ox} (V)	ΔG_0 (eV)	k_q ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Anisole	1.76	−0.01	0.078
3-Methylanisole	1.60	−0.17	0.88
4-Methylanisole	1.52	−0.25	2.57
1,3-Dimethoxybenzene	1.49	−0.28	4.95
1,3,5-Trimethoxybenzene	1.46	−0.31	6.52
Anthracene	1.02	−0.75	13.06
Triphenylamine	0.87	−0.90	13.34
<i>N</i> -Methylaniline	0.81	−0.96	17.00
<i>N,N</i> -Diethylaniline	0.76	−1.01	14.21
<i>N</i> -Methylphenothiazine	0.69	−1.08	16.05
<i>N</i> -Phenylphenothiazine	0.67	−1.10	14.25

absorb at shorter wavelengths compared to $2^{\oplus}\text{BF}_4^{\ominus}$, and hence we can rule out energy transfer quenching taking place in these systems. In the case of the trioxatriangulene salt $1^{\oplus}\text{ClO}_4^{\ominus}$, we have shown earlier that the quenching reactions occurred by an electron transfer mechanism [7]. Hence in the case of $2^{\oplus}\text{BF}_4^{\ominus}$ also, one can invoke an electron transfer mechanism for the observed fluorescence quenching, as shown in Eq. (1), where S^{\oplus} stands for 2^{\oplus} .



The free energy change (ΔG_0) associated with the electron transfer process can be calculated using the Weller equation [22]:

$$\Delta G_0 = E_{\text{ox}} - E_{\text{red}} - E_s + C \quad (2)$$

where C is a coulombic term. $C = -z_{\text{D}}^+ z_{\text{A}}^- e^2 / \epsilon_s d_{\text{cc}}$, where z_{D}^+ and z_{A}^- are the charges on the product ions, ϵ_s is the static dielectric constant of the solvent and d_{cc} is the center-to-center separation distance of the donor and acceptor. Since only charge exchange takes place in the PET reaction in Eq. (1), the coulombic term was neglected in the calculation of ΔG_0 . For the fluorescence quenching reaction, the quenching rate constants k_{q} were obtained using the Stern–Volmer relationship:

$$\frac{I_0}{I} = 1 + k_{\text{q}}\tau[Q] \quad (3)$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, and $[Q]$ is the quencher concentration. In all cases, plots of I_0/I were linear and k_{q} values were calculated from the slopes of these plots. The list of donors, their oxidation potentials, calculated ΔG_0 values and observed k_{q} values for the fluorescence quenching of $2^{\oplus}\text{BF}_4^{\ominus}$ are presented in Table 2 (the redox potentials reported in this paper were either taken from literature [1,2,23] or measured in house).

In order to confirm the electron transfer pathway for fluorescence quenching, we have correlated the observed k_{q} values to the ΔG_0 values using the Rehm–Weller expression [22]:

$$k_{\text{q}} = \frac{k_{\text{diff}}}{1 + 0.25[\exp(\Delta G^{\#}/RT) + \exp(\Delta G_0/RT)]} \quad (4)$$

where k_{diff} is the diffusion rate constant and $\Delta G^{\#}$ is the free energy of activation and is given by Eq. (5).

$$\Delta G^{\#} = \frac{1}{2}\Delta G_0 + [(\frac{1}{2}\Delta G_0)^2 + (\Delta G_0^{\#})^2]^{1/2} \quad (5)$$

$\Delta G_0^{\#}$ in Eq. (5) is the free energy of activation when there is no driving force for the reaction. In Fig. 2, we have presented the experimentally obtained k_{q} values (Δ) along with a theoretical fit (solid line) obtained using Eqs. (4) and (5). Values of $k_{\text{diff}} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $\Delta G_0^{\#} = 0.15 \text{ eV}$ were used in the calculation of the theoretical fit. It can be seen that the fit is very good which suggests that fluorescence quenching of $2^{\oplus}\text{BF}_4^{\ominus}$ by the electron donors occur by an electron transfer mechanism.

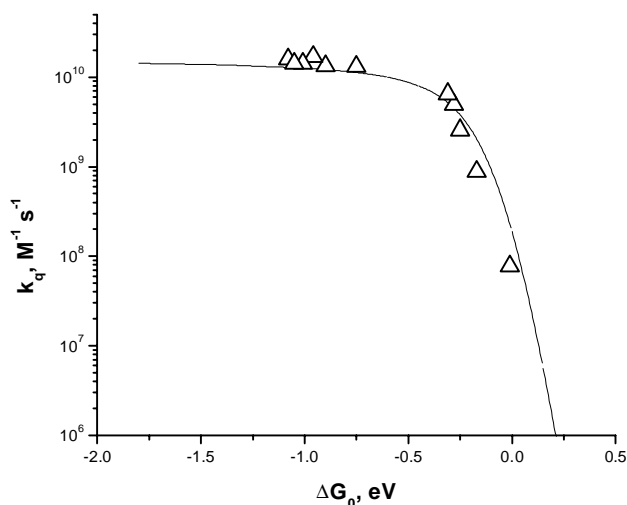


Fig. 2. Plot of k_{q} vs. ΔG_0 for the fluorescence quenching of $2^{\oplus}\text{BF}_4^{\ominus}$. The solid line is a theoretical fit to the Weller equation.

3.2. Fluorescence quenching studies of $3^{\oplus}\text{BF}_4^{\ominus}$

Fluorescence of the diazoxatriangulene $3^{\oplus}\text{BF}_4^{\ominus}$ was also quenched by a few strong electron donors. In this case also one can expect reductive quenching of the singlet excited state of the cation by electron donors as shown in Eq. (1), where S^{\oplus} now stands for 3^{\oplus} . The k_{q} values obtained along with the calculated ΔG_0 values are presented in Table 3. Notice that the driving forces for these PET reactions ($-\Delta G_0$) are considerably lower compared to those for $2^{\oplus}\text{BF}_4^{\ominus}$ and this explains the low k_{q} values. Thus, compared to $2^{\oplus}\text{BF}_4^{\ominus}$, $3^{\oplus}\text{BF}_4^{\ominus}$ is a weak electron acceptor.

It was noted that the fluorescence of $3^{\oplus}\text{BF}_4^{\ominus}$ was quenched efficiently by a few strong electron acceptors (Table 3). For these cases also, the fluorescence quenching reactions obeyed the Stern–Volmer relationship described in Eq. (3) and we obtained quenching rate constants k_{q} from plots of I_0/I versus $[Q]$. Molecules such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrachloro-1,4-benzoquinone (chloranil) are very good electron acceptors. These molecules absorb at shorter wavelengths compared to $3^{\oplus}\text{BF}_4^{\ominus}$, which suggest that fluorescence quenching is not due to an energy transfer mechanism. The fluorescence spectrum of $3^{\oplus}\text{BF}_4^{\ominus}$ in the presence of the quenchers did not exhibit any long wavelength bands that can be attributed to exciplexes and hence we can rule out exciplex formation as a possible reason for fluorescence quenching. Thus, in all probability, quenching of the fluorescence of $3^{\oplus}\text{BF}_4^{\ominus}$ by the acceptor molecules occur by an electron transfer mechanism as shown in Eq. (6):



where the cation 3^{\oplus} (S^{\oplus} in Eq. (6)) now plays the role of an excited state electron donor. In these cases also, the free

Table 3

List of quenchers, their redox potentials (vs. SCE), ΔG_0 and k_q values for the fluorescence quenching of $3^{\oplus}\text{BF}_4^{\ominus}$

Quencher	E_{ox} (V)	E_{red} (V)	ΔG_0 (eV)	k_q ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
Donors				
3-Methylanisole	1.60		+0.29	0.0013
4,4',4''-(Trisbromophenylamine)	1.05		-0.26	2.50
Triphenylamine	0.87		-0.44	5.40
Diphenylamine	0.78		-0.53	6.70
N-Methylphenothiazine	0.69		-0.62	7.80
N-Phenylphenothiazine	0.67		-0.64	9.22
Acceptors				
1,3-Dinitrobenzene		-0.90	+0.03	0.16
1,4-Benzoquinone		-0.54	-0.33	4.28
Methyl viologen		-0.47	-0.40	3.90
Chloranil		+0.02	-0.89	12.42
DDQ		+0.51	-1.38	10.31

energy changes for the PET processes were calculated using Eq. (2). Since there is a net change in charge in the PET reaction described in Eq. (6), the coulombic term could not be neglected. We have calculated the coulombic term assuming $d_{\text{cc}} = 7 \text{ \AA}$ and using this value the ΔG_0 values were calculated. ΔG_0 and k_q values along with the list of acceptors for the fluorescence quenching of $3^{\oplus}\text{BF}_4^{\ominus}$ are presented in Table 3.

For both the reductive and oxidative quenching reactions of $3^{\oplus}\text{BF}_4^{\ominus}$, the k_q values were correlated with ΔG_0 values using Eqs. (4) and (5). Fig. 3 shows the experimental k_q values (Δ) for reductive quenching and (\blacktriangle) for oxidative quenching and a theoretical fit (solid line). For the theoretical fit, values of $k_{\text{diff}} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $\Delta G_0^{\#} = 0.15 \text{ eV}$ were used in the calculation. It can be seen that the fit is good suggesting that the fluorescence quenching of $3^{\oplus}\text{BF}_4^{\ominus}$ by donors and acceptors occur by electron transfer mechanisms.

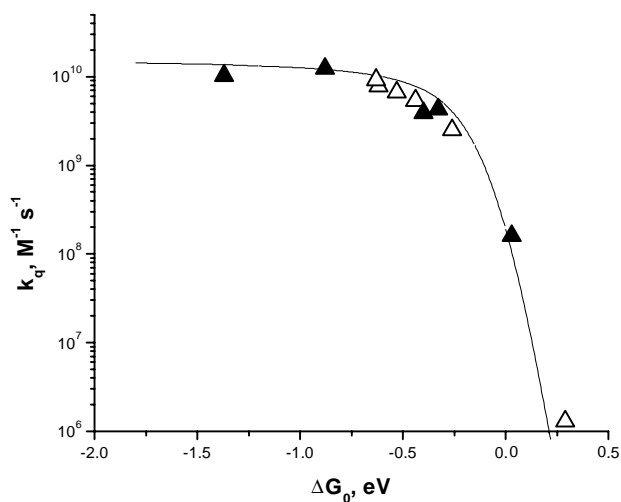


Fig. 3. Plot of k_q vs. ΔG_0 for the fluorescence quenching of $3^{\oplus}\text{BF}_4^{\ominus}$. The solid line is a theoretical fit to the Weller equation.

3.3. Fluorescence quenching studies of $4^{\oplus}\text{BF}_4^{\ominus}$

Fluorescence of $4^{\oplus}\text{BF}_4^{\ominus}$ is quenched by strong electron donors such as *N*-methylphenothiazine and *N*-phenylphenothiazine. For the quenching of $4^{\oplus}\text{BF}_4^{\ominus}$ fluorescence by *N*-phenylphenothiazine, we obtained $k_q = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is much lower than the corresponding values for $2^{\oplus}\text{BF}_4^{\ominus}$ and $3^{\oplus}\text{BF}_4^{\ominus}$. This showed that $4^{\oplus}\text{BF}_4^{\ominus}$ is a weak electron acceptor compared to $2^{\oplus}\text{BF}_4^{\ominus}$ and $3^{\oplus}\text{BF}_4^{\ominus}$. Several acceptor molecules, on the other hand, readily quenched the fluorescence of $4^{\oplus}\text{BF}_4^{\ominus}$. Thus $4^{\oplus}\text{BF}_4^{\ominus}$ could participate in PET reactions as an excited state electron donor as shown in Eq. (6), where S^{\oplus} now stands for 4^{\oplus} . The quenching rate constants k_q were obtained by the Stern–Volmer method, and these along with the reduction potentials of these quenchers and calculated ΔG_0 values, are presented in Table 4.

The experimental k_q values were correlated to ΔG_0 values using Eqs. (4) and (5). In Fig. 4 we have presented the k_q values (\blacktriangle) along with a theoretical fit (solid line). For the fit, values of $k_{\text{diff}} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $\Delta G_0^{\#} = 0.15 \text{ eV}$ were used. It can be seen from Fig. 4 that the fit is very good, which indicates that the fluorescence quenching of $4^{\oplus}\text{BF}_4^{\ominus}$ by electron acceptors proceed by an electron transfer mechanism.

It is interesting to note that for all the three azatriangulenium salts the quenching data could be fitted adequately

Table 4

List of electron acceptors, their reduction potentials (vs. SCE), ΔG_0 and k_q values for the fluorescence quenching of $4^{\oplus}\text{BF}_4^{\ominus}$

Quencher	E_{red} (V)	ΔG_0 (eV)	k_q ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
2-Nitrotoluene	-1.26	+0.06	0.06
Nitrobenzene	-1.15	-0.05	0.75
1,3-Dinitrobenzene	-0.90	-0.30	7.14
1,4-Benzoquinone	-0.54	-0.66	12.11
Methyl viologen	-0.47	-0.73	12.30
Chloranil	+0.02	-1.22	15.55
DDQ	+0.51	-1.71	21.19

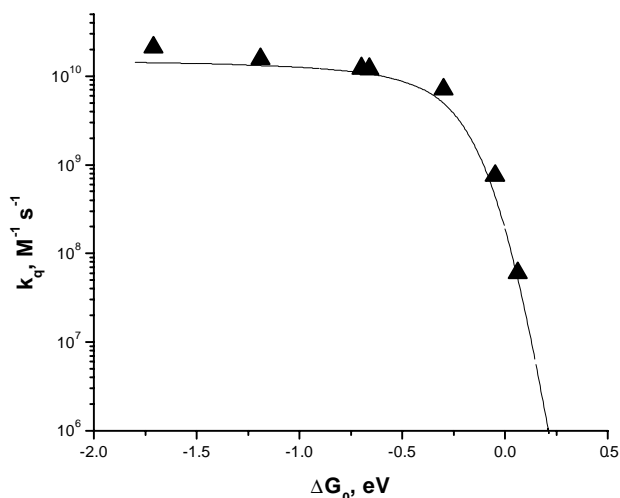


Fig. 4. Plot of k_q vs. ΔG_0 for the fluorescence quenching of $4^{\oplus}\text{BF}_4^{\ominus}$. The solid line is a theoretical fit to the Weller equation.

using $\Delta G_0^{\#} = 0.15$ eV. $\Delta G_0^{\#}$ is generally taken as equal to $\lambda/4$, where λ is the reorganization energy. In this way one obtains $\lambda = 0.6$ eV for the electron transfer reactions discussed above. The reorganization energy λ is the sum of an inner sphere term λ_{in} , involving vibrational energy changes between reactant and product states, and an outer sphere term λ_{out} involving the solvent orientation and polarization.

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{out}} \quad (7)$$

λ_{out} is given by [1,2]

$$\lambda_{\text{out}} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2r_{\text{T}}} + \frac{1}{2r_{\text{Q}}} - \frac{1}{d_{\text{cc}}} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right) \quad (8)$$

where r_{T} and r_{Q} are the radii of the triangulenium salts and quenchers, respectively, and ϵ_{op} and ϵ_{s} are the optical and static dielectric constants of the solvent. For calculating λ_{out} we have used $r_{\text{T}} = 7$ Å and $r_{\text{Q}} = 4$ Å. Since the azatriangulenium salts are highly planar, d_{cc} was taken as 7 Å. Substituting in Eq. (8) we obtained $\lambda_{\text{out}} = 0.43$ eV. From Eq. (7) it follows that $\lambda_{\text{in}} = 0.17$ eV. The azatriangulenium ions are very rigid, planar structures and electron transfer, whether oxidative or reductive, in such systems is not expected to alter the bond angles or bond lengths significantly. The small value of λ_{in} supports this conclusion.

3.4. Laser flash photolysis studies

Fluorescence quenching studies described above suggested that $2^{\oplus}\text{BF}_4^{\ominus}$ acts as an excited state electron acceptor and $4^{\oplus}\text{BF}_4^{\ominus}$ mainly acts as an excited state electron donor. $3^{\oplus}\text{BF}_4^{\ominus}$ can, on the other hand, act as an excited state electron acceptor as well as excited state electron donor. Laser flash photolysis of these cations in the presence of various quenchers corroborated this argument. Thus, laser flash photolysis of $2^{\oplus}\text{BF}_4^{\ominus}$ or $3^{\oplus}\text{BF}_4^{\ominus}$ in the presence of

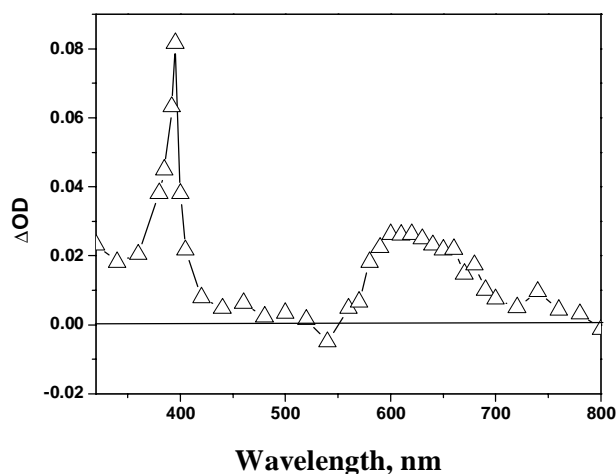


Fig. 5. Transient absorption spectrum obtained at 1.5 μs in the laser flash photolysis of $3^{\oplus}\text{BF}_4^{\ominus}$ (1×10^{-5} M) in the presence of MV^{2+} (1×10^{-3} M) in acetonitrile solution.

4,4',4''-(tribromophenylamine) resulted in the formation of the radical cation of the amine ($\lambda_{\text{max}} = 710$ nm, [24]) suggesting that excited states of $2^{\oplus}\text{BF}_4^{\ominus}$ and $3^{\oplus}\text{BF}_4^{\ominus}$ were capable of accepting an electron from this amine. Flash photolysis of $3^{\oplus}\text{BF}_4^{\ominus}$ or $4^{\oplus}\text{BF}_4^{\ominus}$ in the presence of methyl viologen (MV^{2+}), on the other hand, led to the formation of $\text{MV}^{\bullet+}$. Fig. 5 gives the transient absorption spectrum of the $3^{\oplus}\text{BF}_4^{\ominus}/\text{MV}^{2+}$ system. The absorption maxima at 390 and 610 nm can be attributed to the well-known $\text{MV}^{\bullet+}$ [25], and these experiments confirm that $3^{\oplus}\text{BF}_4^{\ominus}$ and $4^{\oplus}\text{BF}_4^{\ominus}$ indeed act as excited state electron donors. Carbocations 2^{\oplus} – 4^{\oplus} thus present an interesting case, where successive replacement of oxygen atoms by *N*-alkyl groups lead to a gradual shift of the PET property from an excited state acceptor to that of an excited state donor.

4. Conclusions

In this paper we have investigated the electron transfer properties of azatriangulenium salts 2^{\oplus} – 4^{\oplus} . The azadioxa derivative 2^{\oplus} is a good electron acceptor in its singlet excited state. This molecule can accept an electron even from a relatively weak electron donor such as anisole. The diazoxa derivative 3^{\oplus} is a poor electron acceptor in its singlet excited state. This molecule also exhibited properties of a poor electron donor. The triaza derivative 4^{\oplus} is a very weak electron acceptor as it could accept electrons only from the strongest of electron donors. This molecule, on the other hand, exhibited moderate electron donating abilities. Thus upon going from the azadioxa to the triaza derivative, we see a gradual shift of PET property, from an excited state acceptor to an excited state donor. In general, carbocations are good electron acceptors in PET reactions. To the best of our knowledge, the possibility of carbocations acting as donors in PET reactions has not been explored previously.

Carbocations exhibiting electron-donating abilities could be very rare and the diazaoxa- and triazatriangulenium cations belong to this small group of electron-donating carbocations.

Acknowledgements

The authors wish to thank the Council of Scientific and Industrial Research (CSIR), Government of India, and the Department of Science and Technology (DST), Government of India, for financial support.

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