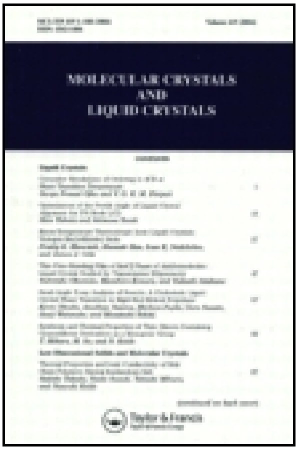

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Fluorescence Quenching and External Spin-Orbit Coupling Effects

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Abstract—The quenching of the fluorescence of anthracene and some of its meso-derivatives by "heavy atom quenchers" in various solvents has been shown to be dependent on the solvent, the quencher, and especially on the nature of the substituent. Anthracene shows good agreement with the Stern-Volmer equation in all solvents even in the presence of very high concentrations of quencher. However, marked deviations from this equation are observed for certain anthracene derivatives and in some cases the heavy atom "quencher" leads to an increase rather than to a decrease in the fluorescence.

Possible reasons for this behavior are discussed and bimolecular rate constants for quenching are given where appropriate.

1. Introduction

Radiative and non-radiative transition probabilities between electronic energy levels of different multiplicity are increased in the presence of atoms with high atomic number, "*heavy atoms*", either substituted directly into the molecule or present in the solvent, due to *internal* or *external* spin-orbit coupling effects[1]. These effects have been shown to increase the probability of T ↔ S processes in many organic phosphors leading to

(i) An increase in singlet-triplet absorption.[1, 2]
(ii) A decrease in the lifetime of phosphorescence.[3]
(iii) An increase in the rate of non radiative decay from the lowest triplet state[4].
(iv) An increase in the quantum yield of triplet state formation in fluid media[5] and of phosphorescence in rigid media.[6]
(v) A decrease in the quantum yield of fluorescence.[6]

Halogen derivatives of anthracene show normal internal heavy atom effects enhancing the rate of non radiative intersystem crossing from the lowest triplet state in viscous paraffin solution. Bromination is ten times more effective than chlorination at the same position and halogenation at the 9 or 10 positions has four times the effect of a halogen at any other position[4]. However the fluorescence yields show no clear trends as illustrated by the following values for φ_F in benzene at room temperature.[7] These are, 0.26, 0.065, 0.65, 0.05, 0.22, for anthracene, 1,5-dichloroanthracene, 9,10-dichloroanthracene, 9-bromoanthracene and 9,10-dibromoanthracene respectively. The fluorescence yields of these derivatives show marked solvent and temperature dependencies[8] and in this paper the effect of an external heavy atom environment is examined.

2. Experimental

Materials

Anthracene B.D.H. Analytical Standard was used without further purification. 9-Phenylanthracene had been twice chromatographed. 9-Bromoanthracene was prepared from anthracene and "Analar" cupric bromide in carbon tetrachloride[9] and was twice chromatographed M.Pt. 101°C open up 9,10-Dibromoanthracene was B.D.H. reagent grade and wastwice chromatographed, M.Pt. 226°C.

B.D.H. "Analar" benzene and B.D.H. reagent grade ethyl iodide and bromobenzene were twice distilled. 95% Spectroscopic ethanol, B.D.H. spectroscopic hexane and B.D.H. "Analar" potassium iodide were used without further purification. Xenon gas (99%—balance Krypton) was purchased from the British Oxygen Company.

Fluorescence Measurements

An Aminco-Bowman Spectrophotofluorometer was used for all fluorescence intensity measurements. No corrections were applied to allow for changes in refractive index since equal concentrations of solute were used. The number of quanta arriving in the cell compartment was measured as a function of wavelength and slit settings using the ferrioxalate actinometer[10]. The photomultiplier was an R.C.A. IP 28 and its sensitivity had been determined from the absolute spectrum of quinine sulphate[11]. Fluctuations in lamp intensity were allowed for by using a 5×10^{-6} M solution of quinine sulphate in 0.1 N sulphuric acid as a fluorescence standard taken before and after each measurement.

The fluorescence was measured at right angles to the exciting light. A calibration graph of fluorescence intensity of 9,10-dibromoanthracene in ethanol versus the peak optical density for the 4020 Å band with the excitation monochromator set at this peak, and with slit arrangement number 2[12], is shown in Figure 1. All measurements were made at peak

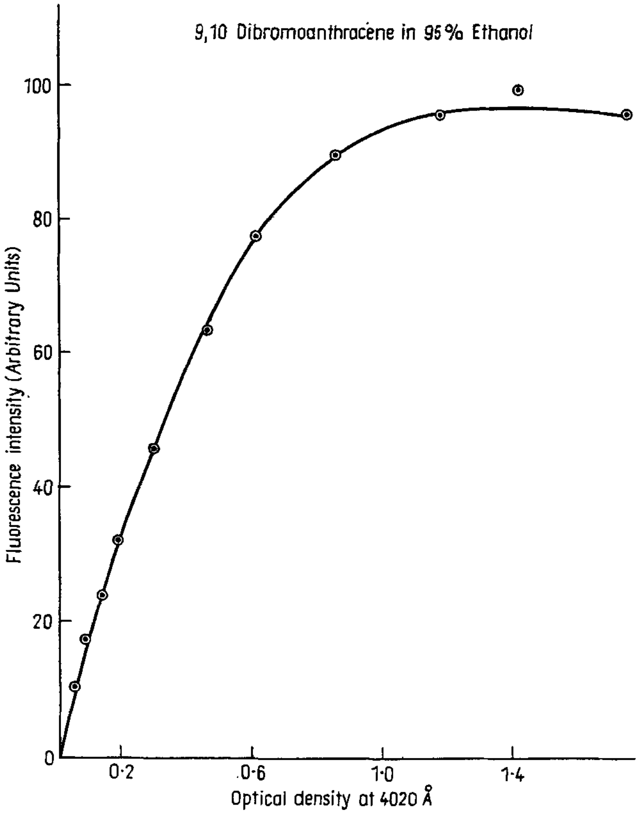

Fig.1

Figure 1. Variation in fluorescence intensity of 9,10-dibromoanthracene in 95% ethanol with increasing absorbance at 4020 Å.

optical densities less than 0.4. Absorption spectra of all solutions were taken on a Unicam SP 800 spectrophotometer.

Degassing Procedure

Anthracene and 9-phenylanthracene solutions were deoxygenated by repeated cycles of freezing, pumping, thawing and shaking. As 9-bromoanthracene and 9,10-dibromoanthracene show only a small increase in fluorescence upon degassing some of the runs using these solutes were done in aerated solvents.

All experiments were carried out at 21 ± 1°C.

3. Results

Figure 2 shows the Stern-Volmer plots for quenching of anthracene fluorescence in deaerated ethanol by bromobenzene, xenon, ethyl iodide

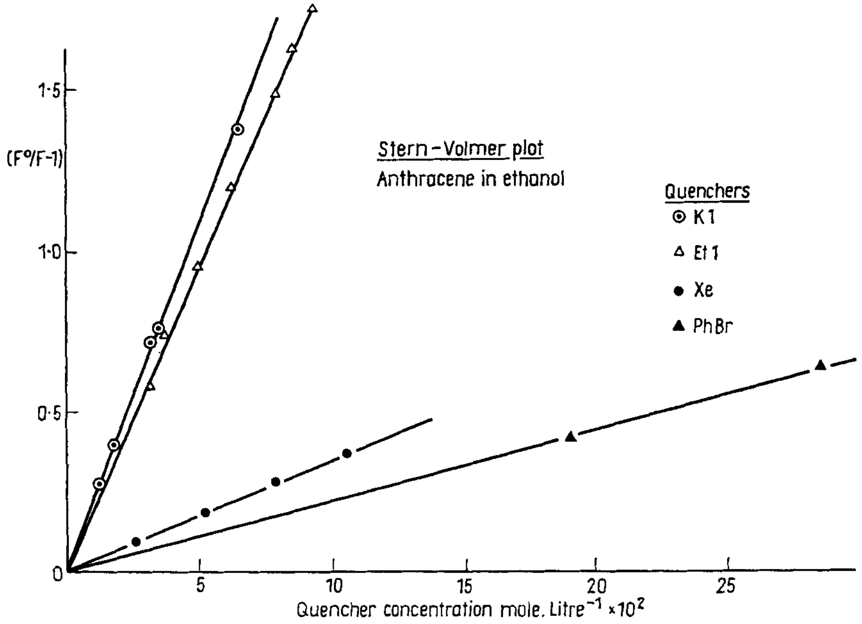

Figure 2. Fluorescence quenching of anthracene in ethanol by ⊙ potassium iodide, △ ethyl iodide, ● Xenon, ▲ bromobenzene

and potassium iodide. The ratios F°/F, where F° and F are the fluorescence intensities in the absence and presence of heavy atom quencher respectively, were the same for each of the main emission peaks. Anthracene was excited at 3740 Å and the results are summarized in Table 1.

The effects which high concentrations of bromobenzene have on the fluorescence of anthracene and three derivatives in degassed hexane solution are illustrated in Fig. 3. The anthracene derivatives were

TABLE 1

Conc. of anthracene (M/l)	Quencher	Quencher conc. (M/l)	($F^0/F - 1$)
3.96×10^{-5}	Bromobenzene	0.1904	0.415
		0.2856	0.640
		0.4761	1.120
		0.7617	1.700
		0.9520	2.160
3.96×10^{-5}	Ethyl Iodide	0.0310	0.580
		0.0372	0.738
		0.0496	0.957
		0.0620	1.200
		0.0780	1.490
		0.0860	1.630
		0.0930	1.770
		0.1116	2.180
		0.1860	3.460
2×10^{-5} and 4×10^{-5}	Potassium Iodide	0.0128	0.276
		0.0173	0.395
		0.0319	0.720
		0.0346	0.760
		0.0638	1.380
		0.0852	1.970
2×10^{-5} and 1×10^{-4}	Xenon	0.0260	0.090
		0.0526	0.180
		0.0789	0.280
		0.1057	0.370

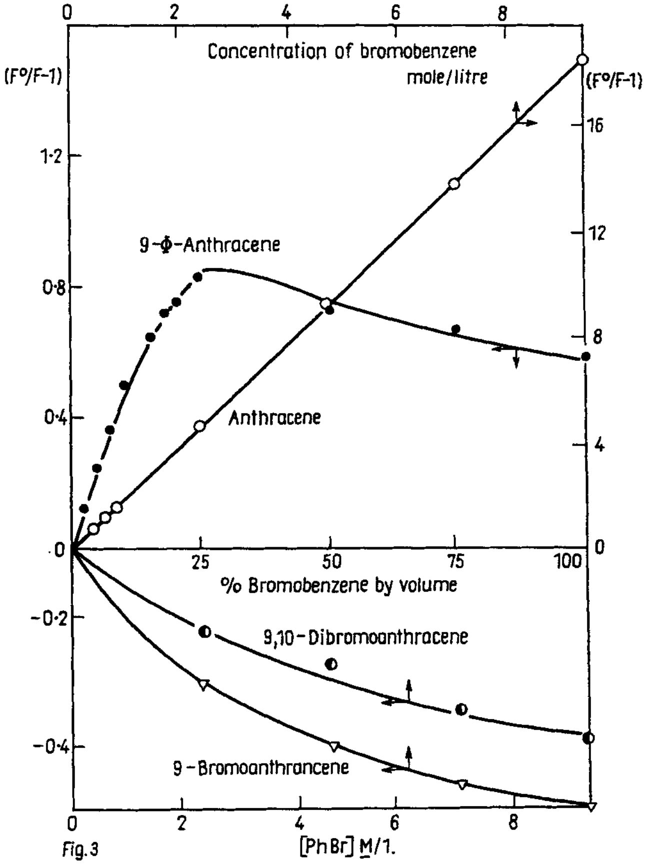

Figure 3. Relative fluorescence intensities upon changing the solvent from hexane to bromobenzene for ○ anthracene, ● 9-phenylanthracene, ◐ 9,10-dibromoanthracene, △ 9-bromoanthracene.

excited at the maximum of their respective 0, 0 bands, which were found to undergo a red shift of 60 Å in each case as the solvent nature changed from 100% hexane to 100% bromobenzene.

The fluorescence spectra also showed a similar red shift but no corrections were applied as the changes in the lamp output and photomultiplier response tended to compensate each other and in any case both were less than 4% over the range studied.

The maximum extinction coefficient of the 0, 0 band for each derivative decreases slightly in the presence of bromobenzene but there is a corresponding broadening of the band which will compensate for this because of the low dispersion of the fluorometer, as illustrated by the linearity of the plot for quenching of anthracene. Full allowance for all the above factors would make no significant difference to the shapes of the curves in Fig. 3. Table 2 gives the relevant excitation wavelengths for each degassed solution.

TABLE 2

Solute	Solute concentration (moles/litre)	Exciting wavelength	Concentration bromobenzene (moles/litre)	$(F^0/F - 1)$
Anthracene	4×10^{-5}	374	0.1904	0.222
		374	0.4760	0.940
		374	0.7617	1.580
		376	2.383	4.58
		377	4.765	9.25
		378	7.148	13.80
		380	9.530	18.40
9-phenyl-anthracene	2.3×10^{-5}	382	0.238	0.12
		382	0.476	0.25
		382	0.715	0.36
		383	0.953	0.50
		383	1.430	0.65
		384	1.670	0.72
		384	1.910	0.76
		384	2.383	0.84
		385	4.765	0.73
		387	7.148	0.67
		388	9.530	0.58
9-Bromo-anthracene	3×10^{-5}	391	2.383	−0.420
		392	4.765	−0.604
		394	7.148	−0.717
		395	9.530	−0.786
9,10-dibromo-anthracene	3×10^{-5}	404	2.383	−0.255
		405	4.765	−0.355
		407	7.148	−0.499
		408	9.530	−0.580

The effect of changing solvent nature on the fluorescence of 9,10-dibromoanthracene together with the quenching obtained by potassium iodide in ethanolic solution is shown in Fig. 4 for aerated solutions. Bathochromic shifts of absorption and emission spectra were obtained as the solvent changed from ethanol through benzene, bromobenzene or ethyl iodide and again slight changes in the extinction and the shapes of the absorption spectra were observed but these can be shown using Fig. 1 to lead to expected changes of less than 10% in the fluorescence intensity, much less than observed. The qualitative nature of the plots in Fig. 4 is not affected by the presence of oxygen. The increase in fluorescence on degassing is about 3% in hexane and ethanol, 10% in benzene and ethyl iodide and 15% in bromobenzene.

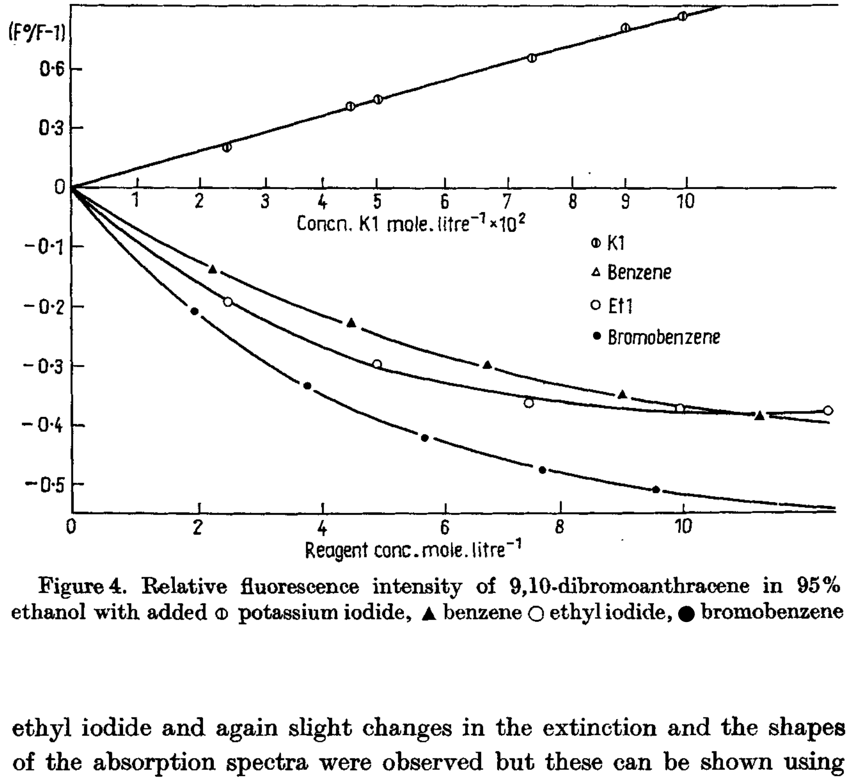

Figure 4. Relative fluorescence intensity of 9,10-dibromoanthracene in 95% ethanol with added ⦶ potassium iodide, ▲ benzene ○ ethyl iodide, ● bromobenzene

No quenching of 9-bromoanthracene or 9,10-dibromoanthracene fluorescence could be detected in ethanol or bromobenzene solutions with xenon concentrations of ~0.1 moles/litre. (Saturated solution, 1 atmosphere partial pressure.)

TABLE 3

Concentration 9,10-dibromo-anthracene (moles/litre)	Added reagent	Exciting wavelength (mμ)	Reagent concentration (moles/litre)	$(F^0/F - 1)$
1.2×10^{-5}	Potassium Iodide	402	0.0249	0.195
		402	0.0450	0.410
		402	0.0498	0.450
		402	0.0746	0.655
		402	0.0900	0.830
		402	0.0995	0.900
1.2×10^{-5}	Bromobenzene	404	1.906	—0.208
		405	3.812	—0.334
		406	5.718	—0.422
		407	7.624	—0.475
		408	9.530	—0.506
1.2×10^{-5}	Benzene	403	2.25	—0.135
		404	4.50	—0.225
		405	6.75	—0.290
		405	9.00	—0.345
		406	11.25	—0.380
1.2×10^{-5}	Ethyl Iodide	403	2.48	—0.190
		405	4.96	—0.295
		405	7.44	—0.360
		406	9.92	—0.365
		406	12.40	—0.370

4. Discussion

The following mechanism

$$
\begin{array}{llr}
{}^1A + h\nu & \rightarrow {}^1A^* & 1 \\
{}^1A^* & \rightarrow {}^1A + h\nu_F & 2 \\
{}^1A^* & \rightarrow {}^3A^* & 3 \\
{}^1A^* & \rightarrow {}^1A & 4 \\
{}^3A^* & \rightarrow {}^1A & 5 \\
{}^1A^* + Q & \rightarrow {}^3A^* + Q & 6 \\
{}^1A^* + Q & \rightarrow {}^1A + Q & 7
\end{array}
$$

where an asterisk represents a molecule in an electronically excited state and the superscript the multiplicity, explains the linear Stern-Volmer plots shown in Fig. 2 as predicted by the equation

$$\frac{F^\circ}{F} - 1 = K_{SV}[Q]$$

where F° and F are the fluorescence intensities as described above, Q is the heavy atom quencher and, K_{SV}, the Stern-Volmer constant, is equal to $k_q \tau_0 \varphi_F$ where k_q is the bimolecular quenching rate constant, τ_0 is the true radiative lifetime and φ_F is the quantum yield of fluorescence.

The values of k_q, calculated by taking $\tau_0 = 15.5$ nanoseconds and $\varphi_F = 0.27$ in ethanol[7] are given in Table 4.

TABLE 4

Quencher	Solvent	K_{SV} (litre mole^{-1})	k_q (litre mole^{-1} sec^{-1})	Heavy atom	$\Sigma\, \xi_i^2$ (cm^{-2})
Bromobenzene	Hexane	2.06	4.3×10^8	Br	6.06×10^6
Bromobenzene	Ethanol	2.25	5.4×10^8	Br	6.06×10^6
Ethyl Iodide	Ethanol	19.3	4.6×10^9	I	2.54×10^7
KI	Ethanol	21.8	5.2×10^9	I	2.54×10^7
Xenon	Ethanol	3.5	8.4×10^8	Xe	5.02×10^7

Vassil'ev[14] has shown that the rate constants for intermolecular energy transfer by a spin forbidden process, and the rate constants for intramolecular intersystem crossing of halogenated anthracene derivatives in solution are proportional to $\Sigma \xi_i^2$ where ξ_i is the radial part of the matrix element for spin-orbit coupling, ⟨Hso⟩, for each atom.

The values of ξ_i for isolated atoms are obtained from atomic spectra and the approximation that the ξ value for a molecule may be taken as the sum of the ξ_i values of the constituent atoms was first made by McClure.[3]

In recent studies we have shown that the four quenchers given in Table 4 lead to catalysed conversion of anthracene derivatives to their triplet states.[15] If the conversion is due to spin-orbit coupling factors alone it is difficult to account for the relatively low values of k_q for xenon since the values for I^- and ethyl iodide are close to those expected for diffusion controlled reactions.

On the basis of the effect on quencher power of electron withdrawing substituents in alkyl and aryl bromides, Melhuish and Metcalf[16] have suggested that electrons move towards the quencher in the quenching process. The relative values of k_q for ethyl iodide and I^- do not support this suggestion. The fact that xenon has a quenching efficiency closer to bromobenzene than ethyl iodide however supports the suggestion that spin-orbit coupling factors are not the only ones to be considered.

We have shown previously[5] that $\varphi_F + \varphi_T = 1$ for several anthracene derivatives and if this is assumed to be true for the haloanthracenes given in Table 5, the rate constants for intersystem crossing $S_1 \rightarrow T_1$ in benzene solution may be calculated from the results of Bowen[8] and Melhuish.[7] The rate constants increase on halogenation but show a marked decrease when substitution is in both the 9 and 10 positions. This positional effect is the reverse of that found by Hoffman and Porter[4] for the other intersystem crossing process $T_1 \rightarrow S_0$. (See Table 5.)

TABLE 5

compound	$k_{T_1 \rightarrow S_0} \times 10^{-2}$ sec^{-1} (4) in viscous paraffin at room temperature	$k_{S_1 \rightarrow T_1} \times 10^{-8}$ sec^{-1} in benzene at room temperature
Anthracene	1.1	2.36
1-chloroanthracene	2.8	8.44
1,5-dichloroanthracane	5.6	13.6
9,10-dichloroanthracene	20	0.528
9-bromoanthracene	90	13.2
9,10-dibromoanthracene	220	2.83

Meso-substituted anthracenes usually show large fluorescence yields which are very solvent and temperature dependent.[7] Recent work has shown that there is a converse dependence on solvent[15] and temperature[17] of the fluorescence and triplet state yields. It appears, so far as the first excited singlet state is concerned, that spin orbit coupling is small in anthracene and 9,10-dibromoanthracene, but quite large in 9-bromoanthracene.

It was decided to enquire further into external heavy atom effects to check the suggestion of McGlynn,[2] based on theoretical and experimental results for $S_0 \rightarrow T_1$ absorption, that the external heavy atom effect is larger the greater the internal spin-orbit coupling in the molecule. The results are shown in Fig. 3. It is clear that bromobenzene does not quench the fluorescence of either 9-bromo or 9,10-dibromoanthracene and the fluorescence intensities are actually greater in pure bromobenzene than in pure ethanol or hexane. Anthracene fluorescence is quenched in complete agreement with the Stern-Volmer equation despite the change in solvent nature, while the fluorescence of 9-phenylanthracene is quenched by low concentrations of bromobenzene but at higher concentrations the fluorescence intensity starts to increase again.

Figure 4 illustrates that 9,10-dibromoanthracene fluorescence is not quenched even in pure ethyl iodide, the fluorescence intensity again being greater than in ethanol. It appears that the heavy atom solvents bromobenzene and ethyl iodide are causing a change in the fluorescence yield comparable with the changes observed in solvents such as benzene[7] and toluene (see Fig. 4).

Although xenon has no effect on the fluorescence of 9, bromo and 9,10-dibromoanthracenes at a concentration of 10^{-1} moles litre^{-1}, quenching is obtained by a similar concentration of potassium iodide. Taking φ_F of 9,10-dibromoanthracene in ethanol to be 0.11[7] and τ_0 to be 12.5 nanoseconds[7], the rate constant for bimolecular quenching, k_q, is 6.5×10^9 l. mole^{-1} sec^{-1}, a value very similar to that obtained for anthracene. (See Table 4.)

All values of k_q are subject to errors of up to 20% by virtue of the uncertainty in the φ_F and τ_0 values.

These observations illustrate that it is not possible to explain heavy atom quenching effects by a consideration of spin-orbit coupling parameters alone. Those molecules which exhibit a large solvent dependence of fluorescence yield seem somehow able to increase these yields even in heavy atom solvents, possibly by some form of complex formation, or it could be that the activation energy for fluorescence reduction[8] is increased in these solvents outweighing any increase in the pre-expotential factor caused by spin-orbit effects. The lowering of S_1 relative to S_0 as witnessed by the red shift observed in the absorption spectra in these solvents might be supporting evidence for this latter suggestion.

However it will be necessary to make further investigations into these effects before the mechanism responsible for the observations can be fully understood.

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