Fluorescence Quenching Studies with Diaryl Sulphones

By **Ali S. Amiri** and **John M. Mellor,*** Department of Chemistry, The University, Southampton SO9 5NH

Fluorescence of diaryl sulphones is quenched by a range of electron donor quenchers including halogenobenzenes and some bromoaliphatic compounds. Bis-4-methoxyphenyl sulphone undergoes efficient self-quenching.

IN an earlier study [1] of the quenching of the excited singlet state of aromatic polysulphones and model diaryl sulphones fluorescence quenching by furan and 2-methylfuran was observed. Although the quenching of fluorescence from aromatic hydrocarbons,[2] nitriles,[3] ketones,[4] and other substrates [5] is now well documented no general study of quenching of fluorescence from sulphones has appeared. We now study a variety of possible quenchers, analyse the factors controlling the rate of fluorescence quenching in sulphones, and finally compare the behaviour of sulphones with that of other aromatic substrates.

EXPERIMENTAL

Materials.—Preparation of sulphones (1)—(4) has been described elsewhere.[1] Bis-4-benzyloxyphenyl sulphone (5), m.p. 190—191.5°, was prepared in 32% yield by reaction of benzyl bromide with the sodium salt of bis-4-hydroxyphenyl sulphone in acetone and subsequent recrystallisation from ethyl acetate. Bis-4-phenoxyphenyl sulphone (6) was prepared by the method of Rose *et al.*[6] in 90% yield. Purification by preparative t.l.c. and recrystallisation from isopropyl alcohol afforded bis-4-phenoxyphenyl sulphone (6), m.p. 141—143° (lit.,[6] 143—143.5°).

For quenching studies cyclohexane (Koch-Light spectroscopic grade) was further purified by passage through a column of silica gel (previously activated at 450 °C for 30 min). No solvent emission was observed at room temperature. All quenchers except 2-thia-adamantane [7] and 1-bromo-3,5-dimethyl-7-t-butyladamantane [8] were commercial samples. All quenchers were purified by recrystallisation or distillation as appropriate.

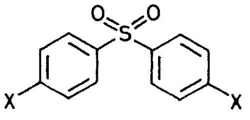
Spectroscopic Methods.—Ionisation potentials were measured by photoelectron spectroscopy on a Perkin-Elmer PS 18 instrument, as described fully elsewhere.[8]

Absorption spectra were recorded using a Unicam SP 800 spectrophotometer. Fluorescence spectra were recorded using a Farrand Mark 1 spectrofluorimeter. Spectra were recorded in cyclohexane after repeated degassing by a freeze–thaw cycle. Quenching was examined by construction of Stern–Volmer plots, which were linear. No new emission bands, suggestive of exciplex emission, were observed. Singlet state lifetimes were measured by single photon counting as described elsewhere.[9]

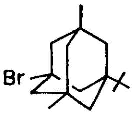
Half-wave Potentials.—Voltammograms were recorded in dry dimethylformamide containing 0.1M-$Bu^n_4NBF_4$ at a working platinum electrode with a cylindrical platinum gauze as secondary electrode, using a standard calomel electrode as reference. A Chemical Electronics potentiostat type TR70/7A was used and recordings made with a Bryan's Series 26000 AS XY recorder.

RESULTS AND DISCUSSION

Absorption and emission characteristics of a series of diaryl sulphones (1)—(6) and polarographic half wave reduction potentials are given in Table 1. Detailed quenching studies were made with the following quenchers, bromobenzene, chlorobenzene, bromoethane, 1-bromopropane, 2-bromopropane, 1-bromo-3,5-dimethyl-7-t-butyladamantane, furan, and tetrahydrofuran. Iodobenzene, iodoethane, triethylamine 1,4-diazabicyclo[2.2.2]octane, and 2-thia-adamantane were examined but rejected as unsuitable for detailed quenching studies as they were not completely transparent at 265 nm, the wavelength of excitation of the diaryl sulphones.



(1) X = H
(2) X = Me
(3) X = OMe
(4) X = Cl
(5) X = OCH_2Ph
(6) X = OPh



(7)

TABLE 1

Absorption and emission data and half-wave reduction potentials for sulphones (1)—(6)

Compound	Absorption (cyclohexane) $\lambda_{max.}$/nm	log s	Emission (cyclohexane) $\lambda_{max.}$/nm	ϕ_f	$E_{\frac{1}{2}}$ (reduction)/V
(1)	236	4.17	298	0.069	1.99
(2)	244.5	4.27	300	0.096	2.18
(3)	236	4.29	302	0.085	2.33
(4)	250	4.39	298	0.02	1.83
(5)	258	4.40	296	0.04	2.11
(6)	260	4.55	299	0.05	2.18

Diamantane (I_p 8.59 eV) and chloroethane (I_p 10.98 eV) failed to quench the fluorescence of diaryl sulphones. An initial survey was made of the quenching efficiency of the remaining quenchers, with bis-4-methylphenyl sulphone (2) in cyclohexane. For each quencher Stern–Volmer plots were constructed and values of $k_q\tau$ and of k_q, assuming the value τ obtained by single photon counting are given in Table 2. With the series of alkyl bromides there is a clear relationship that the lower the ionisation potential of the alkyl bromide, the greater its efficiency as a quencher. The halogenobenzenes quench more efficiently, and furan is a substantially better quencher than tetrahydrofuran. Ionization potential is not the sole parameter of importance in determining quenching efficiency. This is clear from (a) the inefficiency of diamantane as a quencher, (b) the comparison between the bromoadamantane (7) and the halogenobenzenes, and (c) the comparison between tetrahydrofuran and the bromo compounds. The origin of these anomalies cannot be conclusively explained. Different formation constants of ground state complexes between sulphones and the various quenchers might explain the observations. Finding evidence for such complex formation is difficult; in our studies we observe no significant deviations from the Beer–Lambert law. However, in other studies[10] of quenching of aromatic ketone triplet states, for example, benzophenone, aromatic quenchers behaved differently from non-aromatic quenchers. Our study is complicated by the finite absorption of the halogenobenzenes at 265 nm. Either formation of ground state complexes or some excitation of the appropriate halogenobenzenes may account for the diffusion controlled quenching observed with chloro- and bromo-benzene.

TABLE 2

Fluorescence quenching data for compound (2)

Quencher	Ip (quencher)/ eV	$k_q\tau$/ l mol^{-1}	10^{-9} k_q/ l mol^{-1} s^{-1}
1-Bromo-3,5-dimethyl-7-t-butyladamantane	8.5 [c]	29.50	1.98
Bromobenzene [b]	8.98 [d]	512	34.3
Chlorobenzene [b]	9.07 [d]	153	10.2
Furan	8.98 [d]	100	6.7
Tetrahydrofuran	9.55 [e]	24.4	1.6
Bromoethane	10.29 [f]	10.3	0.68
1-Bromopropane	10.18 [f]	15.3	1.02
2-Bromopropane	10.07 [f]	17.6	1.18

[a] A value of τ = 14.9 ns was determined by single photon counting. [b] With excitation at 265 nm absorption by the quencher is low. [c] Ref. 8. [d] D. W. Turner 'Molecular Photoelectron Spectroscopy', Wiley, New York, 1970. [e] A. D. Bain, J. C. Bunzli, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 1973, **95**, 291. [f] L. S. Levitt and B. W. Levitt, *Tetrahedron*, 1973, **29**, 941.

The most important feature of the results in Table 2 is the relation between the electron availability of the quenchers and the magnitude of the quenching rate constant for a limited series of related quenchers. Noting the above anomalies a low I_p favours a high k_p value. This result suggests a component of electron transfer in the quenching process and implies that with a given quencher the quenching rate constant will be related to the electron affinity of the sulphone. Results in Table 3 and Figure 1 show that this is the case with the exception of an anomalously high k_q value for bis-4-methoxyphenyl sulphone. This anomaly is discussed below.

TABLE 3

Fluorescence quenching data for diaryl sulphones

Diaryl sulphone	Quencher	$k_q\tau$/ l mol^{-1}	10^{-9} k_q/ l mol^{-1} s^{-1}
(1)	Bromoethane	10.3	1.18
(2)	Bromoethane	10.3	0.68
(3)	Bromoethane	2.22	0.58
(4)	Bromoethane	6.85	2.13
(1)	(7)	67.5	7.75
(1)	1-Bromopropane	13.8	1.59

[a] Values of τ determined by single photon counting: (1), τ 8.7 ns; (2), τ 14.9 ns; (3), τ 3.9 ns; (4), τ 3.2 ns.

Evans[11] has successfully shown that in quenching of excited singlet states by processes involving charge transfer a modification (1) of the normal Stern–Volmer equation (2) may be applied for the process where ϕ_0 and

$$'\mathrm{M} + \mathrm{Q} \underset{k_{-q}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} \underset{\text{encounter complex}}{'(\mathrm{M}\cdots\mathrm{Q})} \xrightarrow{k_r} \underset{\text{solvated ion pair}}{(\overset{-}{\mathrm{M}^0}\ \overset{+}{\mathrm{Q}^0})}$$

$$\phi_o/\phi = 1 + \{k_{\text{diff}}k_r/(k_{-q} + k_r)\tau_s[\mathrm{Q}]\} \qquad (1)$$

$$\phi_o/\phi = 1 + k_q'\tau_s[\mathrm{Q}] \qquad (2)$$

ϕ are the quantum yields for fluorescence in the absence and presence of quencher, k_{diff} is the rate constant for diffusion of 'M and Q to form an encounter complex, k_{-q} is the rate constant for diffusion from the encounter complex out of the solvent cavity and k_r is the rate constant for the quenching reaction, k_q' is the apparent rate of quenching of the excited molecule 'M by quencher, and τ_s is the singlet lifetime of 'M. It follows that $k_q' = k_{\text{diff}}k_r/(k_{-q} + k_r)$. k_q' can be measured and k_{diff} calculated.

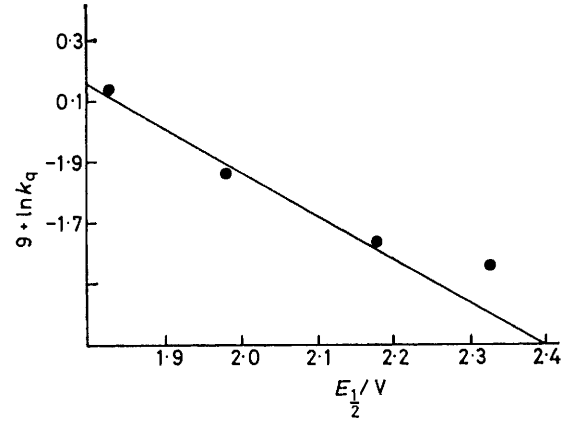


FIGURE 1 Plot of lnk_q *versus* $E_{\frac{1}{2}}$ for diazyl sulphones with bromoethane (see Table 3)

If it is assumed within a series of compounds that k_{-q} is determined only by the properties of the solvent then relationship (3) is obtained where ΔG is the free energy of activation for the electron transfer reaction. Thus for a given sulphone with a series of quenchers relationship (4) has been derived where I_p is the ionisation potential of the quencher and C is a constant related to the solvation of pairs of ions and hence a plot of $\ln[k_q'/(k_{\text{diff}} - k_q')]$ against I_p of the quencher is expected to be linear if charge transfer quenching is operative. For a series of compounds of closely related I_p the approximate constancy of C can be assumed.

$$\ln[k_q'/(k_{\text{diff}} - k_q')] \propto \Delta G \qquad (3)$$

$$\Delta G \propto I_p + \mathrm{C} \qquad (4)$$

Using a value for $k_{\text{diff}} = 1.1 \times 10^{10}$ l mol^{-1} s^{-1} the term $\ln[k_q'/(k_{\text{diff}} - k_q')]$ has been calculated for quenching of bis-4-methylphenyl sulphone (2). Data are presented in Table 4 and Figure 2. Hence the direction of electron transfer in the quenching of the fluorescence of diaryl sulphones is shown in two separate experiments. Quenching is facilitated for a given sulphone by quenchers having reduced ionisation potentials, and for a given quencher the quenching efficiency for a series of diaryl sulphones is determined by their electron affinities.

TABLE 4

Fluorescence quenching data for compound (2)

Quencher	$10^9\ k_q'/\text{l mol}^{-1}\ \text{s}^{-1}$	$\ln \dfrac{k_q'}{k_{\text{diff}} - k_q'}$	Ionisation potential of quencher (eV)
Tetrahydrofuran	1.64	−1.74	9.41
Bromoethane	0.68	−2.71	10.3
1-Bromopropane	1.02	−2.28	10.2
2-Bromopropane	1.18	−2.11	10.1
Furan	6.71	0.44	8.89

From these results we conclude that the diaryl sulphones are quenched by a charge-transfer process with the quencher acting as donor. The general features of this process are closely related to those involving donor quenchers interacting with other excited states, notably aromatic hydrocarbons [2] and ketones.[4,10]

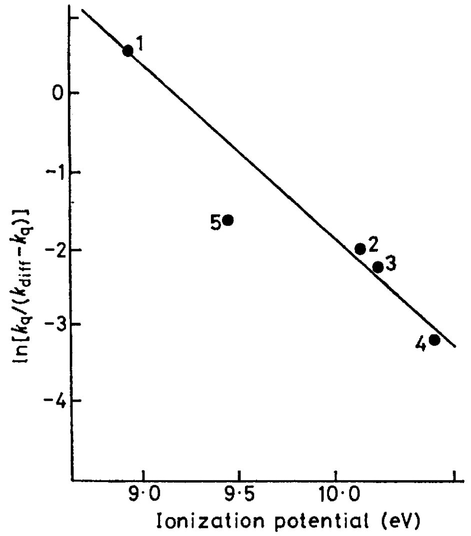


FIGURE 2 Fluorescence quenching of bis-4-methylphenyl sulphone with 1, furan; 2, 2-bromopropane; 3, 1-bromopropane, 4; bromoethane; 5, tetrahydrofuran

It was noted that an exception to the general trend was observed with bis-4-methoxyphenyl sulphone; the observed k_q value is higher than expected. We have examined this compound more closely and conclude the deviation originates from self-quenching of fluorescence by this sulphone (**3**). The fluorescence intensity was monitored as a function of concentration of (**3**) and at low concentrations $<10^{-5}$ mol l^{-1} the intensity was a linear function of concentration. Above 10^{-5} mol^{-1} l^{-1} the intensity tended to a constant value with increasing sulphone concentration. At these concentrations the non-linearity cannot be due to self-absorption but is clearly attributable to a self-quenching phenomenon. Although we have not been able to measure the ionisation potential of sulphone (**3**) directly it is to be expected that the methoxy substituent will substantially lower the ionisation potential of (**3**) relative to the other diaryl sulphones examined. It is therefore not surprising that (**3**) alone shows self quenching.

[7/1857 *Received*, 21*st October*, 1977]

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