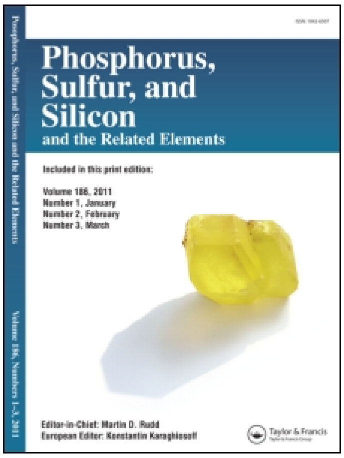

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A STUDY OF THE PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF THE S_8 MOLECULE The Quenching of Benzene, Naphthalene and Pyrene Fluorescence by S_8 Molecules in S_8 Liquid Methanol System. I

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A STUDY OF THE PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF THE S_8 MOLECULE

The Quenching of Benzene, Naphthalene and Pyrene Fluorescence by S_8 Molecules in S_8 + Liquid Methanol System. I

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The energy of the first excited singlet state S_1 of S_8 is estimated as 89 ± 3 kcal · mole^{-1}. S_8 does not exhibit fluorescence, but quenches the fluorescence of certain sensitizers (benzene, naphthalene, pyrene) acting as an energy acceptor in the energy transfer process from the S_1 state of the sensitizer. The process of the quenching of donor fluorescence by S_8 was analysed using the Stern–Volmer equation.

INTRODUCTION

The photophysical and photochemical properties of the cyclic S_8 molecule in the gas phase have not yet been fully investigated. This is particularly true of the mechanism of excitation and decomposition of S_8.[1–7] Relatively more information is available on the structure of S_8,[8–18] the electronic structure,[8, 19–22] the bond,[3, 13, 23–26] dissociation[26, 27–30] and the ionization energy.[31–32] S_8 absorption spectra in the visible and ultraviolet,[1, 2, 8, 33–37] the infrared absorption spectra and Raman spectra[17, 18, 38–48] have all been described.

There are, however, very few data about the photochemical processes occurring in the liquid phase in S_8 + solvent systems.[4] Also, the possibility of using S_8 as a source of sulphur in photochemical synthesis has not been fully explored.

The present work is concerned with solutions of S_8 in methanol. Part I is devoted to an investigation of the S_8 + methanol system in order to obtain information on the excited state of S_8 molecule. S_8 in the ground state, S_0, acts as an energy acceptor in energy transfer processes, taking up energy from sensitizers in the excited S_1 state. S_8 itself does not exhibit fluorescence in the visible or near UV, but it quenches the fluorescence of certain sensitizers introduced into the system. Other sulphur compounds such as disulphides,[49–54] sulphides,[55] carbon sulphoxide,[56] mercaptans[57] and dimethyl sulphoxide[58] also have this ability or, for some sensitizers, the ability to quench phosphorescence.

Part II describes an investigation of the photochemistry of the S_8 + methanol system and of the kinetics of the reactions which take place in the presence of sensitizers under the same conditions as those described here. On the basis of the results obtained mechanisms are proposed to account for the reaction observed.

RESULTS AND DISCUSSION

The Energy of the S_1 State of S_8

The approximate value of energy of the excited singlet state of S_8, E_{S_1}, was obtained from the absorption spectrum of S_8 in liquid methanol, shown in Figure 1. The method of Lewis and Kasha[59] was used. This gave $E_{S_1} = 89 \pm 3$ kcal · mole^{-1}, which is consistent with the value of energy calculated from the difference between the orbitals for the ground and the excited S_1 state of S_8.[2]

The Quenching of Benzene, Naphthalene and Pyrene Fluorescence by S_8.

In order to elucidate the mechanism of quenching of fluorescence and the process of energy transfer to S_8 when S_8 acts as a quencher of fluorescence, the sensitizers were chosen so that the energies of their excited singlet states E_{S_1} should cover a certain range. The energies of the S_1 states of benzene and naphthalene lie above that of the S_1 state of S_8, while

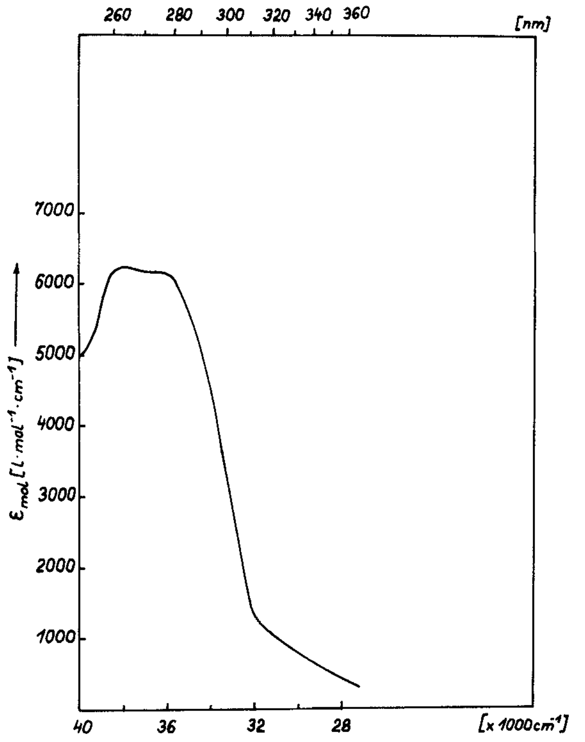

FIGURE 1. Absorption spectrum of S_8 in liquid methanol.

that of the S_1 state of pyrene lies below it. The spectroscopic data for these molecules and S_8 are given in Table I.

The value of E_{S_1} estimated for S_8 (89 kcal.mol^{-1}) has been confirmed by energy transfer process from the S_1 state of the sensitizers to the S_0 state of S_8 in this system. This value falls between the E_{S_1} values for naphthalene (92 kcal·mol^{-1}) and pyrene (77 kcal·mol^{-1}).

S_8 is an efficient quencher for these molecules. It was assumed that in the tracings of the fluorescence spectra the area under the curve was in each case proportional to the quantum efficiency for the fluorescence.[60,61] The quenching of fluorescence by S_8 was analysed using the Stern-Volmer equation:

$$\frac{I_0}{I} = \frac{\phi_0}{\phi} = 1 + k_q \cdot \tau_D [Q]$$

where I and I_0 are intensities of fluorescence of the donor with and without the quencher, ϕ and ϕ_0 are the respective quantum yields, k_q is the rate constant for the quenching process, τ_D is the lifetime of the excited donor molecule and $[Q]$ the concentration of the quencher, in moles·l^{-1}. For all donors tested, plots of ϕ_0/ϕ v. $[Q]$ are linear. The slopes calculated by the least squares method were combined with the known lifetimes of the excited donors, to yield the rate constants k_q for the quenching by S_8. The results are presented in Table II. The calculations were carried out with corrections[62–65] for the partial absorption of the exciting radiation ($\lambda \sim 254$ nm) by S_8, and for the absorption by S_8 of the fluorescence radiation emitted by the donors.

The spectral distribution of the fluorescence radiation was identical irrespective of whether the fluorescence was partially quenched or not.

The value of k_q for benzene given in Table II is appreciably higher than k_d, the rate constant for the diffusion controlled bimolecular reaction which takes place in pure methanol ($k_q/k_d = 3.38$; $k_d = 1.8 \times 10^{10}$ l·mole^{-1}·s^{-1}).[66] k_q for naphthalene is similar to k_d($k_q/k_d = 1.38$), and k_q for pyrene is lower than k_d($k_q/k_d = 0.33$). In the case of the quenching of benzene fluorescence by S_8, the process most probably occurs through long-range interactions (of the dipole-dipole type).[67–68] This is not a diffusion controlled process, since it is faster, but diffusion may be a contributory factor. Energy interchange

TABLE I

Spectroscopic and other data for the sensitizers

Molecules	E_{S1} (kcal · mol^{-1})	ε for $\lambda \sim 254$ nm (l · mol^{-1} · cm^{-1})	ϕ for fluorescence	$\tau_D^{S_1}$ (ns)	E_{T_1} (kcal · mol^{-1})	Concentration of solution in CH_3OH (mol · l^{-1})	Range of fluorescence (measurement for λ) (nm)
Benzene	109[a]	195 ± 4	0.06[c,d]	31[b]	84.3[b]	4.7×10^{-2}	260–320 (278)
Naphthalene	92[b]	2900 ± 60	0.205[b]	105[b]	60.9[b]	1.5×10^{-2}	310–400 (337)
Pyrene	77[b]	11000 ± 250	0.53[b]	475[b]	48.1[b]	8.3×10^{-4}	360–500 (395)
S_8[d]	89	5250 ± 110					

E_{S_1}—energy of excited singlet state; ε—molar extinction coefficient for $\lambda \sim 254$ nm, calculated for solutions in CH_3OH: ϕ—the quantum yield of fluorescence; $\tau_D^{S_1}$—lifetime of the excited singlet state of the donor molecule; E_{T_1}—energy of excited triplet state.
[a] Data from ref. 70; [b] data from ref. 66; [c] data from ref. 71 and 72; [d] data from this work included for comparison.

TABLE II

Data obtained from the Stern–Volmer equation for the quenching of fluorescence

Donor	Slope of plot $\times 10^3$ ($1 \cdot mol^{-1}$)	k_q ($1 \cdot mol^{-1} \cdot s^{-1}$)
Benzene	19.00 ± 1.6	6.1×10^{11}
Naphthalene	2.65 ± 0.25	2.5×10^{10}
Pyrene	2.90 ± 0.25	6.1×10^{9}

The values of $\tau_D^{S_1}$ are given in Table I.

between singlet states in solution should also be considered—this would also tend to make k_q higher.[67]

The value of k_q for the quenching of naphthalene fluorescence by S_8 in methanol (Table II) is close to the value of rate constant for the bimolecular, diffusion controlled reaction taking place in pure methanol. The values of E_{S_1} for naphthalene (92 kcal·mole^{-1}) and S_8 (89 kcal·mole^{-1}) are close, however, the slight excess of energy makes the energy transfer process, from the S_1 state of naphthalene to the S_0 state of S_8, possible.

The value of k_q for pyrene (Table II) is lower than k_d. Taking into account the values E_{S_1} for pyrene (77 kcal·mole^{-1}) and S_8 (89 kcal·mole^{-1}) the process is seen to be endothermic[69] by as much as about 12 kcal·mole^{-1}, which would lead one to expect the quenching to be even less efficient than it in fact is. It is possible that in addition to collisional energy transfer, there is another, more effective transfer process, which could be via an excited complex (S_8 pyrene).*

EXPERIMENTAL

Reagents.

The purity of liquid reagents was checked spectrophotometrically (uv absorption) and using gas chromatography.

The sulphur was obtained as recrystallized analytical grade crystals from the "Ogorzelec" Chemical Works and from Hopkin and Williams Ltd. It was ground in a mortal, washed with distilled water in order to remove traces of oxygen-containing sulphur compounds and dried at room temperature.

The methanol was made by Merck (fluorescence grade). It was dried using molecular sieves (Linde, type 3A, made by Union Carbide) and redistilled, using of a rectification column. The fraction boiling at 64.8°C was collected.

The benzene was also made by Merck (fluorescence grade)—it was used without further purification. The fluorescence spectrum of the benzene was identical with the accepted standard.

Naphthalene and pyrene—both made by Fluka—were purified by recrystallising them from methanol 3 times.

Apparatus

The exciting uv radiation was obtained from a low pressure mercury lamp—it was practically monochromatic, with $\lambda \sim 254$ nm. The lamp was made by Hanau, type NK 6/20.

Absorption spectra of the reactants and products were registered in the visible and uv using a Zeiss spectrophotometers types VSU-1, VSU-2 and Specord.

Fluorescence spectra were obtained using a Perkin–Elmer spectrofluorimeter, type MPF-3 coupled with a recorder. Optimum conditions for recording fluorescence spectra (the exciting wavelength, entrance and exit slit widths and signal amplification) were kept constant for each series of measurements.

Methods of work

Spectroscopic data for the energy donors used in quenching experiments, benzene, naphthalene and pyrene and for comparison, for S_8 are given in Table I. This Table also gives the concentrations of the methanolic solutions employed. The concentrations of the quencher, S_8, in systems containing naphthalene and pyrene were between 4.0×10^{-4} and 0.25×10^{-4} mole·l^{-1}, and for the system with benzene, between 3.0×10^{-4} and 0.031×10^{-4} mole·l^{-1}.

The quenching of the fluorescence emitted by the donors were always observed under the same experimental conditions.

Air was removed from all solutions used for fluorescence measurements by passing through them a stream of deoxygenized helium (which had been passed over heated metallic copper). The measurements were carried out at 20 ± 0.5°C.

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