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Quenching of Excited Singlet and Triplet States of Some Polyfused Arenes by Dihalobenzenes

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External heavy atom effect on the emission spectra of naphthalene, phenanthrene, and chrysene by perturbers dihalobenzenes are investigated to estimate different nonradiative rate constants associated with the depletion of the singlet and the triplet states of the fluorescers. The bimolecular fluorescence quenching rate constant k_q has been evaluated at 300 K by applying Stern–Volmer relation. The dihalobenzene quenchers have triplet states lying below the singlet states of the fluorescers and the overall quenching rate k_q is composed of two rate constants, namely, the intramolecular intersystem crossing rate k_q^{ISC} and the singlet-triplet energy transfer rate constant k_q^{ST}. The relative magnitudes of the two rate constants k_q^{ISC} and k_q^{ST} have been examined in the light of the energy conditions controlling the associated processes. At 77 K, the phosphorescence decay curve of the fluorescers in the presence of dihalobenzenes is biexponential and the triplet decay of the perturbed fraction of the fluorescers is exponential. It is concluded that at the low temperature, heavy atom interaction in the systems studied mainly proceeds through CT mechanism. Speculative suggestion has been made to account for enhancement of phosphorescence emission of polyfused arenes in EtOH solution.

It is generally believed that the quenching of the excited singlet states of aromatic molecules (AM) in presence of another molecular species containing heavy atom like Cl, Br, and I proceeds via intermediate contact exciplex of charge transfer (CT) nature.[1–15] This CT exciplex is formed in a singlet state which may be higher than the singlet S_1 of the fluorescer AM. The reported observations were made mainly in dilute solutions and in a few cases in vapour phase[10,11] also. This intermediate contact CT exciplex increases the spin-orbit coupling as a result of which the spin forbiddeness of the intercombinational process decreases and consequently intramolecular intersystem crossing (ISC) rate increases. This intramolecular ISC $T_1 \leftsquigarrow S_1$ rate depends upon the energy gap between the singlet S_1 and triplet T_1 of the fluorescer AMs, the closer the gap, the greater will be the nonradiative transition probability from singlet to triplet.[16,17] In the presence of external heavy atom perturber another mechanism may be operative in causing depletion of singlet state. This is intermolecular singlet–triplet energy transfer depicted by the scheme[18]

$$S_d^1 + S_q^\circ \to\to S_d^\circ + T_q^1 \tag{1}$$

where the subscripts d and q stand for donor and quencher molecules respectively. This transfer occurs by means of an exchange mechanism and is of short range nature. A required condition is that the triplet T_1 of the quencher should lie well-below the singlet S_1 of the fluorescer.

Heavy atom perturbation also modifies phosphorescence spectra of AMs[19–30] through the second order interactions which proceed via (1) electron exchange and (2) CT mechanism. There is still some controversy whether CT or electron exchange mechanism would be dominant in spin orbit interaction. Castino et al.[31] proposed exchange mechanism for pyrene-iodine system in cyclohexane solution. Lessard and Durocher[32] studied phosphorescence decay of indole and concluded that when halocarbons were used as quenchers heavy atom interaction proceeded through CT exciplex formation whereas in the case of the quencher propyl bromide the electron-exchange mechanism prevailed. Najbar et al.[28] stressed on second order electron exchange mechanism for the external heavy atom interaction between several AMs and KI.

The present paper reports the emission spectra of naphthalene, phenanthrene, and chrysene in ethanol (EtOH) at 300 and 77 K in presence of different concentrations of *p*-dichlorobenzene (DCB), *p*-dibromobenzene (DBB), and *p*-diiodobenzene (DIB). One of the objectives was to estimate the rates of the bimolecular fluorescence quenching proceeding via intramolecular ISC and intermolecular singlet–triplet energy transfer processes. It was also intended to determine the various photophysical parameters involved in the heavy atom interaction and to examine the role of CT or electron exchange in inducing depletion of singlet and triplet states of the fluorescer molecules.

Experimental

Source and method of purification of naphthalene, phenanthrene, and chrysene (used as fluorescer) were the same as described in our previous paper.[14] Both *p*-dichlorobenzene (DCB) and *p*-dibromobenzene (DBB) obtained from BDH were used after vacuum sublimation. *p*-Diiodobenzene (DIB) from Aldrich Chemical Ltd. was used without further purification. Solvent EtOH (E. Merck) of spectroscopic grade was used as such. 1,2-Dichloroethane (1,2-DCE) obtained from B D H London (LR Grade) was treated with calcium chloride for two days and then distilled over P_2O_5. 1,3-Dibromopropane (1,3-DBP) purchased from the same source was fractionally distilled at atmospheric pressure before use. The samples, quenchers, and solvents were tested for any possible interfering emission.

The concentrations of naphthalene, phenanthrene, and chrysene were chosen approximately at 10^{-4} mol dm^{-3} for all emission experiments at 300 and 77 K. The concentrations of the perturbers DCB, DBB, and DIB were varied between

0.32—2.30, 10^{-2}—0.25, and 10^{-4}—10^{-2} mol dm^{-3} respectively and those of 1,2-DCE and 1,3-DBP varied between 10^{-2}—10^{-1} and 0.41—4.00 mol dm^{-3} respectively.

The fluorescence and phosphorescence spectra were recorded with a Perkin Elmer model MPF 44 A fluorescence spectrophotometer provided with corrected spectra unit and the absorption spectra with a Shimadzu UV-VIS spectrophotometer model 210 A.

Naphthalene, phenanthrene, and chrysene were excited at 300, 295, and 320 nm, respectively when fluorescence and phosphorescence spectra were recorded both at 300 and 77 K. For phosphorescence decay study the emission wavelengths of naphthalene, phenanthrene, and chrysene were chosen at 469, 497, and 540 nm, respectively. After the phosphorescence intensity achieved a steady state, the exciting radiation was cut off to obtain the dark decay on the recorder.

Results and Discussion

The intensity of fluorescence emission of naphthalene, phenanthrene, and chrysene in EtOH falls off in a regular way when DCB, DBB, and DIB are added gradually (Fig. 1) to the binary mixtures. But the same dihalogen molecules do not produce any change in the absorption spectra of the polyfused arenes in EtOH. So, for these systems the static quenching may be ignored and the dynamic fluorescence quenching rate constant can be determined from the well-known relation (2)

$$f_o/f = 1 + K_{SV}[Q] = 1 + k_q\tau_o[Q]. \qquad (2)$$

Here f_o and f refer to relative fluorescence intensities of fluorescer in EtOH without quencher [Q] and with quencher of concentration [Q] respectively, and K_{SV} is the Stern-Volmer (S-V) constant. Figure 2 gives the S-V plots and in Table 1 are given the k_q values measured in ternary solutions containing the dihalogens and also in solutions containing monohalogen quenchers chlorobenzene (ClB), bromobenzene (BrB), and iodobenzene (IB). The dihalogen perturbers are seen to be more efficient than the monohalogens in quenching fluorescence. The dependence of quenching efficiency on the number of chlorine, bromine, or iodine atoms in the quencher molecules or in other words on the electron affinities of the quencher molecules indicates that a possible route of depletion of the excited states of the fluorescer polyfused arenes is through contact exciplex of CT nature formed between fluorescer and quencher molecules. In the systems under study, the transfer of charge necessary for CT exciplex formation would be from the electron donor naphthalene, phenanthrene, or chrysene to the electron acceptor DCB, DBB, or DIB molecules. The CT interaction would induce large ISC with rate constant k_q^{ISC} in the chromophore. Another possible mechanism for nonradiative deactivation capable of significant con-

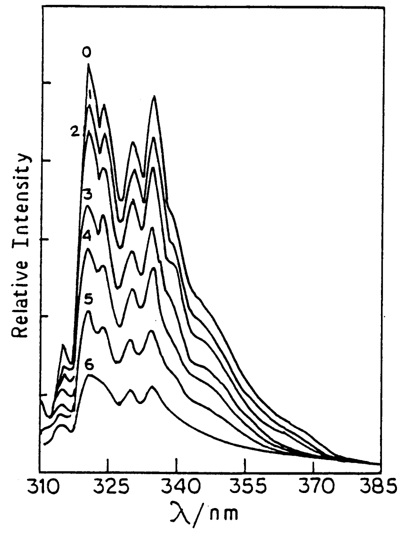

Fig. 1. Fluorescence spectra of naphthalene in EtOH (9.75×10^{-4} mol dm^{-3}) at 300 K (excitation wavelength: 300 nm). Concentration (mol dm^{-3}) of DBB in O,O; 1, 1.18×10^{-2}; 2, 1.96×10^{-2}; 3, 3.93×10^{-2}; 4, 6.56×10^{-2}; 5, 0.11; 6, 0.18.

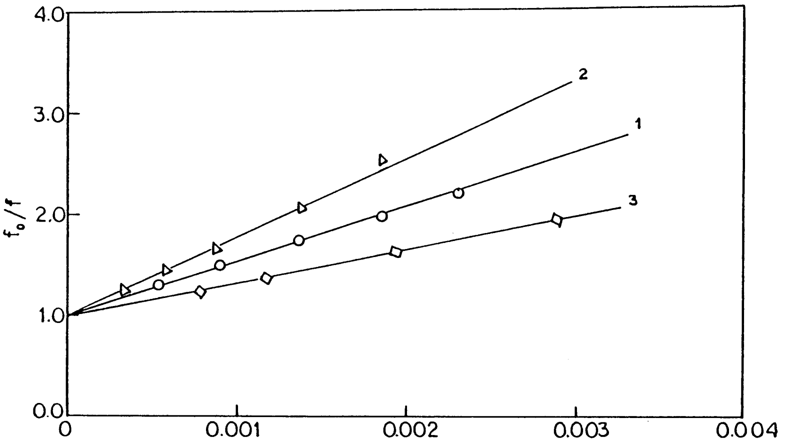

Fig. 2. f_o/f vs. [Q] relations for (1) naphthalene-DIB, (2) phenanthrene-DIB, and (3) chrysene-DIB.

Table 1. Values of Stern-Volmer Constant K_{SV} and Bimolecular Fluorescence Quenching Rate Constant k_q for the Systems of the Electron Donors Naphthalene, Phenanthrene, and Chrysene and Some Halobenzene Acceptors (Quenchers) in EtOH Solution at 300 K

Molecule	τ_0[a]/ns	Quencher	K_{SV}/ $dm^3\,mol^{-1}$	k_q/ $dm^3\,mol^{-1}\,s^{-1}$	k_q'/ $dm^3\,mol^{-1}\,s^{-1}$	k_q^{ISC}/ $dm^3\,mol^{-1}\,s^{-1}$	k_q^{ST}/ $dm^3\,mol^{-1}\,s^{-1}$
Naphthalene	96.0	1) ClB[a]		No quenching			
		2) DCB	0.70	7.29×10^6	—	1.67×10^6	5.62×10^6
		3) 1,2-DCE	0.16	—	1.67×10^6	1.67×10^6	—
		1) BrB[a]	7.0	7.30×10^7	—	—	—
		2) DBB	24.8	2.58×10^8	—	1.25×10^8	1.33×10^8
		3) 1,3-DBP	12.0	—	1.25×10^8	1.25×10^8	—
		1) IB[a]	155.0	1.60×10^9	—	—	—
		2) DIB	543.7	5.66×10^9	—	—	—
Phenanthrene	57.5	1) ClB[a]		No quenching			
		2) DCB	0.35	6.09×10^6	—	2.61×10^6	3.48×10^6
		3) 1,2-DCE	0.15	—	2.61×10^6	2.61×10^6	—
		1) BrB	1.8	3.20×10^7	—	—	—
		2) DBB	7.0	1.22×10^8	—	6.09×10^7	6.11×10^7
		3) 1,3-DBP	3.5	—	6.09×10^7	6.09×10^7	—
		1) IB[a]	55.5	9.70×10^8	—	—	—
		2) DIB	772.3	1.34×10^{10}	—	—	—
Chrysene	42.6	1) ClB[a]		No quenching			
		2) DCB	0.14	3.28×10^6	—	2.35×10^6	0.93×10^6
		3) 1,2-DCB	0.10	—	2.35×10^6	2.35×10^6	—
		1) BrB[a]	2.4	5.60×10^7	—	—	—
		2) DBB	5.0	1.17×10^8	—	9.39×10^7	2.31×10^7
		3) 1,3-DBP	4.0	—	9.39×10^7	9.39×10^7	—
		1) IB	61.5	1.40×10^9	—	—	—
		2) DIB	106.90	2.52×10^9	—	—	—

[a] Ref. 14.

tribution is singlet-triplet energy transfer, with rate constant k_q^{ST}, from the chromophore to the quencher. This energy transfer occurs through exchange mechanism and is of short range nature.[18] The dynamic rate constant may be assumed to be composed of mainly two independent rate constants k_q^{ISC} and k_q^{ST} and one may write

$$k_q = k_q^{ISC} + k_q^{ST}. \tag{3}$$

For the polyfused arene-dihalobenzene systems studied, it is not possible to estimate individual contribution of k_q^{ISC} and k_q^{ST} to k_q. Therefore, the fluorescence spectra of naphthalene, phenanthrene, and chrysene in EtOH have been measured with 1,2-DCE and 1,3-DBP as quenchers. In these aliphatic molecules the halogen atoms are well separated from each other by CH_2 group and, what is more important, these two molecules do not have any singlet or triplet state lying near the fluorescent state of naphthalene, phenanthrene, or chrysene. Therefore, energy transfer between the fluorescers and 1,2-DCE or 1,3-DBP should have no role in the deactivation process and only ISC would be operative through CT mechanism. The measured dynamic quenching rate constants, k_q', of the fluorescer in these aliphatic solvents (Table 1) would be composed of only k_q^{ISC}. If the k_q^{ISC} values of the aromatic fluorescers in dihalobenzene solvents are assumed to have the same values as k_q' then an estimate of k_q^{ST} for these systems may be made from the relation (3). The k_q^{ST} values thus determined are included in Table 1. The analysis of the rates k_q^{ST} and k_q^{ISC} so made, can only be very approximate and admittedly the procedure is open to criticism because it involves the tacit assumption that the external heavy atom effects induced by the aliphatic dihalogens and the aromatic dihalogens are the same. At the same time all other possible deactivation processes are disregarded. Nevertheless, such analysis may give a qualitative idea about the relative importance of the two processes in these systems and the relative magnitudes of the rate constants k_q^{ST} and k_q^{ISC} determined by the above procedure may be examined in the light of the energy condition controlling the associated processes. The triplet state T_1 of DCB and of DBB lies well below the singlet state S_1 of naphthalene and phenanthrene (Table 2) and the rate constant k_q^{ST} is large for two fluorophores in DCB and DBB, whereas T_1 states of DCB and DBB have energies higher than S_1 of chrysene and the singlet-triplet energy transfer process is less probable. Expectedly, for chrysene-DCB and chrysene-DBB systems the estimated k_q^{ST} is smaller than k_q^{ISC}. The intramolecular ISC rate k_{ISC} is, in general, large or small depending on whether the singlet-triplet energy interval ($\nu_f - \nu_p$) in a fluorescer is small or large. The k_q^{ISC} values of naphthalene, phenanthrene, and chrysene perturbed by DCB are in the expected order (Table 3), but in DBB the

Table 2. Difference in Energy ($\Delta\nu$) between the Singlet (S_1) of the Fluorescer and the Triplet (T_1) of the Quencher and k_{ST} values

Quencher	ν_p[a)]/cm^{-1}	Molecule	ν_f[b)]/ cm^{-1}	$d\nu(=\nu_f-\nu_p)$/ cm^{-1}	k_q^{ST}/ dm^3 mol^{-1} s^{-1}
DCB	27890[d)]	Naphthalene	32249[c)]	4359	5.62×10^6
		Phenanthrene	28893[c)]	1003	3.48×10^6
		Chrysene	27692[c)]	−198*	0.93×10^6
DBB	27910[e)]	Naphthalene	32249	4339	1.33×10^8
		Phenanthrene	28893	983	6.11×10^7
		Chrysene	27692	−218*	2.31×10^7

* −Ve sign indicates that the triplet level of the quencher lies above the singlet level of the fluorescer.

a) ν_p denotes the phosphorescence 0-0 band (T_1) of quenchers. b) ν_f denotes the fluorescence 0-0 band (S_1) of fluorescers. c) Ref. 33. d) Ref. 34. e) Ref. 35.

Table 3. Difference between Singlet (ν_f) and Triplet (ν_p) Energy Levels of the Naphthalene, Phenanthrene, and Chrysene and k_q^{ISC} Values with Dihalobenzene Quenchers at 300 K in EtOH Solution

Molecule	ν_f^*/cm^{-1}	ν_p^*/cm^{-1}	$(\nu_f-\nu_p)$/cm^{-1}	k_q^{ISC}/dm^3 mol^{-1} s^{-1}	
				DCB	DBB
Naphthalene	32249	21274[a)]	10975	1.67×10^6	1.25×10^8
Chrysene	27692	19800[a)]	7892	2.35×10^6	9.39×10^7
Phenanthrene	28893	21730[a)]	7163	2.61×10^6	6.09×10^7

* ν_f and ν_p denote the 0-0 bands of S_1 and T_1 levels of the polyfused arenes, respectively.
a) Ref. 36.

values calculated for naphthalene, phenanthrene, and chrysene are not so. Perhaps in the case of the aliphatic and aromatic quenchers containing bromine, the objections noted above are more valid. So far as relative magnitudes of k_q^{ST} and k_q^{ISC} for the individual polyfused arene fluorophores in DCB and DBB are concerned the following facts may be noted. For naphthalene in DCB as heavy atom perturber with large $(\nu_f-\nu_p)$ and $\Delta\nu$ (Tables 2 and 3), the k_q^{ST} rate process is more important than k_q^{ISC} (Table 1) while in the case of phenanthrene, the k_q^{ISC} is only marginally smaller than k_q^{ST}. In DBB, on the other hand, k_q^{ST} and k_q^{ISC} are of nearly the same magnitude for both naphthalene and phenanthrene. In the case of chrysene, where the energy condition for energy transfer from the singlet of the fluorescer to the triplet states of the heavy atom perturbers DCB and DBB is unfavourable, k_q^{ST} is smaller than k_q^{ISC} in both DCB and DBB. It is seen from Table 3 that k_q^{ST} is small when $\Delta\nu$ is small. This dependence of k_q^{ST} on $\Delta\nu$ is consistent with the expectation that small energy gap between the singlet of the fluorescer and the triplet of the quencher facilitates back transfer from the latter to the former. It is to be pointed out here that 1,2-diiodoethane or any other suitable aliphatic iodo compound of desired purity and stability, which does not have singlet or triplet level below S_1 state of the polyfused arenes, was not available. So individual contribution of k_q^{ST} and k_q^{ISC} with DIB as quencher could not be determined seperately. But it may be speculated that because of favorable energy condition, the S-T energy transfer (k_q^{ST}) in the case of chrysene in DIB will be larger than in DCB or DBB. The proposed quenching process may be represented by,

$$ {}^1A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^1(A^{\delta+}\cdots\cdots Q^{\delta-})^* \xrightarrow{k_{ISC}} {}^3A^* + Q \rightarrow {}^1A + Q \tag{3a} $$

The dihalobenzenes have favorable π-electronic structure efficiently forming CT complex and indicating quenching via process (3a). The low temperature measurements at 77 K discussed below favor this reaction.

Another process that might have some role is

$$ {}^1A^* + Q \rightarrow\rightarrow {}^1A + {}^3Q^* \tag{3b} $$

because the fluorescers and the quenchers have singlet and triplet states with favorable condition for energy transfer. But no direct evidence of ^3Q could be found. It may be pointed out that careful examination showed that the halobenzenes in EtOH did not phosphoresce at 300 K and even at 77 K, emission from these molecules was very weak.

The two second order mechanisms, charge transfer and electron exchange, through which external heavy atom perturbation by the dihalobenzenes on emission of the polyfused arenes proceeds, are known to affect the lowest triplet state of the aromatic polyfused arene fluorescers. Generally, these processes enhance the radiative character of $S_0 \leftarrow T$ transition of aromatic molecules (AM).[28,37] Study of decay of emissions from the molecules and kinetic analysis of photophysical parameters of the singlet and triplet states of the molecules would therefore be expected to yield interesting information. With this idea in mind, the luminescence emissions of naphthalene, phenanthrene, and chrysene in EtOH rigid glass matrix at 77 K have been measured with and without addition of dihalobenzenes. When DCB is added to the binary mixture of phenanthrene or chrysene in EtOH at 77 K, both the fluorescence and phosphorescence emissions are reduced (Fig. 3). Only in the case of naphthalene, fluorescence is quenched and the phosphorescence is enhanced (Fig. 4). With DBB as quencher, fluorescence emission of all three polyfused arene fluorescers is quenched but their phosphorescence emission is enhanced (Fig. 5) while DIB quenches both the fluorescence and phosphorescence of the polyfused arenes (Fig. 6). In all the systems studied no change occurs in the shape and position of emission bands. The phosphorescence decay curves of polyfused arene-dihalobenzene systems are of biexponential nature. In the decay curve given in Fig. 7, $I_P(t)$ and $I_P(0)$ refer to time-dependent and stationary state phosphorescence intensity respectively. After a considerable time the decay curves become linear and identical with the unperturbed decay. The perturbed decay function which is obtained by subtracting the exponential decay component from the observed phosphorescence decay function is of exponential nature (Fig. 7). This lends support to the conclusion that the dominant process in external heavy atom perturbation in the systems investigated is charge transfer, because a nonexponential perturbed decay function would mean that major contribution comes through electron exchange mecha-

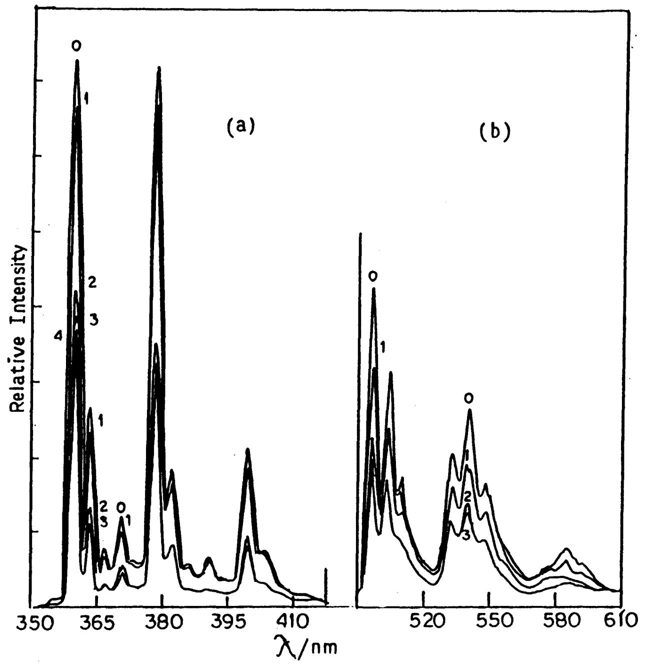

Fig. 3. Fluorescence (a) and phosphorescence (b) spectra of chrysene in EtOH (1.80×10^{-4} mol dm^{-3}) at 77 K (excitation wavelength: 320 nm). Concentration (mol dm^{-3}) of DCB in 0,0; 1, 0.34; 2, 0.67; 3, 0.81.

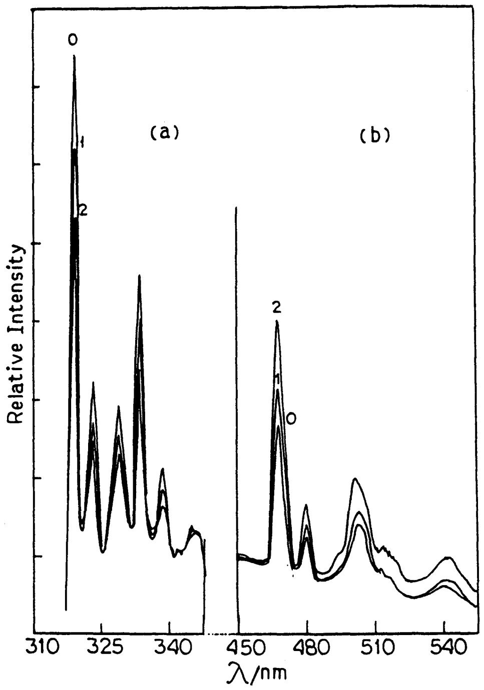

Fig. 4. Fluorescence (a) and phosphorescence (b) spectra of naphthalene in EtOH (5.20×10^{-4} mol dm^{-3}) at 77 K (excitation wavelength: 300 nm). Concentration (mol dm^{-3}) of DCB in 0,0; 1, 0.57, 2, 1.13.

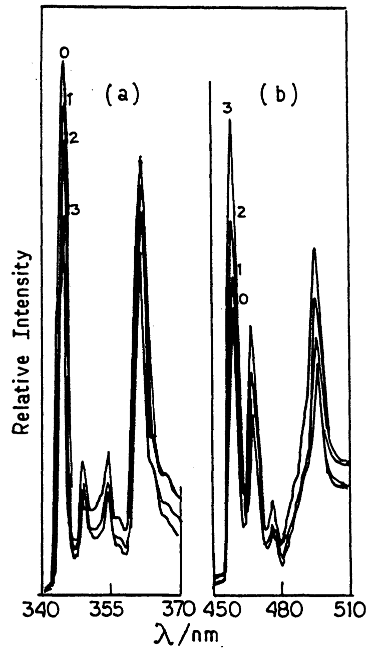

Fig. 5. Fluorescence (a) and phosphorescence (b) spectra of phenanthrene in EtOH (3.50×10^{-4} mol dm^{-3}) at 77 K (excitation wavelength: 295 nm). Concentration (mol dm^{-3}) of DBB in 0,0; 1, 0.11; 2, 0.18; 3, 0.25.

nism.[28,32] Referring to the decay curves, the phosphorescence intensity can be expressed as[13,22]

$$I_p(t)/I_p(0)=\beta e^{-t/\tau_p}+(1-\beta)e^{-t/\tau_p'}. \tag{4}$$

From the biexponential nature of the phosphorescence decay curve it is evident that the CT complex which may be formed in excited singlet state is also formed in the triplet state. But absence of any change in shape and position of phosphorescence bands of the polyfused arenes after addition of *p*-dihalobenzenes may mean that the triplet complex quickly dissociates into free molecules. With regard to possible phosphorescence emission from perturbed complex which has its own decay rate it may be that the peak positions and structure of phosphorescence spectra of the complex molecules are similar to those of the electron donor polyfused arenes. Cases of complexes showing donor type phosphorescence have been discussed and reviewed by previous authors.[32,38]

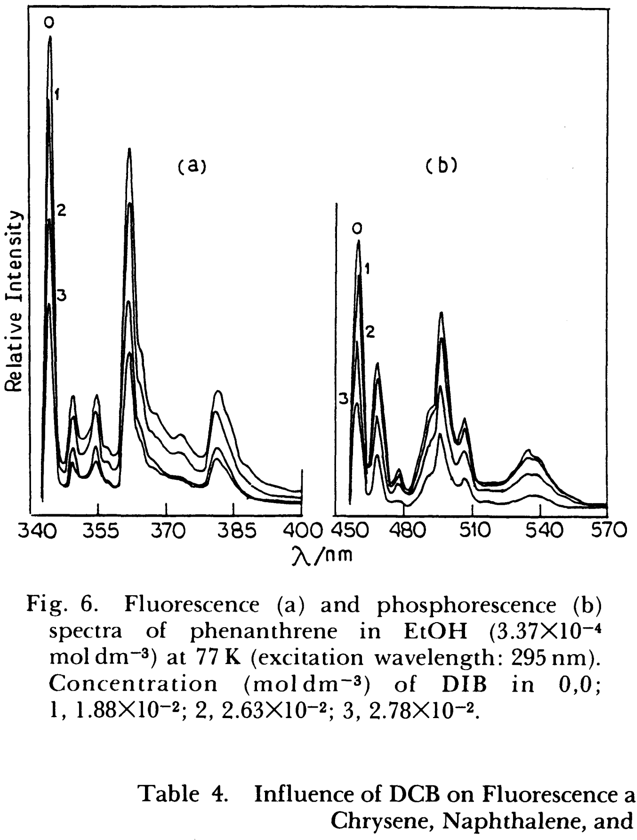

Fig. 6. Fluorescence (a) and phosphorescence (b) spectra of phenanthrene in EtOH (3.37×10^{-4} mol dm^{-3}) at 77 K (excitation wavelength: 295 nm). Concentration (mol dm^{-3}) of DIB in 0,0; 1, 1.88×10^{-2}; 2, 2.63×10^{-2}; 3, 2.78×10^{-2}.

The values of β and other photophysical parameters are obtained by usual methods described earlier[13] are given in Tables 4—6. The photophysical parameters are all found to depend on concentration of the quenchers. The phosphorescence decay time τ_p' of a perturbed fluorescer molecule decreases regularly with increase of quencher concentration (Tables 4—6). Concomitantly relative intramolecular ISC rate k_i'/k_i (Prime sign denoting perturbed species) and the triplet

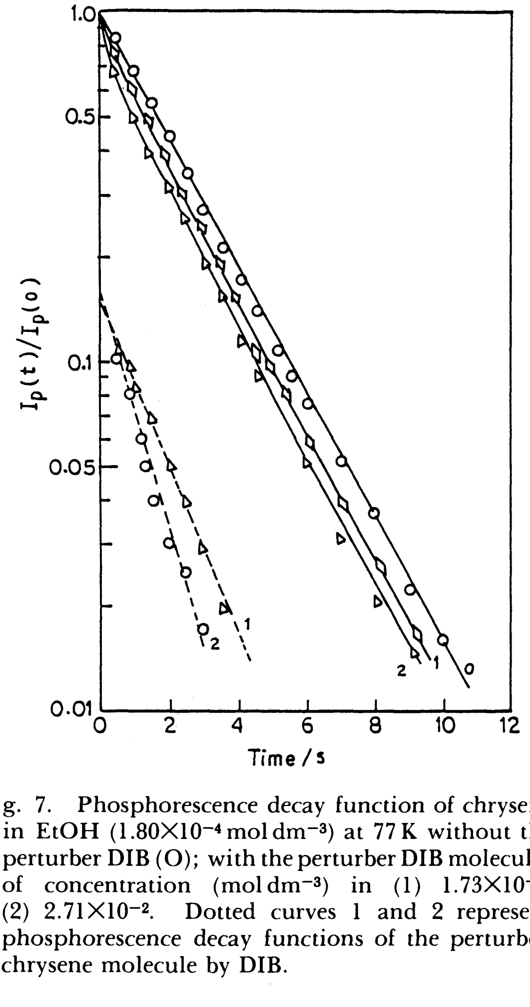

Fig. 7. Phosphorescence decay function of chrysene in EtOH (1.80×10^{-4} mol dm^{-3}) at 77 K without the perturber DIB (O); with the perturber DIB molecules of concentration (mol dm^{-3}) in (1) 1.73×10^{-2}; (2) 2.71×10^{-2}. Dotted curves 1 and 2 represent phosphorescence decay functions of the perturbed chrysene molecule by DIB.

Table 4. Influence of DCB on Fluorescence and Phosphorescence Photophysical Parameters of Chrysene, Naphthalene, and Phenanthrene in EtOH at 77 K

Compound	C_{DCB}/mol dm^{-3}	I_f/I_f°	I_p/I_p°	β	τ_p/s	τ_p'/s	α[a)]	k_i'/k_i	k_p'/k_p	k_{ip}'/k_{ip}	Φ_t'/Φ_t	Φ_t'
Chrysene	0.34	0.93	0.73	0.78	2.38	1.73	0.57	1.25	0.49	1.46	1.05	0.81
	0.67	0.48	0.53	0.73	2.38	1.52	0.39	8.50	0.30	1.69	1.26	0.97
	0.81	0.41	0.45	0.71	2.38	1.44	0.32	9.51	0.25	1.79	1.26	0.97
Naphthalene	0.57	0.88	1.23	0.70	2.38	1.23	0.86	10.52	3.08	1.86	1.50	0.95
	1.13	0.78	1.50	0.50	2.38	1.15	0.75	12.64	4.08	1.93	1.52	0.96
	1.58	0.75	1.80	0.40	2.38	1.01	0.72	14.22	5.98	2.11	1.52	0.96
Phenanthrene	0.34	0.95	0.87	0.85	3.61	1.88	0.74	1.27	0.95	2.05	1.03	0.90
	1.13	0.77	0.77	0.80	3.61	1.80	0.62	2.76	0.75	2.17	1.09	0.95
	1.58	0.63	0.67	0.75	3.61	1.73	0.50	4.27	0.62	2.28	1.11	0.97

a) $\alpha=(I_p/I_p^\circ)\,\beta$.

Table 5. Influence of DBB on Fluorescence and Phosphorescence Photophysical Parameters of Chrysene, Naphthalene, and Phenanthrene in EtOH at 77 K

Compound	$\frac{C_{\mathrm{DBB}}}{\mathrm{mol\,dm^{-3}}}$	$\frac{I_f}{I_f^\circ}$	$\frac{I_p}{I_p^\circ}$	β	$\frac{\tau_p}{\mathrm{s}}$	$\frac{\tau_p'}{\mathrm{s}}$	α	$\frac{k_i'}{k_i}$	$\frac{k_p'}{k_p}$	$\frac{k_{ip}'}{k_{ip}}$	$\frac{\Phi_t'}{\Phi_t}$	Φ_t'
Chrysene	0.10	0.96	1.15	0.82	2.38	1.73	0.94	3.60	3.94	1.12	1.20	0.92
	0.14	0.93	1.25	0.72	2.38	1.58	0.90	4.03	4.32	1.21	1.21	0.93
	0.17	0.89	1.33	0.65	2.38	1.30	0.86	5.76	4.92	1.52	1.23	0.95
Naphthalene	0.04	0.85	1.20	0.68	2.38	1.23	0.82	8.94	2.78	1.88	1.49	0.94
	0.11	0.75	1.50	0.48	2.38	1.15	0.72	14.23	3.79	1.95	1.52	0.96
	0.18	0.66	1.57	0.40	2.38	1.01	0.63	18.99	3.91	2.25	1.54	0.97
Phenanthrene	0.11	0.96	1.09	0.87	3.30	1.59	0.95	5.60	5.26	1.66	1.12	0.97
	0.18	0.90	1.25	0.70	3.30	1.51	0.88	6.75	6.08	1.68	1.13	0.98
	0.25	0.80	1.48	0.52	3.30	1.44	0.77	8.28	6.27	1.77	1.13	0.98

Table 6. Influence of DIB on Fluorescence and Phosphorescence Photophysical Parameters of Chrysene, Naphthalene, and Phenanthrene in EtOH at 77 K

Compound	$\frac{C_{\mathrm{DIB}}}{\mathrm{mol\,dm^{-3}}}$	$\frac{I_f}{I_f^\circ}$	$\frac{I_p}{I_p^\circ}$	β	$\frac{\tau_p}{\mathrm{s}}$	$\frac{\tau_p'}{\mathrm{s}}$	α	$\frac{k_i'}{k_i}$	$\frac{k_p'}{k_p}$	$\frac{k_{ip}'}{k_{ip}}$	$\frac{\Phi_t'}{\Phi_t}$	Φ_t'
Chrysene	1.16×10^{-2}	0.77	0.89	0.73	2.38	1.88	0.65	3.49	0.73	1.32	1.20	0.92
	1.73×10^{-2}	0.66	0.87	0.70	2.38	1.73	0.61	9.83	0.73	1.44	1.26	0.97
	2.71×10^{-2}	0.50	0.73	0.67	2.38	1.23	0.49	32.80	0.71	2.06	1.29	0.99
Naphthalene	1.85×10^{-3}	0.88	0.93	0.75	2.38	1.59	0.70	2.06	0.93	1.54	1.24	0.78
	2.31×10^{-3}	0.81	0.73	0.80	2.38	1.44	0.58	2.31	0.45	1.74	1.27	0.80
	2.89×10^{-3}	0.68	0.44	0.86	2.38	1.30	0.38	2.69	0.14	1.95	1.30	0.82
Phenanthrene	1.88×10^{-2}	0.85	0.87	0.90	3.30	2.02	0.78	3.46	0.58	1.77	1.10	0.96
	2.63×10^{-2}	0.65	0.65	0.86	3.30	1.87	0.59	7.70	0.37	1.95	1.13	0.98
	2.78×10^{-2}	0.43	0.41	0.83	3.30	1.80	0.34	8.28	0.17	2.05	1.13	0.98

yield Φ_t' increase. The k_{ISC} rate is highly sensitive to concentration of the quencher (Tables 4—6). It has been noted above, that DBB enhances the intensity of phosphorescence bands of all three polyfused arenes whereas DCB enhances the phosphorescence of naphthalene only. On the other hand, DIB quenches phosphorescence of all three compounds. According to Eisenthal[39] electronic mixing of the donor triplet with the CT singlet may lead to an enhancement of the 0-0 band as well as all successive totally symmetric vibrational bands of the donor fluorescer molecule through borrowing of intensity from CT interaction by $S_0 \leftarrow T$ transition of the fluorescer. The mixing of the donor triplet with the CT singlet of the complex occurs via the CT triplet of the complex provided the mixing of the donor and CT triplets is permitted. A necessary condition is that the phosphorescence of the fluorescer is polarized parallel to the CT absorption.[39] It is tempting to speculate that these conditions are satisfied in the cases of those polyfused arene-dihalogen systems in which enhancement of intensity of phosphorescence emissions of polyfused arenes due to external heavy atom effect has been observed. These conditions might not be satisfied in the other systems such as phenanthrene and chrysene in DCB and the three polyfused arenes in DIB. In the case of these systems, addition of heavy atom quencher DCB or DIB to arenes concerned reduces phosphorescence radiative rates k_p'/k_p and simultaneously increases the nonradiative rates k_{ip}'/k_{ip} (Tables 4 and 6). The net result is quenching of phosphorescence on complexation in the triplet state.

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