The Fluorescence of Some Dipolar *NN*-Dialkyl-4-(dichloro-1,3,5-triazinyl)anilines. Part 1. Solvent Effects and Solvent Exciplex Formation

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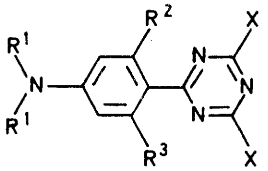
The fluorescence emissions of the title compounds occur from highly charge-transfer excited states and, in cyclohexane solution, the fluorescence quantum yields ϕ_F are high. In aprotic solvents of low to moderate polarity ϕ_F is much reduced, mainly by an increase in the non-radiative rate constant k_{NR} with solvent polarity increase. The decay channel is thought to be intersystem crossing from the singlet to the triplet intramolecular charge transfer excited state. The formation of a 1 : 1 solvent exciplex between acetonitrile and the excited dipolar triazine system in aliphatic hydrocarbon solvents has been investigated and found to be diffusion controlled.

THE optical absorption and emission characteristics of many dipolar aromatic systems D–Ar–A, where D is a π-electron donor and A is an electron acceptor, have been described.[1-3] Recently more detailed and systematic measurements, especially for systems in which conformational changes occur, *e.g.* intramolecular exciplexes, have been reported.[4-6] The solvent medium is often found to exert a dramatic influence on the luminescence of the highly dipolar excited states in many instances.[1,6-10]

We have reported previously [11-13] on the luminescence of nitrostyrenes ($Ar{-}A = C_6H_4CH{=}CHNO_2$). When D is Me_2N increase of solvent polarity in mobile, but not in rigid, media leads to fluorescence initially but subsequently to a marked fall-off in emission without much additional shift in the emission band maxima. However, the detailed interpretation in this instance is complicated by the existence of n,π^* excited states in close proximity to the π,π^* charge-transfer excited state.

We report here on the fluorescence characteristics of a series of triazine derivatives (I)—(V) in which the donor moiety D is a di-n-alkylamino group and the acceptor A is a *sym*-triazinyl system. These compounds proved to be more suitable than the nitro compounds for an examination of the way in which dipolar singlet excited states are quenched in polar solvents. Furthermore, attention is again being drawn to the discrete nature of many excited solute–solvent interactions following the lead of Chandross [14,15] in establishing the existence of solvent exciplexes (although few reports [16,17] of such behaviour exist). Evidence is adduced here that the triazine derivatives (I)—(V) form such solvent exciplexes. Finally, the compounds investigated by us are closely related to some dipolar systems, *e.g.* $D = NR_2$, $Ar = C_6H_4$, $A = C{\equiv}N$ or COR, which exhibit dual luminescence and about which much controversy has arisen.[18] It was hoped that some clarification could be made of some of the problems associated with this debate.



(I) $R^1 = Et, R^2 = R^3 = H, X = Cl$
(II) $R^1 = Et, R^2 = Me, R^3 = X = H$
(III) $R^1 = Et, R^2 = R^3 = Me, X = H$
(IV) $R^1 = Pr^n, R^2 = R^3 = H, X = Cl$
(V) $R^1 = Bu^n, R^2 = R^3 = H, X = Cl$

EXPERIMENTAL

All the compounds were kindly supplied by Professor R. A. Shaw, Birkbeck College, London. Their preparation and purification is described elsewhere.[19]

All solvents, mainly Merck UVASOL grade, were checked before use and found to be non-emissive under the excitation wavelengths (360—420 nm) used in this study.

Uncorrected fluorescence spectra were recorded, for solutions <0.05 in optical density at the excitation wavelength for 10 mm path length, on a Perkin-Elmer MPF-2A instrument. Both emission and excitation band widths were 2 nm.

For fluorescence quantum yield determinations, spectra were corrected on the basis of a sensitivity curve calibrated by the fluorescence of quinine bisulphate solutions. The reference standard was 9,10-diphenylanthracene in deoxygenated cyclohexane at room temperature (22 ± 2 °C) for which a quantum yield of fluorescence [20] of 0.83 was assumed. The excitation wavelength in the quantum yield determinations was 380 nm, since this coincided with a slight shoulder in the absorption spectra of the triazine compounds in many solvents and thus minimised errors due to finite excitation bandwidth.

U.v. absorption spectra of *ca.* 1×10^{-5}M solutions were measured on a Pye–Unicam SP 8000 A instrument.

In a few cases, as noted in the Tables, fluorescence lifetimes were measured by phase fluorimetry in the laboratory of Dr. Prochorov, Institute of Physics, Polish Academy of Sciences, Warsaw.

Most lifetimes were estimated by the oxygen quenching method as follows. Fluorescence intensities of the compound in a given solvent were measured for a sample successively nitrogen-flushed, air-saturated, and oxygen-flushed. From several such determinations and knowing the solubility of oxygen in the solvent [21] Stern–Volmer quenching constants were derived. The fluorescence lifetimes were calculated knowing the rate constant k_{O_2} for oxygen quenching in the solvent. This constant was taken to be the mean of such values given in the literature,[22] or in the absence of such data, was estimated on the basis of solvent viscosity taking $k_{O_2} = 2.3 \times 10^{10}$ mol^{-1} dm^3 s^{-1} for cyclohexane as a reference. The latter value gave a lifetime τ°_{F} for (I) in cyclohexane of 1.35 ± 0.13 ns by this method whereas the lifetime (in the absence of quenching) determined by phase fluorimetry was 2.22 ± 0.04 ns, and that from the known ϕ°_{F} and k_F estimated *via* the Strickler–Berg relationship was 2.80 ns. In an absolute sense the derived lifetimes could be in error, therefore, by a factor of two, but the relative values should be subject to much less error (20%).

RESULTS AND DISCUSSION

Absorption and Fluorescence in Neat Solvents.—Absorption. The u.v. spectra have been noted briefly elsewhere.[19] All the compounds (I)—(V) dissolved in cyclohexane have an intense long wavelength absorption band in the region 388—400 nm. Vibrational structure of spacing *ca.* 700 cm^{-1} and maximum intensity in the 0,1 band is readily apparent except in the case of compound (III), and to a much lesser extent compound (II). In these cases the absorption band is broader and red-shifted, resembling the absorption of the other compounds (I), (IV), and (V) as solutions in slightly polar media. The effects can be attributed to the twist about the phenyl ring–triazine ring bond brought about by the methyl substituent(s) in the phenyl ring as is observed in analogous systems.

The absorption spectrum of (I) dissolved in solvents of increasing polarity (measured, for example, by the empirical Dimroth E_T parameter)[23,24] consists of the same intense long wavelength band which shifts to the red with polarity increase (Table 2) but vibrational fine structure is lost and the maximum intensity appears to lie in the submerged 0,2 component.

The nature of the absorptive transition was judged to remain unchanged with change of solvent, namely a highly allowed charge-transfer excitation. For example, the oscillator strengths of the transition for (I) in cyclohexane and methanol were 0.67 and 0.69 respectively.

Fluorescence. (a) Cyclohexane solution. The fluorescence spectra showed a good mirror-image relationship to the absorption spectra with regard to the intensity distribution envelope but the vibrational spacing was *ca.* 1 000 cm^{-1}. The quantum yields of fluorescence ϕ°_{F} were high for all the compounds studied (Table 1). The fluorescence lifetimes of (I)—(III) were measured directly by pulse fluorimetry and thus the radiative (k_F) and non-radiative (k_{NR}) rate constants could be evaluated (Table 1).

TABLE 1

Emission characteristics of the triazine derivatives in cyclohexane at room temperature

Compound	$\bar{\nu}_F$/kK	ϕ°_{F}	τ°_{F}/ns †	$10^{-8}k_F$/s^{-1}	$10^{-8}k_{NR}$/s^{-1}
(I)	25.13	0.81	2.22 (4)	3.62	0.89
(II)	24.70	0.82	2.47 (3)	3.32	0.72
(III)	23.30	0.60	3.80 (6)	1.57	1.05
(IV)	25.06	0.94			
(V)	25.00	0.86			

† Pulse fluorimetry; ( ) = error.

$\bar{\nu}_F$ = Fluorescence band maxima, ϕ°_{F} = fluorescence quantum yield, τ°_{F} = fluorescence lifetime, k_F = radiative rate constant (fluorescence), k_{NR} = non-radiative rate constant.

With increasing twist about the donor moiety–acceptor moiety bond the radiative rate constant decreases as expected [also reflected in the molar absorption coefficients of (I)—(III)]. The non-radiative rate constant is less sensitive to this internal rotation, for the non-polar solvent environment.

TABLE 2

Emission properties of compound (I) with changes in the polarity of the solvent

						$K_{sv}(O_2)$/	$10^{-10}k_{O_2}$/l mol^{-1} s^{-1}				
No.	Solvent	E_T	$\bar{\nu}_A$/kK	$\bar{\nu}_F$/kK	ϕ°_{F}	l mol^{-1}	*a*	*b*	τ°_{F}/ns	$10^{-8}k_F$/s^{-1}	$10^{-8}k_{NR}$/s^{-1}
1	Iso-octane	31.0	25.91	25.51	0.80	39 (4)		5.1	0.77	10.4	2.6
2	Cyclohexane	31.2	25.74	25.13	0.81	31 (3)	2.30	[2.30]	1.35	6.0	1.4
3	Decalin			25.19							
4	Carbon tetrachloride	32.5	25.51	24.57	0.44	27 (3)		2.42	1.11	4.0	5.0
5	Carbon disulphide	32.6		23.81							
6	Toluene	33.9	25.32	23.58	0.54	36 (4)	4.0 (1.2)	4.0	0.90	6.0	5.1
7	Benzene	34.5	25.19	23.31	0.62	41 (5)	3.2 (3)	3.6	1.28	4.8	3.0
8	Di-n-butyl ether	33.4		23.70							
9	Di-isopropyl ether	34.0		23.87							
10	Diethyl ether	34.6	25.64	23.36	0.42	18 (3)		10.0	1.8	2.3	3.3
11	Dioxan	36.0	25.51	22.73							
12	Anisole	37.2	24.94	22.57	0.12	14 (2)		1.8	0.78	1.5	11.3
13	1,1,1-Trichloroethane			23.53	0.45	25 (2)		2.0	1.25	3.6	4.4
14	Tetrahydrofuran	37.4	25.06	22.37	0.026	7 (2)		5.0	0.14	1.8	70
15	Chlorobenzene	37.5	25.06	22.78	0.32	24 (3)		2.93	0.82	3.9	8.3
16	Ethyl acetate	38.1	25.32	22.42			4.3 (1.0)	5.1			
17	Chloroform	39.1	25.00	22.55	0.11	8 (1)	3.3 (7)	4.0	0.24	4.6	37
18	Cyclohexanone	40.8		22.22							
19	Ethyl methyl Ketone	41.3		22.17							
20	Acetone	42.2		22.17			5.1 (1.0)	7.3			
21	Benzonitrile	42.0		22.07							

E_T = Dimroth polarity parameter (kcal mol^{-1}), $\bar{\nu}_A$ = absorption band maxima, $K_{sv}(O_2)$ = Stern–Volmer quenching constant for oxygen, k_{O_2} = bimolecular rate constant for oxygen quenching, other parameters as in Table 1.

[a] From ref. 22. [b] Estimated from viscosity.

Lengthening of the alkyl chains of the R_2N group produced only minor perturbations on the fluorescence yield (Table 1).

(b) Solvents of low to moderate polarity. The fluorescence emission in aprotic solvents consists of a structureless band appreciably red-shifted relative to that observed in aliphatic hydrocarbon solvents (Table 2). The quantum yield of fluorescence declines markedly with moderate increase in the polarity of the solvent medium such that in acetone the yield is extremely low and reliable measurements of fluorescence become impossible thereafter. Protic solvents were not considered for this reason and also on account of their tendency, confirmed by u.v. absorption studies, to hydrogen bond to the triazine dye ground state.

Application of the Lippert–Mataga formula [1,6] involving the solvent polarity function $f(\varepsilon,n)$ [equation (1)]

$$f(\varepsilon,n) = \left[\frac{2(\varepsilon - 1)}{2\varepsilon + 1} - \frac{(n^2 - 1)}{2n^2 + 1}\right] \qquad (1)$$

to the data (Table 2) enabled a value of *ca.* 18 D to be derived for the increase in the molecular dipole moment on excitation, $\mu(S_1) - \mu(S_0)$, assuming an effective molecular radius of 0.60 nm. The correlation of $(\bar{\nu}_A - \bar{\nu}_F)$ with $f(\varepsilon,n)$ was relatively poor over the range of solvent polarities capable of study. The correlation with the empirical Dimroth E_T parameter, based on the electronic charge-transfer absorption band of a betaine, was significantly better [24] (see Figure 1). There can be no doubt as to the high charge-transfer character of the emitting excited state, as expected for such a good electron donor group as R_2N and a moderate electron acceptor, the triazinyl group, reckoned to be between COMe and NO_2 in electron-withdrawing power.[19]

For a representative series of solvents the fluorescence lifetimes of compound (I) were obtained by the oxygen quenching method outlined in the Experimental section. The lifetimes thus obtained should reflect in a relative sense the changes in the actual lifetimes and the derived values of k_F and k_{NR} should be understood on this basis.

A downward trend in k_F with increase in solvent polarity is perhaps significant. A least-squares analysis gives $k_F = 10^8\ (25.46 - 0.60\ E_T)\ s^{-1}$ with a mean residual of 1.88×10^8.

Such a decrease in k_F should arise from a reduction in the conjugation between the donor D and acceptor A parts of the excited molecule. There exists now increasing evidence to suggest that such a reduction in conjugation, caused for example by a rotation of D relative to A, leads also to a greater transfer of electric charge.[18] That is, the resultant excited state becomes more dipolar, an event assisted by solvent polarity increase, or even induced thereby.

The gross increase in the non-radiative rate constant k_{NR} with increase in solvent polarity is clear. The data can be fitted to equation (2) with a mean residual of 0.28 in $\log_{10} k_R$.

$$\log_{10} k_{NR} = 3.395 + 0.156\ E_T \qquad (2)$$

The nature of the non-radiative relaxation process(es) is uncertain. Internal conversion $S_0 \leftarrow S_1$ as the dominant mode is highly unlikely in view of the moderate energy gap and the marked dependence of k_{NR} on the excited singlet state energy coupled with the magnitude of k_{NR}. The internal conversion $S_1 \rightarrow S_1^1$, where S_1^1 is a non-emitting singlet excited state formed by an internal conformational change or bond breakage, is not excluded. Compound (I) is quite photostable in solution and thus the latter possibility seems unlikely.

Internal rotation of the dialkylamino group to a perpendicular configuration with respect to the benzene ring would produce an excited state of essentially zero emissive capability and of great dipole moment,[18] which could be identified with S_1^1.

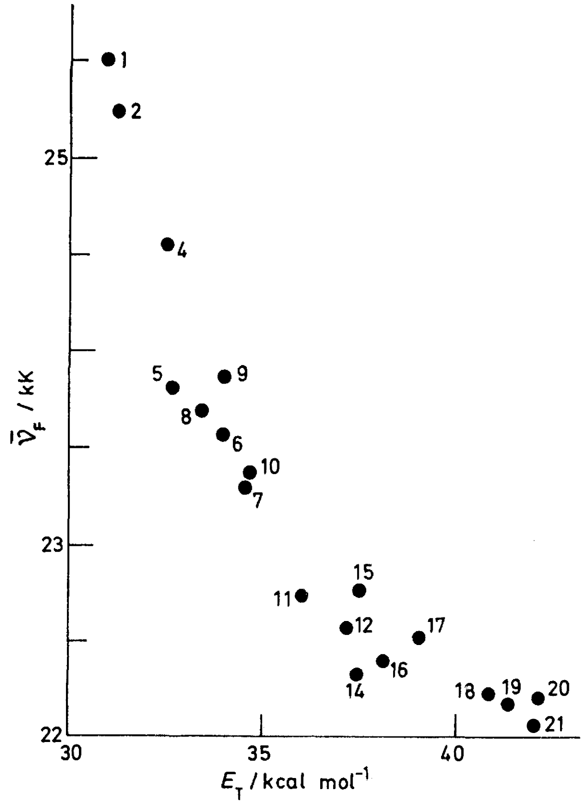


FIGURE 1 Plot of wavenumber of the fluorescence band maxima of compound (I) *versus* solvent polarity expressed on Dimroth E_T (kcal mol^{-1}) scale. Numbers denote solvents as in Table 2

An alternative explanation, and one perhaps to be favoured, would ascribe the major contribution in k_{NR} to intersystem crossing.

The corresponding charge-transfer triplet state T_n(CT) must lie below the S_1(CT) state. It is possible that the non-radiative decay route involves $S_1(CT) \rightsquigarrow T_n(CT)$ followed by $T_n(CT) \rightsquigarrow T_1$ where T_1 is the lowest energy, mainly locally excited, π,π^* triplet level.

Some circumstantial evidence can be gained from studies of the phosphorescence emission. In rigid n-propanol glass at 77 K, compounds (I)—(III) show weak phosphorescence at *ca.* 18.5, 18.5, and 19.1 kK respectively whereas strong fluorescence is observed at 22.6, 22.5, and 21.7 kK (maxima) respectively. The phosphorescence to fluorescence ratio for (III) is *ca.* 0.05 whereas that of (I) and (II) is *ca.* 0.01. The phosphorescence lifetimes (of the order of seconds) seem indicative of a normal locally excited aromatic π,π^* triplet state.

Thus, twist about the donor D–acceptor A linkage leads to an increase in the population of T_1, even in rigid media.

In the limit of 90° mutual twist between donor D and acceptor A the formal singlet and triplet complete charge-transfer states would be nearly degenerate. The solvent polarity increase effect on k_{NR} could arise either from the induced twist leading to a more dipolar state, thus bringing S_1(CT) and T_n(CT) closer together, or to a greater solvation of the planar S_1(CT) state relative to the T_n state, with the same result. In practice, T_n will consist of mainly CT with some locally excited (LE) contribution, and *vice versa* for T_1. Hence T_n may be less dipolar than S_1(CT).

The questions can be clarified only by further study of temperature and viscosity effects on the luminescence. The importance lies in the obvious generality of such behaviour to be expected in charge-transfer systems.

Absorption and Fluorescence in Binary Mixtures of Aliphatic Hydrocarbons and Acetonitrile.—Upon addition of small quantities of polar species P, *e.g.* acetonitrile to cyclohexane solutions of (I), a quenching of the distinctive structured fluorescence band of the triazine dye monomer M* occurs with the simultaneous rise of a broader band *ca.* 1 000 cm^{-1} to the red; at low concentrations of acetonitrile ([P] <0.05M) an isoemissive point is apparent at 403 nm. At higher concentrations of acetonitrile the characteristic major peak of M* in fluorescence disappears completely, the new band shifts further to the red, and is itself weakly quenched (Figure 2).

Concurrent with the changes in fluorescence emission some changes are observable in the u.v. absorption spectrum. For the concentrations of acetonitrile in cyclohexane studied (limited by solubility) the u.v. absorption band maxima showed negligible shift in position but an appreciable decline in intensity (Table 3) in an asymptotic fashion. Since the fluorescence quenching could arise *via* a static (ground-state association) mechanism it was desirable to estimate quantitatively the association of ground-state (I) with acetonitrile in cyclohexane.

TABLE 3

U.v. absorption of (I) in cyclohexane with added acetonitrile

[MeCN]/M	d	$(d_0 - d)/(d - d_\infty)$
0	0.170	0
0.032	0.164	0.13
0.064	0.156	0.39
0.128	0.145	1.00
0.192	0.140	1.50
0.256	0.134	2.26
0.320	0.130	4.00
∞	0.120 *	

d_0, d, d_∞ = optical density (1 cm path length) at 389 nm at zero, given, and infinite concentration of acetonitrile in the solution respectively.

* This value estimated by extrapolation. The error in d is ± 0.002. $[(\text{I})] = 1.64 \times 10^{-5}$M.

Analysis of U.v. Absorption Data.—Let M = solute molecule, P = polar molecule, and MP$_n$ = complex of solute M with n polar molecules P in the 'inert' hydrocarbon medium.

If d = optical density at the absorption maximum of M of a solution whose *total* solute concentration is C_0 and whose polar additive concentration is [P], $d_0 = \varepsilon_{\text{M}} C_0$ and $d = \varepsilon_{\text{M}} C_{\text{M}} + \varepsilon_{\text{MP}} C_{\text{MP}} + \cdots$ where ε_{M}, ε_{MP}, $\cdots$ are the molar extinction coefficients of M, MP, $\cdots$ MP$_n$ and the Cs are their actual concentrations in solution.

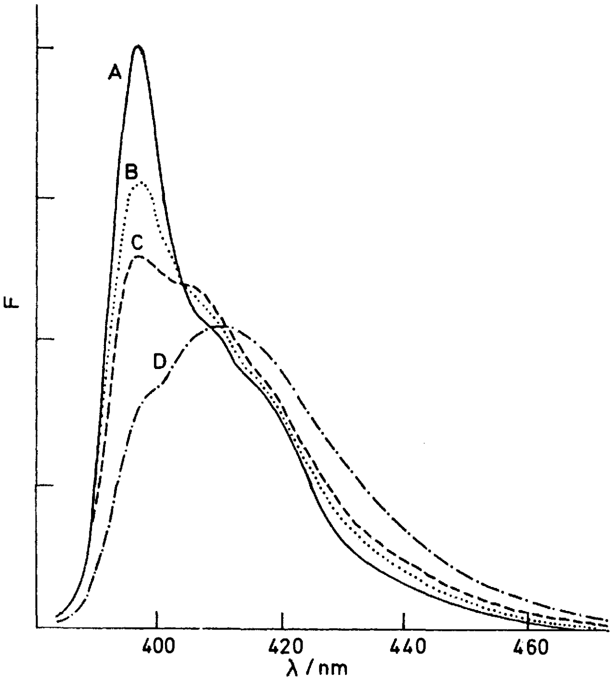


FIGURE 2 Uncorrected fluorescence spectra of compound (I) in cyclohexane containing various concentrations of acetonitrile: A, 0; B, 0.0128; C, 0.0256; D, 0.064M. $[(\text{I})] = 1 \times 10^{-6}$M in every case. I_F is the fluorescence intensity in arbitrary units

Considering only a 1 : 1 association (3) and assuming $[\text{P}] >> C_0$, it can be shown that equation (4) applies

$$\text{M} + \text{P} \rightleftharpoons \text{MP} \tag{3}$$

$$K_1[\text{P}] = \frac{(\varepsilon - \varepsilon_{\text{M}})}{(\varepsilon_{\text{MP}} - \varepsilon)} = \frac{(d - d_0)}{(d_\infty - d_0)} \tag{4}$$

where K_1 is the association constant, ε is the apparent molar extinction coefficient of M in a given solution, and d_0 and d_∞ are the optical densities at zero and, by extrapolation, infinite concentrations of polar additive P, respectively.

Analysis of the data (Table 3) in this manner was satisfactory and a value for K_1 of 7.5 ± 1.0M^{-1} was obtained for comparison with the Stern–Volmer fluorescence quenching constant.

Above *ca.* 0.25M-acetonitrile strong deviation from the simple relationships for 1 : 1 association was present as expected, thus indicating the participation of higher aggregates MP_n.

Analysis of Fluorescence Spectra.—The following method was applied to the data (Table 4) for (I) in cyclohexane with added acetonitrile. The assumptions appear to hold for the range of acetonitrile concentration (0— *ca.* 0.07M) important with respect to monomer M fluorescence quenching.

TABLE 4

Fluorescence intensities of (I) in cyclohexane with added acetonitrile

[MeCN]/M	I (395)	I (420)	I_M	I_E	I_M°/I_M
0	76.4	27.0	76.4	0.0	1.00
0.0128	59.0	28.0	57.4	7.8	1.33
0.0256	49.0	30.0	46.2	13.7	1.65
0.0448	37.0	31.0	33.2	19.3	2.29
0.064	27.0	33.0	22.0	25.3	3.46
0.128	13.0	30.0	7.5	27.4	10.15
0.192	8.0	25.3	3.2	24.2	23.80
0.256	5.3	21.3	1.1	20.8	
0.320	3.7	16.3	0.4	16.2	
0.384	3.0	14.7	0.0	14.7	

I (395) and I (420) are the experimental intensities of fluorescence (arbitrary units) at 395 and 420 nm respectively. I_M is the intensity of fluorescence at 395 nm ascribable to the triazine dye molecule (I). I_E is the intensity of fluorescence at 420 nm ascribable to the triazine dye–acetonitrile 1 : 1 solvent exciplex. The excitation wavelength was 380 nm. The optical density at this wavelength remained essentially constant for the additions of acetonitrile necessary to produce appreciable quenching of the dye fluorescence (I_M).

The total emission was considered to be the sum of the monomer M* emission and the new emission, denoted by E, arising from a 1 : 1 association of M* with P.

The total emission intensities at two wavelengths λ_1 and λ_2, $I(\lambda_1)$ and $I(\lambda_2)$, were known experimentally for various concentrations of polar additive P at a constant concentration of dye M.

The two wavelengths were chosen to correspond as far as possible to the band maxima of M* and MP* (E), namely 395 and 420 nm in the above experimental case (see Figure 2).

The actual contributions of dye monomer emission at λ_1, I_m, and MP* emission at λ_2, I_E, can be found from the easily derived formulae (5) and (6) where A is the ratio of emission intensities $I(\lambda_2) : I(\lambda_1)$ for the monomer

$$I_E(\lambda_1) = I(\lambda_1) - AI(\lambda_2)/(1 - AB) \qquad (5)$$

$$I_M(\lambda_2) = I(\lambda_2) - AI(\lambda_1)/(1 - AB) \qquad (6)$$

M spectrum, known experimentally from the spectrum in pure cyclohexane, and B is the ratio of the emission intensities $I((\lambda_1) : I(\lambda_2)$ for the MP* spectrum. The latter was estimated in two ways. (i) The emission spectrum of MP* was taken to be that spectrum obtained when the emission of M* was >95% quenched but before substantial further quenching of MP*, and small further shift in band position (*cf.* ref. 14) by polar additive P had occurred, *i.e. ca.* 0.26M-P. Hence B could be closely approximated. (ii) For an assumed value of B, values of I_M were calculated and thence, point wise, Stern–Volmer quenching constants, using the formula (7). This was repeated for stepwise increments in B, the mean value of K_{sv} with its uncertainty for the five

$$I_M{}^{\circ}/I_M = 1 + K_{sv}[P] \qquad (7)$$

lowest concentrations of P evaluated ($[P] \leqslant 0.07$M), and that value of B giving the lowest spread in values for K_{sv} chosen.

In practice, I_M was found to be insensitive to any reasonable choice of B, and the two approximation methods gave a value of 25 ± 3 for the Stern–Volmer quenching constant of the monomer emission (MeCN–C_6H_{12}).

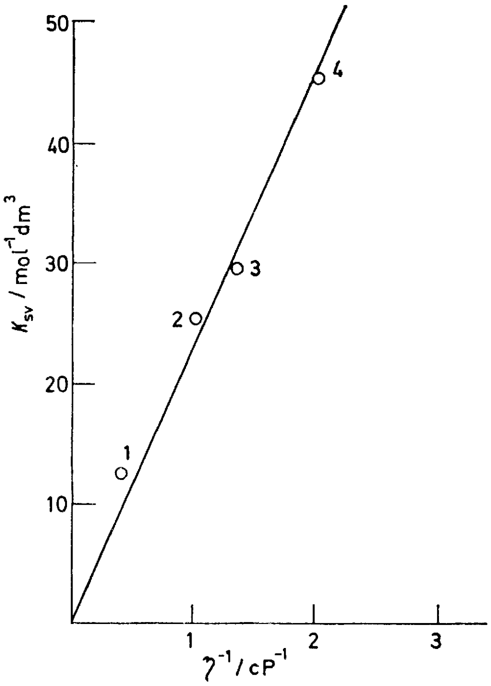


FIGURE 3 Correlation of the apparent Stern–Volmer constant, for the fluorescence quenching of compound (I) by acetonitrile, with reciprocal viscosity of aliphatic hydrocarbon solvent: 1, decalin; 2, cyclohexane; 3, methylcyclohexane; 4, isooctane

The Stern–Volmer quenching constants for (I) in other aliphatic hydrocarbon solvents upon addition of acetonitrile were determined in like manner (see Figure 3).

Formation of 1 : 1 *Solvent Exciplex.*—The association of the polar molecule P with the highly dipolar excited species M* at low concentrations of P (<0.07M) appears to be in a simple 1 : 1 ratio as judged by the linearity of the Stern–Volmer plot in this range. Further good evidence of the assumptions inherent in the analysis is given by the good linearity of the plot of I_M *versus* I_E in this range of concentration (see Table 4).

Above *ca.* 0.07M-P deviations arise, as expected, due to (a) quenching of MP* by P, (b) static quenching, and (c) formation of multiple aggregates MP_n.

The question arises of the interpretation to be given to the measured K_{sv}. K_{sv} is much larger than the static association constant K_1 determined from the optical absorption. In the case of acetonitrile as polar additive P, K_{sv} is not to be identified either with K_1 or with an equilibrium constant for the excited state association K_1^*, as the following argument shows. The intrinsic quantum yield of fluorescence ϕ°_E of the exciplex MP*, *i.e.* in the absence of quenching by polar P molecules, can be estimated by extrapolation of the exciplex emission intensity (for polar additive concentrations where M* quenching is essentially complete) to a hypothetical zero concentration of P. After allowance for instrumental factors ϕ°_E is estimated to be 0.45 by comparison with ϕ°_M. If the radiative rate constant $k^E_F \approx k^M_F$ (3.5×10^8 s^{-1}), then reciprocal τ^E_0 (sum of exciplex decay constants, $k^E_F + k^E_{NR}$) is 7.7×10^8 s^{-1}.

Since static quenching of M* is not effective the formation of MP* must be at least diffusion controlled, or slower. For cyclohexane at 22 °C, the diffusion-controlled second-order rate constant $k_{diff.}$ is *ca.* 1×10^{10} mol^{-1} dm^3 s^{-1}. Thus if $K_{sv} = 25$ mol^{-1} dm$^3 = K^*$, then the dissociative first-order rate constant of the exciplex MP*, k_d, would be $\leqslant 4 \times 10^8$ s^{-1}, and less than $(k^E_F + k^E_{NR})$; this is inconsistent with the establishment of a true equilibrium. Caution has been advised on this point regarding exciplex kinetics in general, and in the evaluation of exciplex enthalpies of formation in particular.[25] From the experimentally determined fluorescence lifetime of M*, $\tau^\circ_F = 2.22$ ns, the formation rate constant, k_P, of the solvent exciplex is 1.12×10^{10} mol dm^{-3} s^{-1} if K_{sv} measures simply the direct quenching. This value is close to that for diffusion control, k_{diff}.

Measurement of the Stern–Volmer constants for the fluorescence of (I) quenched by acetonitrile in hydrocarbon solvents of various viscosities confirms that the exciplex formation is diffusion controlled. A plot of K_{sv} *versus* η^{-1} (reciprocal viscosity) is *linear* (Figure 3).

The solvent exciplex appears to derive its stability from the direct μ–μ and induced μ–μ interactions[16] of the M* molecule ($\mu \geqslant 18$ D) with the polar molecule P (μ 3.92 D; acetonitrile). This aspect requires closer investigation *via* a study of other additives, since Chandross claims[15] that ability to solvate positive charge may be the dominant requirement.

Finally, the photophysical characteristics of the solvent exciplex are of interest in view of the fact that in acetonitrile as solvent, the fluorescence yield of (I) is negligible.

The fluorescence band maxima of the exciplex is shifted *ca.* 1 000 cm^{-1} to the red of that of (I) in neat cyclohexane. From the correlation of $\bar{\nu}_F$(M) with solvent polarity parameter E_T (Figure 1) and the correlation of $\log_{10} k_{NR}$(M) with E_T, a shift of 1 000 cm^{-1} to the red should increase $\log_{10} k_{NR}$ by *ca.* 0.30, *i.e.* $\phi^\circ_E \approx 0.5\ \phi^\circ_M$, if $k^E_F \approx k^E_M$. Thus the observed exciplex properties are consistent with the results obtained for the dye (I) in neat solvents, and do not require a special explanation.

Studies of the interaction of the highly suitable intramolecular charge-transfer excited triazine dye with other polar additives are in progress.

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