Fluorescence of Some Dipolar *N,N*-Disubstituted 4-(Dichloro-1,3,5-triazinyl)anilines. Part 4.* Internal and Molecular Rotations in Homogeneous and Inhomogeneous Media

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Radiative and non-radiative decay constants have been obtained for the *N,N*-diethyl and *N,N*-diphenyl derivatives of the title compounds (DETA and DPTA, respectively). DETA fluorescence occurs from a planar conjugated excited singlet state which decays by an internal rotation about the anilino nitrogen–carbon bond at a rate close to the polar solvent dielectric relaxation rate. By contrast, the detectable emission from DPTA is from a twisted species, and its decay is an order of magnitude slower than that of the DETA emission.

The molecular tumbling of the DPTA molecule in homogeneous solvents is deduced to be isotropic. Preliminary studies on the applicability of the triazine dyes as fluorescence probes are reported. In aqueous neutral or alkaline media the dyes undergo hydrolysis but the product fluorescence can be utilised. Hydrolysed DPTA probe rotation in egg lecithin unilamellar vesicles is probably isotropic and has an activation barrier of 26 kJ mol^{-1} in the liquid crystalline phase.

DPTA dye is adsorbed strongly onto porous Vycor glass but the fluorescence emission is complex.

Relaxation of photoexcited intramolecular charge-transfer systems has been studied more closely of late with particular attention to solvent dielectric relaxation.[1-6] The effects of solvent viscosity on the rates of radiative and non-radiative decay of excited solutes able to undergo internal conformational changes, while familiar in outline, are being explored in some detail as being relevant to the very rapid sub-nanosecond photophysical decays of laser and other dyes in polar solutions.[5 13] The rotational anisotropies of such large dyes, with or without attached solvent molecules, have been scrutinized in attempts to probe and test models of rotational diffusion.[14-16]

We have reported previously [17-19] on the photophysical characteristics of various *para*-substituted *N,N*-dialkylanilines possessing a 1,3,5-triazinyl group as an electron acceptor, and have concluded that the behaviour is best rationalised on the basis of a twisted intramolecular charge-transfer (TICT) model.[13,18,20]

Direct determination of the fluorescence lifetimes in a variety of media allows us now to discuss more clearly the roles of solvent viscosity, solvent dielectric relaxation, and dye molecular structure in determining the formation and decay of highly dipolar TICT states *via* internal rotation.[1,2,5,6,13,21] The overall molecular tumbling of the dyes has been investigated in various, mainly alcoholic, media.

The wide range of (micro) viscosity over which either the internal or the overall rotation of the dyes produced significant changes in the fluorescence emission characteristics suggested application of these dyes as probes of microenvironment.

Preliminary findings, relevant to the potential use of the dyes as new fluorescence probes, are reported for doped egg lecithin vesicles and porous Vycor glass. The advantages and limitations of these dyes as fluorescence probes are assessed.

Experimental

The triazine dyes were prepared and purified as described by Shaw *et al.*[22,23] Solvents of good spectroscopic quality were checked and found to be non-emissive under the excitation wavelengths, 350—430 nm, used for the fluorescence studies. Uncorrected fluorescence spectra, polarisations, and quantum yields were measured under normal optical conditions as described previously, except that the instrument used was a model 4800 S Phase Fluorimeter (SLM Instruments Inc., Urbana, U.S.A.). Fluorescence lifetime measurements were made usually in the delta phase mode, *i.e.* the phase and modulation of the sample emission and of a dilute Ludox solution light scatterer were compared in turn with a second reference light scattering Ludox solution. Each reported lifetime is the average of at least eight alternate accumulations of ten successive data samples for sample and reference solutions, in order to minimise errors due to drift in modulation depth and phase. The lifetimes are reproducible to ±5% or ±0.05 ns, whichever is the greater, on the basis of experimental observation, in agreement with the manufacturer's specifications. Scattered light effects were minimised by the use of narrow-band excitation (0.5 nm bandpass) and a 400/420 nm cut-off filter on the sample emission. The emission monochromator was set at zero order with a bandpass of 4—8 nm.

Fluorescence lifetimes were determined from both phase and modulation data obtained at 30 and at 18 MHz, and in a few cases also at 6 MHz, modulation frequency. The presence, or absence, of multi-component/non-exponential fluorescence decay was thus ascertained. In cases where two (or more) components were suspected the relevant data were processed on a two-component exponential-decay basis according to the moments analysis given by Weber.[24]

Egg lecithin unilamellar vesicles doped with triazine dye were prepared by colyophilisation and sonication. Egg lecithin in chloroform (Sigma; 3 mg in 30 μl) with an appropriate amount of the triazine dye dissolved in chloroform or acetonitrile, was evaporated under nitrogen to a solid film in a 15 mm diameter Pyrex tube. Aqueous buffer (3.0 ml; pH 8.1; 50 mM-Tris, 20mM-KCl) was added and the solution was flushed with nitrogen, then vortexed for 10—20 s. Sonication for 5—10 min at *ca.* 0 °C yielded clear solutions containing the doped vesicles.

Porous Vycor glass [25] (No. 7930, Corning) in the form of flat thin discs/rectangles was decolourised by treatment with 30% hydrogen peroxide solution at 100 °C, and then stored under distilled deionized water. When required, samples were oven-dried at 60 °C for 1 h, then baked at 180 °C for 2 h. After cooling, the porous glass sample was immersed briefly in

* Part 3, ref. 19.

Table 1. Fluorescence of DETA at 295 K in homogeneous organic solvents

Solvent	τ_F [a]/ns	φ_F	$10^{-8}\ k_F$/ s^{-1}	$10^{-8}\ k_{NR}$/ s^{-1}
Cyclohexane	1.74	0.81	4.2	1.0
Toluene	1.75	0.54	2.8	2.9
Chloroform	1.25	0.11	0.88	9.1
Tetrahydrofuran	0.45	0.030	0.67	22
Methylene dichloride	0.45	0.031	0.69	21
Decan-1-ol	0.86	0.10	1.16	10.5
Octan-2-ol	0.52	0.083	1.6	18
Hexan-1-ol	0.19	0.028	1.5	50
Butan-1-ol	0.10	0.012	1.2	99
Propan-2-ol	0.13	0.019	1.5	77
Cyclohexanol	0.45	0.054	1.2	21
Glycerol	1.37	0.066	0.5	6.8

[a] Lifetimes for air-saturated solutions; small corrections for oxygen quenching have been applied in the calculation of k_F and k_{NR}.

Table 2. Fluorescence of DPTA at 295 K in homogeneous organic solvents

Solvent	τ_F [a]/ns	φ_F	$10^{-8}\ k_F$/ s^{-1}	$10^{-8}\ k_{NR}$/ s^{-1}
n-Hexane	4.51	0.62	1.08	0.67
Toluene	5.35	0.53	0.75	0.67
Chloroform	4.69	0.14	0.23	1.44
Chlorobenzene	5.60	0.24	0.32	1.02
Tetrahydrofuran	3.18	0.063	0.17	2.5
Methylene dichloride	2.49	0.050	0.18	3.3
Decan-1-ol	3.35	0.084	0.21	2.3
Octan-2-ol	2.29	0.053	0.20	3.6
Hexan-1-ol	1.42	0.019	0.13	6.4
Butan-1-ol	0.95	0.0084	0.08	9.3
Ethanol	0.65	0.0048	0.07	15
Cyclohexanol	1.17	0.029	0.23	7.8

[a] Air-saturated solutions; small corrections for oxygen quenching have been applied in the calculation of k_F and k_{NR}.

chloroform before being brought into contact with a chloroform solution of the triazine dye for 30 min. The dye-doped glass was air-dried at 50 °C for 1 h before fluorescence measurements were made on the optically clear sample.

Results and Discussion

(1) *Dye Photophysics and Internal Rotation.*—Tables 1 and 2 give the measured τ_F and φ_F values with the derived radiative (k_F) and non-radiative (k_{NR}) decay constants for two triazinyl dyes *N,N*-diethyl- and *N,N*-diphenyl-4-(dichloro-1,3,5-triazinyl)aniline, hereafter referred to as DETA and DPTA, respectively. The similarity of the trends in the variations of τ_F and φ_F with polarity and viscosity of the homogeneous organic solvent media for DETA and DPTA is deceptive in that the major components of the observed emissions are deduced to have related, but different, origins.

The u.v. absorption band maxima of DETA and DPTA are close in energy to 400 ± 5 nm in all solvents examined, with molar absorption coefficients of 50 000 ± 3 000 (DETA) and 29 000 ± 2 000 l mol^{-1} cm^{-1} (DPTA). Thus there is no evidence to suggest changes in ground-state conformation of the dyes with change in solvent polarity. If in the dye DETA the amino nitrogen is fully conjugated with the aromatic ring, as seems likely, then in DPTA some twist about the Ph_2N–C bond in the ground state is indicated (θ *ca.* 40° ?, based on $\cos^2\theta$ = 29 000/50 000). DPTA is expected to adopt a propeller-like conformation. The u.v. absorption data suggest conjugation of the tertiary nitrogen centre with the electron-acceptor-substituted aryl ring in preference to the two phenyl rings. The latter appear to perturb the ICT absorption band energy very little as compared with the *N,N*-diethyl derivative, DETA.

For DETA in toluene, the observed radiative rate constant k_F agrees closely with the Strickler–Berg estimate of 2.9 × 10^8 s^{-1}, but in solvents of higher polarity the apparent k_F declines to *ca.* 1.5 × 10^8 s^{-1} for the alcohols and is somewhat lower for aprotic, less viscous solvents (Table 1). The decline in apparent k_F for DPTA from the Strickler–Berg estimate of 1.6 × 10^8 s^{-1} is more marked and, significantly, the k_F values (Table 2) are an order of magnitude smaller than those of DETA in the same solvent media (Table 1). The low k_F values for DPTA of 0.1 to 0.2 × 10^8 s^{-1} found in the more polar media (ε > 4) indicate an orthogonality of the donor and acceptor components in the emitting species of DPTA. This could be achieved by a rotation of the triazinyl acceptor relative to the aryl ring, but then it is unclear why similar behaviour is absent in the dye DETA. A preferred interpretation is that considerable rotation of the Ph_2N– group relative to the $-C_6H_4-C_3N_3Cl_2$ moiety occurs in DPTA prior to emission. The formation of a weakly emitting 'twisted intramolecular charge-transfer' (TICT) state would be assisted by the stabilisation of the electron-deficient tertiary nitrogen centre by the two phenyl substituents as they are released to rotate into better conjugative interaction by the main internal rotation about the Ph_2N–C bond. In this context, a significant difference of *ca.* 4 000 cm^{-1} exists between the fluorescence maxima of DETA and DPTA despite the near-coincidence of their absorption maxima.

The decays of the fluorescence emission of the dye DETA in non-polar and weakly polar media were judged to be good simple exponentials, but instrumental limitations due to the very short lifetimes did not permit tests in the medium to highly polar solvent media (ε ≥ 8). The excited singlet DETA, having a geometry not far removed from that of the ground state, decays by a fast solvent-dependent non-radiative channel which we assign to internal rotation of the Et_2N– group. This results in a further separation of electronic charge with production of a TICT state. For DETA in alcoholic media, where the relevant data are available, a linear correlation exists between k_{NR}^{-1} and an appropriate constant charge * dielectric relaxation time $\tau_D{}'$ of the solvent, as has been noted by Kosower *et al.*[6,26] for the fluorescence decay of a 6,2 ANS derivative.† The slope of the correlation line is near 2.0 however, rather than the value of unity expected if solvent dielectric relaxation is the limiting factor to the linear charge flow (equivalent to a dipole rotation of 180°) in the excited solute. At the molecular level the dielectric relaxation mode of the solvent may be akin to the solvent movement pertaining to viscous flow. If this is the case then the apparent activation energies for the fluorescence quenching of DETA in ethanol (11 kJ mol^{-1}), butan-1-ol (16 kJ mol^{-1}), and ethylene glycol (25 kJ mol^{-1}) determined previously,[18] may relate to either solvent dielectric relaxation or solvent viscous resistance to internal rotation in the solute. It was hoped that this ambiguity would be resolved by the data for DPTA, for which internal rotation involves more bulky phenyl groups but an electronic situation closely similar to that of DETA. In the event the comparison proved to be

* $\tau_D{}' = \tau_D n^2/\varepsilon$ where n is the solvent refractive index, ε the solvent bulk dielectric constant, and τ_D the constant field dielectric relaxation time of the alcohol.

† 6-(4-Methylphenyl)aminonaphthalene-2-(*NN*-dimethylsulphonamide).

Table 3. DPTA in decan-1-ol: rotational anisotropy test

T/K	τ_F [a]/ns	P [b]	tan Δ [c]
278	4.30	0.280	0.1299
285	3.84	0.270	0.1395
286	3.91	0.257	0.1418
296	4.48	0.218	0.1566
298	3.95	0.212	0.1610
305	3.79	0.192	0.1688
313	4.03	0.208	0.1596
323	4.14	0.203	0.1598

[a] Measured for vertically polarised excitation and 55° emission polariser angle; τ_F(mean) = 4.05 ± 0.20 ns. [b] P = polarisation; P_0 = 0.45, r_0 = 0.353. [c] Calculated from τ_F and P_0 for a 30 MHz modulation frequency; theoretical tan $\Delta_{max.}$ = 0.163 for an isotropic rotor, based on P_0 = 0.45 and τ_F = 4.05 ns.

invalid since the major emission detectable from excited DPTA occurs from a (TICT) species which has already undergone internal rotation. The non-radiative decay constants k_{NR} for this excited DPTA species follow a smooth progression with increase in solvent dielectric constant but are one order of magnitude smaller than those found for the DETA emitting species in all but non-polar media (Tables 1 and 2).

The formation rate of the highly twisted emitting species of the dye DPTA should be equal to, or even greater than, the observed non-radiative decay rate of the observed DETA-dye-excited singlet species, and greater by an order of magnitude than its subsequent decay rate (to twisted ground state mainly). A similar situation appears to prevail in the formation and decay of a high charge-transfer state of the 6,2 ANS derivative reported by Kosower *et al.*[26]

(2) *Molecular Rotation in Homogeneous Media.*—The nature and relationship of the molecular tumbling of the triazine dyes to the micro-environment, relevant to the use of the dyes as fluorescent probes, was examined for homogeneous solvent media.

For DPTA dye dissolved in decan-1-ol, reasonably accurate fluorescence decay times for vertically and horizontally polarised emissions under vertically polarised excitation could be measured over the temperature range 278—313 K (Table 3) and were analysed using expressions given by Lakowitz and Prendergast.[27]* The maximum 'tangent defect', tan Δ, of 0.169 found at a temperature of 305 K agreed well with the theoretical maximum of 0.163 expected for DPTA as an isotropic rotor. Consideration of the molecular shape of the DPTA molecule, a triphenylamine system, would lead one to expect a near isotropic rotation of the molecule in fluid media. For the more elongated DETA dye the situation is less clear but unfortunately no direct evidence was obtainable on this point.

Rotational correlation times, derived on the basis of the Perrin expression for an isotropic rotor using polarisation data, are related in a reasonably linear fashion to the macroscopic viscosity η of the homogeneous, mainly alcoholic, solvents (Table 4). The gradients for DPTA and DETA dyes are 1.07 and 0.39 ns cP^{-1}, respectively, whereas the expected gradients at 295 K are 0.56 and 0.36 ns cP^{-1}, respectively,

* Lifetimes of DETA dye were too short, and thereby inaccurate for meaningful analysis, and for DPTA in other solvents the accessible viscosity range around ambient temperature was inappropriate for the test for isotropic rotation of the probe molecule.

Table 4. Fluorescence polarisation at 295 K in homogeneous solutions [a]

Solvent	Viscosity (cP)	DETA $10^3 P$	DETA θ/ns	DPTA $10^3 P$	DPTA θ/ns
Methylene dichloride	0.42			14.8	0.50
Tetrahydrofuran	0.48	107	0.48	13.2	0.25
Chloroform	0.56	46	0.35	13.9	0.39
Toluene	0.58	21	0.22	9.5	0.30
Chlorobenzene	1.67			14.8	0.50
Ethanol	1.10			237	1.92
Dioxane	1.25	63	0.48		
Propan-2-ol	2.30	348	1.00		
Butan-1-ol	2.75	340	0.81	237	3.08
Hexan-1-ol	4.8	323	1.10	274	7.17
Octan-2-ol	6.2	284	2.13	194	5.36
Decan-1-ol	12.3	327	5.40	262	12.5
Cyclohexanol	60	412	9.7	374	16.2

[a] Rotational correlation times, θ, were estimated from the Perrin expression:

$$\left(\frac{1}{P} - \frac{1}{3}\right) = \left(\frac{1}{P_0} - \frac{1}{3}\right)\left(1 + \frac{3\tau_F}{\theta}\right)$$

relating observed polarisation P under vertically polarised excitation, limiting polarisation P_0 (assumed to correspond to glycerol solutions for which polarisation values of 0.458 and 0.443 are found for DETA and DPTA, respectively), and fluorescence lifetimes τ_F (see Tables 1 and 2).

assuming the Debye–Stokes–Einstein expression for a spherical rotor with slip of $\theta_{iso} = 3Vr\eta/kT$ and estimated molecular volumes of 0.75 and 0.49 nm^3 for DPTA and DETA, respectively. The correspondence is good for DETA, but DPTA appears to rotate more slowly than expected. It is likely that (alcohol) solvent molecules associate with the twisted emitting state of the DPTA dye and increase its effective rotational volume.[14,15] The results for cyclohexanol solutions do not lie on the linear correlation lines, the rotations of both DPTA and DETA being much faster than expected on the basis of the bulk viscosity.

(3) *Fluorescence Probes of Inhomogeneous Environments.*—The utility of the triazine dyes DETA and DPTA as probes of local environment polarity and fluidity has been explored and evaluated in preliminary studies. Two representative examples are given here.

(a) *Egg lecithin vesicles.* The dyes were taken up efficiently into the unilamellar egg lecithin vesicles. Contribution to the fluorescence emission by dye remaining in the aqueous phase was judged to be very small [unlike that found for cetyltrimethylammonium bromide (CTAB) micellar systems], the fluorescence quantum yields were moderate, and the fluorescence decays were good single exponential in form.[24]

However, the apparent absorption band maxima appeared at *ca.* 370 nm, greatly blue-shifted as compared with that found for DETA or DPTA in neutral organic solvents, water at pH 3—6, or aqueous micellar solutions of sodium lauryl sulphate (*ca.* 400 nm) but corresponding to that found for aqueous CTAB solutions. Initially this phenomenon was thought to be due to complexation of the anilino nitrogen of the dye with the cationic head portion of the phospholipid or surfactant. Further detailed studies, to be reported elsewhere, now prove that the dyes DETA and DPTA undergo ready hydrolysis under neutral or mildly alkaline conditions in aqueous media, *i.e. one* chlorine of the 2,4-dichloro-1,3,5-triazinyl moiety is replaced by a hydroxy group. The process

Table 5. Molecular rotation in egg lecithin unilamellar vesicles containing hydrolysed DPTA dye [a]

T/K	278.7	292.7	308.4
Polarisation P	0.4000	0.3801	0.3569
τ_F/ns	3.49	2.94	2.48
tan Δ (exp.)	0.0824	0.0972	0.107
(theor.)	0.143	0.102	0.106
10^{-6} R/radians s^{-1}	7.0	12.2	20.6

[a] For tangent defect, tan Δ see ref. 28; R is the molecular rotation rate; molar ratio of dye to egg lecithin *ca.* 1 : 300.

is catalysed in cationic surfactant type media and is complete before observation of fluorescence in the doped egg lecithin vesicles.

Thus it was not possible to utilise correlations of fluorescence maxima and quantum yields obtained for DETA and DPTA in earlier studies to ascertain the effective polarity of the probe micro-environment in the lipid vesicles since the probes are chemically modified species. Molecular rotation of the probe can be examined, however, using polarisation data.* The existence, or otherwise, of restricted rotation of hydrolysed DPTA dye in the liquid crystalline phase of egg lecithin vesicles was examined for specifically by using the ' wobbling-in-a-cone ' analysis.[27-29] For low doping of the vesicles the ' tangent defect ' computed from the appropriate decay times was found to attain the theoretical estimate for an isotropic rotor of limiting anisotropy $r_0 = 0.353$. Rotation rates R were evaluated from measured steady-state anisotropies r and the fluorescence lifetimes τ_F (Table 5) using the expression for isotropic rotation, $r_a/r = 1 + 6R\tau_F$.[27] The fluorescence lifetime τ_F shows only a small dependence on temperature, E_a (τ_F) *ca.* 8 kJ mol^{-1}, whereas the molecular rotation rate R has an activation barrier of 26 kJ mol^{-1}. The fluorescence polarisation of hydrolysed DPTA dye ($\lambda_{max.}$ of fluorescence in egg lecithin vesicles *ca.* 470 nm) extrapolates to a value of 0.33 ± 0.01 at the limit of zero dye probe concentration, which together with a fluorescence lifetime of 2.9 ns yields an isotropic rotational correlation time (θ) of 19 ns. On the assumption that the rotation time–viscosity correlation obtained for unhydrolysed DPTA dye also applies to the rotationally very similar hydrolysed dye species, an effective microviscosity η^1 of 18 cP is indicated for the phospholipid bilayer in the vicinity of the dye probe. A similar analysis of the data for the (hydrolysed) DETA dye ($P = 0.38$, τ_F 0.55 ns) gives θ *ca.* 6.8 ns and η^1 *ca.* 17 cP. The effective microviscosity, valid for isotropic rotors as here, is thus consistent for the two dyes. The triazine dyes do appear to yield data amenable to accurate analysis and interpretation. Work is in progress on these and derivative dyes as probes of phase and dynamical changes of lipid bilayers.

(b) *Porous Vycor glass.* DPTA dye is adsorbed rapidly and strongly from chloroform solution onto prepared porous Vycor glass with little shift in absorption band maxima. Fluorescence emission, centred on 555 nm, was broad and indicative of a range of polar environments for the dye akin to that of the lower aliphatic alcohols. This was in keeping with the expected hydroxylic nature of the silica surface. Of greater interest was the extent of surface mobility of the dye probe inside the 4 nm diameter pores of the glass. The fluorescence decay was not single exponential; the approximate apparent lifetime of 0.35 ns was consistent with a highly polar microenvironment. Subtle, but significant, changes in polarisation across the broad fluorescence emission band were found. For λ 520—570 nm, P was 0.343 ± 0.008, while for λ 580—600 nm, P was 0.371 ± 0.011. Thus two or more adsorption sites are indicated differing perhaps in environment polarity and thus in dye lifetimes. For a mean polarisation P of 0 35, a θ (isotropic) value of 3.1 ns and an ' effective microviscosity ' of 3 cP are crudely indicated, bearing some similarity to the dye in butan-1-ol at room temperature. Obviously, detailed multi-component and wavelength-dependent analysis of fluorescence decay curves is essential for reliable interpretation.

The triazine dye DPTA is promising as a probe of such surfaces in view of its strong adsorption onto the glass surface, a result of its high ground-state dipole moment, and its intense optical absorption band which permits low levels of doping. Work has been initiated to study the surfaces of amorphous silica powders.

In conclusion, these preliminary studies have indicated the usefulness of the dye DPTA in particular (DETA fluorescence lifetimes are much smaller and hence more difficult to determine precisely) in probing inhomogeneous microenvironments in view of its physical adsorption, strong optical absorption, and essentially isotropic rotation characteristics. The disadvantage arises in the ready hydrolysis of the dye in contact with neutral-to-alkaline aqueous media. This can be overcome by full fluorescence characterisation of the hydrolysis product with respect to solvent polarity, viscosity effects, *etc.*, or by easy chemical modification of the dye such that the possibility of hydrolysis is removed. The latter modification could be used to advantage, *e.g.* replacement of one Cl by $-NR^1R^2$ where R^1 and R^2 are long alkyl chains, to alter the location of the dye probe in lipid bilayers.

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* This is possible on the reasonable assumption that the limiting polarisation P_0 is the same for the hydrolysed species as for DETA/DPTA. Since P_0 depends on the angle between absorption and emission transition dipoles this is not expected to alter significantly with the chemical modification undergone by the dye.

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