The Fluorescence of Some Dipolar *NN*-Dialkyl-4-(dichloro-1,3,5-triazinyl)anilines. Part 2.† Temperature and Solvent Effects on the Radiationless Decay of an Intramolecular Charge-transfer Excited Singlet State

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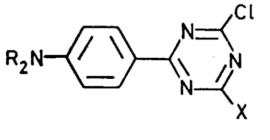
The fluorescence of *NN*-diethyl-4-(2,6-dichloro-1,3,5-triazinyl)aniline is strongly quenched by solvents of even moderate polarity. Reduction of the electron acceptor character of the triazinyl ring system, by substitution of a dimethylamino-group for a chlorine atom, leads to a dramatic decrease in the susceptibility to fluorescence quenching by polar solvents.

The quenching mode is ascribed to a solvent-assisted twist of the *NN*-diethylamino moiety in the intramolecular charge-transfer (ICT) excited singlet state to yield a twisted (TICT) biradicaloid zwitterionic singlet state. At low temperatures, in viscous media, this radiationless decay appears to be limited by the dielectric relaxation rate of the solvent.

RADIATIONLESS decay processes of excited organic charge transfer systems have provoked interest and debate, especially in the case of conformationally mobile intramolecular charge-transfer exciplexes. The solvent medium influences strongly the luminescence characteristics of such highly dipolar excited states.[1-3] Temperature, influencing both effective solvent polarity and solvent relaxation as well as the conformational flux of the emitting solute, is expected to exert a substantial effect on the luminescence but at present little data exists for intramolecular donor–acceptor (D–A) systems.

Arising out of the controversy over the origin of the dual luminescence of *NN*-dialkylaminobenzonitriles and similar systems, and of solvent quenching, the idea has been advanced [4,5] that fluorescence quenching of the initially planar excited singlet state involves an intramolecular twist which places the donor D and acceptor A constituents of the molecule out of mutual conjugation. The result is an increased migration of electronic charge to form a biradicaloid zwitterionic excited state, [$^{+\bullet}$D–A$^{-\bullet}$]. An impressive array of evidence is explicable on this twisted intramolecular charge-transfer (TICT) model.

A preliminary account of the fluorescence characteristics at room temperature of some D–A systems (I)—(III) in which D is an anilino moiety and acceptor A a triazinyl ring has appeared.[6] We report here an extension of those studies to a wider variety of solvents with emphasis on the effects of temperature on fluorescence yields, polarization, and emission bandwidths.



(I) R = Et, X = Cl TA

(II) R = Ph, X = Cl DPTA

(III) R = Et, X = NMe$_2$ TAN

EXPERIMENTAL

The compounds were prepared and purified as described by Shaw *et al.*[7,8]

Solvents were mostly of Merck UVASOL grade and used as received. Other solvents were dried and distilled before use. All solvents showed negligible fluorescence under the excitation conditions (λ_{ex} 350—420 nm).

Uncorrected emission spectra were recorded on a Perkin-Elmer MPF-2A instrument, and were corrected and integrated subsequently by computer utilising a sensitivity curve calibrated by reference to quinine hydrogensulphate solutions.

Quantum yields at room temperature were determined by reference to quinine hydrogensulphate solution as the ultimate standard.[9] For convenience in practice compound TA dissolved in toluene ($\phi_F{}^0$ 0.54, determined separately) was often used as a standard with an excitation wavelength of 390—400 nm. Solutions of optical density <0.05 were contained in 10 mm pathlength rectangular silica cells.

In the variable temperature experiments solutions of the triazine dyes were contained in cylindrical silica tubes of 4 mm internal diameter but errors arising from this geometry were reckoned to be insignificant here.[10] Sample tubes were cooled in a dewar vessel purged by nitrogen gas whose temperature was regulated (to ± 1 °C) by an in-house modified Perkin-Elmer R10 n.m.r.-probe temperature-control system. Sample temperature was measured by a thermocouple immersed in the sample liquid near the observation zone and monitored by a Bailey Instruments model BAT-5 meter.

U.v. absorption spectra were obtained using a Pye–Unicam SP 8000A instrument; variable temperature measurements utilised the temperature control system described above with a modified dewar assembly. Samples were contained in a rectangular fused silica windowed well of 10 mm path length.

Fluorescence quantum yields at low temperatures were normally determined relative to the room temperature value for a given solvent using corrected emission curves, with due allowance made for the small changes in optical density at the excitation wavelength and the variation in solvent refractive index, according to the procedure of Mantulin and Huber.[11] Viscosity [12] and dielectric constant [13] data were obtained from standard compilations.

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† Part 1 is ref. 6.

RESULTS AND DISCUSSION

Fluorescence in Non-viscous Media.—Earlier data[6] on the luminescence and absorption characteristics of TA at room temperature has been extended with the inclusion of, *inter alia*, alcoholic solvents. The latter solvents do not appear to give any anomalous effects due to the likely hydrogen-bonding between the alcohol and the amino-group of the solute.* Table 1 gives quantum yields for TA, DPTA, and TAN at room temperature.

TABLE 1

Fluorescence of TA, DPTA, and TAN at room temperature

		DPTA		TAN	
Solvent	TA[a] ϕ_F	ϕ_F	$\bar{\nu}_F$/kK	ϕ_F	$\bar{\nu}_F$/kK
2-Methylbutane	0.80	0.62	22.09		
Cyclohexane	0.81	0.53	22.00	0.60	27.49
Carbon tetrachloride	0.44	0.51	21.14		
Benzene	0.62			0.48	25.64
Toluene	0.54	0.53	19.90	0.47	25.74
Chlorobenzene	0.32	0.23	18.83	0.47	25.12
Diethyl ether	0.42	0.41	19.23	0.49	25.74
Di-n-butyl ether	0.45				
Ethyl acetate	0.031	0.060	18.69	0.38	24.84
Tetrahydrofuran	0.030	0.063	18.69	0.61	24.85
Dichloromethane	0.031	0.072	18.62	0.12	24.45
Benzonitrile	0.016				
Acetonitrile	0.0006			0.040	25.75
Methanol	0.006				
Ethanol	0.011	0.0048	19.23	0.046	23.81
Propan-1-ol	0.018				
Propan-2-ol	0.019				
Butan-1-ol	0.025	0.069	20.53	0.095	23.92
Ethylene glycol	0.002				

[a] Values of ϕ_F(TA) and $\bar{\nu}_F$(TA) in these and other solvents can be obtained from Tables 2 and 3, and from ref. 6.

Since the fluorescence emission $S_0 \longleftarrow S_1$ for the triazine dyes studied here involves annihilation of a high degree of electronic charge separation, the position of the fluorescence band should reflect the effective polarity of the solvent media at the molecular level (on the assumption that solvent relaxation is faster than the fluorescence decay of the excited solute).

For the solvents of low to moderate polarity, *e.g.* cyclohexane, tetrahydrofuran, the fluorescence maxima correlates with solvent polarity [*e.g.* f(ε,*n*) or Dimroth E_T values[14]]. In media of higher polarity in which ϕ_F and τ_F are very small, the shift in fluorescence band position is not as great as expected and indicates incomplete solvent cage relaxation. The alcoholic solvents seem to fall into this category even at room temperature (see also the comments on the fluorescence polarisation data).

The quantum yield of fluorescence declines as solvent polarity increases, dropping markedly in solvents of dielectric constant ε of 2.5—10, for the compound TA (see Figure 1).

Furthermore, changes in the energy of the ICT transition induced by structural changes in the donor, *e.g.* Ph_2N for Et_2N (DPTA and TA), or in the acceptor, *e.g.* NMe_2 replacing Cl (TAN and TA), result in luminescence behaviour which confirms the general trend that the more polarity in the excited state is favoured the lower becomes the fluorescence quantum yield (see Figure 1).

Thus, TAN is not too sensitive to solvent polarity, even in acetonitrile appreciable fluorescence is observed, whereas TA is very susceptible to the solvent polarity. DPTA behaves similarly to TA.

The dramatic decrease in ϕ_F for TA as solvent polarity increases indicates clearly that a very efficient non-radiative decay channel opens which is related to the charge-transfer nature of the emitting state and which must involve a further increase in excited solute dipolarity during the decay.† That solvent polarity is the governing influence in non-viscous media is substantiated by the results obtained on the variation with temperature of ϕ_F for TA and DPTA (Table 2). The dielectric properties of 2-methylbutane, carbon tetrachloride, and toluene alter little with temperature and the change in ϕ_F is found to be minimal in these solvents. By contrast, the dielectric constants of moderately polar solvents such as diethyl ether, chlorobenzene, ethyl acetate, and tetrahydrofuran increase on cooling while

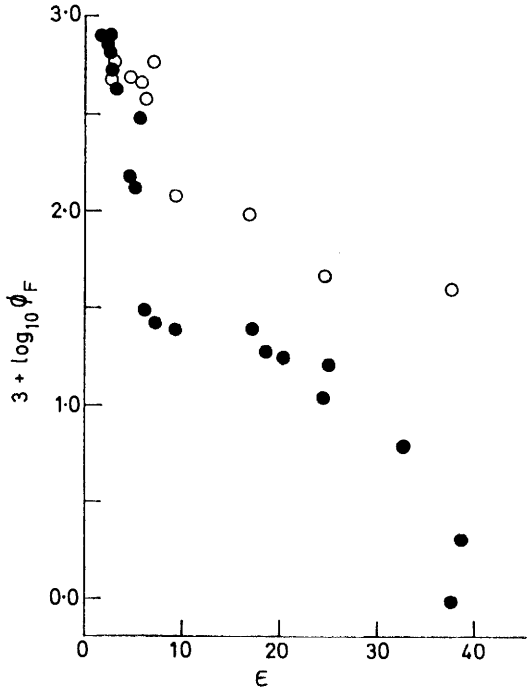

FIGURE 1 Correlation of fluorescence quantum yields and solvent dielectric constant at room temperature for TAN (○) and TA (●)

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* The change in u.v. absorption previously mentioned briefly (ref. 6, p. 486) arises on prolonged standing of the alcohol solutions and is base catalysed. It seems to be due to replacement of chlorine by an alkoxy-group, and is not due to hydrogen bonding as originally stated.

† Oxygen quenching studies have indicated that the radiative rate constant k_F is much less affected by solvent polarity than the non-radiative rate constant k_{NR}.[6]

ϕ_F in these solvents *decreases*, as expected if polarity is the dominant factor. (Note that the variation of ϕ_F with T is here contrary to that commonly found.)

In the light of these observations it seems reasonable to assign the non-radiative decay channel to an intramolecular twist which places the donor and acceptor parts of the ICT molecular system out of mutual conjugation, with a concomitant increase in excited solute dipolarity. The most likely point of rotation is about the carbon–anilino nitrogen bond.

Preliminary studies[15] on the triplet states of the triazine systems indicate that the major decay channel does not involve intersystem crossing but is an internal conversion, *i.e.* $S_1 \longrightarrow S_1(t)$, where $t = 90°$ twisted conformation.

TABLE 2

Fluorescence quantum yields of TA and DPTA. Variation with solvent and temperature

(a) TA

2-Methylbutane		Toluene		Diethyl ether		Ethyl acetate		Tetrahydrofuran	
T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F
293	0.800	299	0.540	298	0.420	296	0.0308	296	0.030
273	0.813	273	0.524	273	0.375	272	0.0268	273	0.0263
236	0.816	249	0.524	236	0.352	260.5	0.0247	237	0.0231
216	0.805	237	0.546	216	0.325	248.5	0.0239	217	0.0229
197[a]	0.797	218	0.564	198	0.278	238.5	0.0229	198	0.0258
181	0.749			180	0.235	218.5	0.0232	181	0.0307
170	0.714			170	0.197	200.5	0.0253	171	0.0363
				77	0.68	191.5	0.0288		
						181.5	0.0410		

(b) DPTA

Carbon tetrachloride		Toluene		Diethyl ether		Ethyl acetate		Tetrahydrofuran		Chlorobenzene	
T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F	T/K	ϕ_F
313	0.481	295	0.528	298	0.407	294	0.0604	294	0.0634	293	0.230
303	0.497	273	0.495	273	0.267	273	0.0457	272	0.0462	273	0.181
297	0.508	238	0.578	238	0.263	256	0.0336	238	0.0298	259	0.168
291	0.493	223	0.579	216	0.101	236	0.0273	216	0.0227	248	0.184
282	0.489	213	0.565	197	0.057	216	0.0258	199	0.0220	238	0.152
273	0.479	198	0.530	180	0.042	196	0.0240	182	0.0206		
261	0.474			170	0.022			171	0.0190		

[a] The slight decline in ϕ below *ca.* 200 K may arise from some ground-state aggregation of the dipolar dye in the non-polar media. Clear evidence for this was obtained for 2-methylbutane solutions at 77 K.

Significant alteration in the twist angle of the electronic ground state amine on cooling is excluded since the u.v. absorption shows only a small red shift with slight intensification and band narrowing with decreasing temperature.[16]

Fluorescence in Viscous Polar Media.—The spectral features of absorption and emission in the alcoholic solvents were similar to those in dipolar aprotic solvents. However, the quantum yield of fluorescence increased monotonically on cooling until a limiting value was reached (Table 3). An upturn in ϕ_F was apparent for compound TA in ethyl acetate and tetrahydrofuran also at quite low temperatures (below −60 °C; see Table 2), suggesting that in the polar-to-moderately polar media the solvent viscosity exerts an influence once the viscosity, η, rises much above *ca.* 2 cP.

Plots of log $(1/\phi_F - 1)$, against inverse temperature, T^{-1}, (Figure 2) had slopes corresponding to activation energies for the non-radiative decay of the excited TA dye in ethanol, n-butanol, and ethylene glycol of 11, 16, and 25 kJ mol^{-1}, respectively (assuming k_F to have zero activation energy). Arrhenius analysis of viscosity data for the same temperature range yields apparent activation energies of 13, 20, and 28 kJ mol^{-1} for the same alcohols, respectively.

Thus medium viscosity in viscous media is crucial as well as polarity.

An interesting question is whether the effects of viscosity derive (a) from the ability of the solvent to relax dielectrically and thus accommodate adequately to the flow of electric charge within the solute during the radiationless decay $S_1 \longrightarrow S_1(t)$. If not, then the flow of charge in the solute will be impeded by the slow response of the solvent reaction field in the cybotactic region.[17] Alternatively, they may derive (b) from the direct degree of resistance to change in the solute molecular geometry (amino-residue rotation), *i.e.* an impedance to change in molecular shape which requires distortion of the solvent cage.[18]

In rigid glasses, independent of polarity, the quantum yield of fluorescence is high. Thus in alcohols at 77 K ϕ_F is $\geqslant 0.5$ reaching almost the value found in non-polar media at room temperature. At room temperature in liquid methyl methacrylate ϕ_F for TA is *ca.* 0.09 while on polymerisation of the medium ϕ_F increases to 0.74.

The high limiting value of ϕ_F is attained concurrently with a stabilisation in the fluorescence band maxima (see Figure 2 and Table 3).

Information on the extent of solvent cage relaxation before light emission by the solute occurs is provided directly by the Stokes' shift of the emission, $\Delta\tilde{\nu}_S = \tilde{\nu}_A - \tilde{\nu}_F$.[19]

At room temperature $\Delta\tilde{\nu}_S$ increases with solvent polarity as expected in non-viscous media, *e.g.* PhMe, 1.58; Et_2O, 1.98; EtOAc, 2.37; THF, 2.58 kK. In the more polar, but much more viscous alcoholic media the Stokes shift remains at *ca.* 2.5 kK which indicates that even at room temperature the alcohol solvent cage relaxation is incomplete before emission.[19,20] This situation pertains for the alcohols at all the temperatures explored in this study. On cooling, τ_{DR} for an alcohol increases and the solvent relaxation about the solute would be dramatically incomplete were it not for a somewhat parallel increase in the emitter lifetime. The net result is that re-orientation relaxation becomes slowly but progressively more incomplete as judged by the small decrease in the observed Stokes shifts. In the range 25 to −100 °C the Stokes' shift in diethyl ether increases on cooling, consistent with polarity increase and a low viscosity. In ethyl acetate and tetrahydrofuran $\Delta\tilde{\nu}_S$ changes very little on cooling, despite an increase in polarity, indicating that solvent relaxation is comparable in rate to the fluorescence emission rate. Significantly τ_F in THF is an order of magnitude smaller than τ_F in Et_2O.

TABLE 3

Fluorescence of TA in alcohols. Variation with temperature

Ethanol			n-Butanol			Ethylene glycol		
T/K	ϕ_F	$\tilde{\nu}_F$/kK	T/K	ϕ_F	$\tilde{\nu}_F$/kK	T/K	ϕ_F	$\tilde{\nu}_F$/kK
294	0.0107	22.58	295	0.0248	22.62	294	0.0021	22.37
273	0.0192	22.52	273	0.0387	22.62	273	0.012	22.37
244	0.031	22.57	241	0.108	22.73	235.5	0.0276	22.47
216.5	0.060	22.53	222.5	0.159	23.09	215.5	0.107	22.52
195	0.105	22.46	213	0.218	23.09	196	0.282	22.73
182.5	0.179	22.46	203	0.266	23.15	180.5	0.386	22.91
170	0.248	22.54	193	0.340	23.20	168	0.400	22.99
151	0.479	22.72	181	0.423	23.31	153	0.479	23.04
			165	0.579	23.39	138.5	0.447	22.88
			155	0.485	23.47	130	0.460	22.83
			145	0.508	23.53			
77	0.63	23.42	77	0.524	23.25	77	0.58	23.40

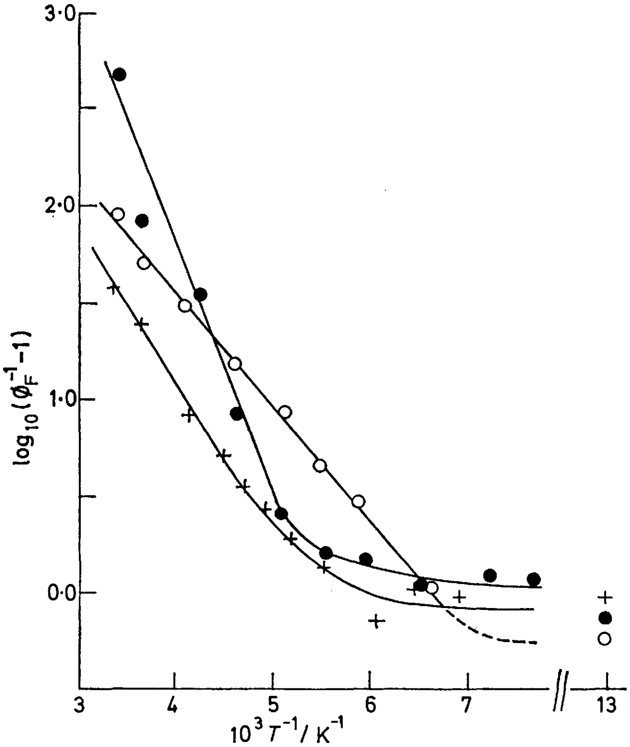

FIGURE 2 Arrhenius analysis of the variation of fluorescence quantum yields of TA in alcohols with temperature: ethanol (○); butan-1-ol (+); ethylene glycol (●)

The parallelisms of fluorescence yields with Stokes' shifts thus indicate that, in media of moderate or greater polarity, the efficiency of the non-radiative decay channel in the dipolar dye depends on the dielectric relaxation rate of the solvent cage, and thereby on the viscosity of the medium.

TABLE 4

Polarisation of fluorescence of TA

	Polarisation P [a,b]			
T/K	Et_2O	THF	Bu^{n}OH	EtOH
296	0.03	0.09	0.28	0.34
273			0.31	
252			0.27	
242		0.21		
223			0.29	
213		0.27		0.36
203	0.07			
193		0.29	0.34	
187	0.10			
177		0.28		
173	0.13		0.34	0.37

[a] $P = (1 - x)/(1 + x)$, $x = (I_{VH}/I_{VV})(I_{HV}/I_{HH})$ where I_{VH} = emission intensity with vertically polarised excitation beam and horizontally polarised emission analyser, *etc.* [b] Each value of P is the mean over the emission band. Errors in P are ±0.02 in most cases.

The exact nature of the dielectric relaxation during reorganisation about the excited solute may differ considerably from that which gives rise to the measured dielectric relaxation of pure solvents. The interpretation of the latter at a molecular level is in any event open to much debate.[21-23,*]

Measurements of fluorescence polarisation, P, exhibited by TA in various solvents and at a series of temperatures (Table 4) reveal a pattern consistent with that deduced from Stokes' shift and quantum yield data.

At room temperature the fluorescence emission is nearly unpolarised for TA in diethyl ether as expected from the low solvent viscosity and the anticipated τ_F value. Significantly, for THF as solvent the polarisation is higher than for diethyl ether, a consequence of the shortened τ_F in THF. Somewhat surprisingly, in the alcohols, the polarisation P is high even at room temperature and increases only slightly with decrease in temperature.

Thus, in the viscous alcohols the overall rotational movement, or libration, of the elongated excited solute molecule [27] is sluggish relative to the very short lifetime of the excited state. This implies, perhaps, that the solute is locked in a relatively immobile cage of hydrogen-bonded alcohol molecules, a feature which would accord with the slow dielectric relaxation of the alcohol solvent itself.

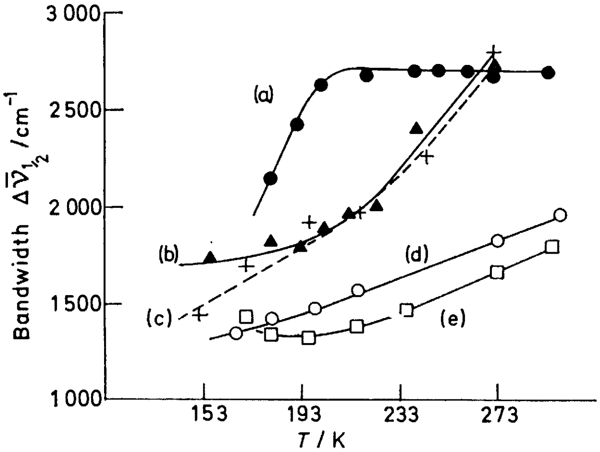

FIGURE 3 Variation of fluorescence bandwidth with temperature for TA in (a) ethyl acetate (●); (b) n-butanol (▲); (c) ethanol (+); (d) diethyl ether (○); and (e) toluene (□)

Decay Modes of the TICT Singlet State.—The photophysical properties of the product state following quenching of the initial planar emitting state are of some interest. We are unable to assign with any confidence a definite fluorescence emission ascribable to a transition such as $S_0(t) \longleftarrow S_1(t)$. In view of the expected low energy gap (*ca.* 15 kK?) and thus high internal conversion rate, together with a low value of the radiative rate constant $k_F(t)$ due to the orthogonality of the donor and acceptor units ($\leqslant 10^6$ s^{-1}?) the absence of a distinct emission of reasonable intensity is perhaps not surprising.[4] However, substantial changes in fluorescence band halfwidths with solvent and temperature are apparent (Figure 3).

At low temperatures, where the fluorescence quantum yield ϕ_F is high and thus the quenching process(es) inefficient, in all solvents the bandwidth approaches a value of *ca.* 1 400 cm^{-1}. For the polar solvents, as temperature is increased and ϕ_F decreases sharply, the bandwidth rises such that at room temperature it is *ca.* 1 000 cm^{-1} broader than observed for the low polarity solvent media, *e.g.* Et_2O, PhMe at room temperature where ϕ_F is still high. Thus, under circumstances in which strong fluorescence quenching occurs an additional weak fluorescence emission to lower energy may be present and may come from the twisted excited solute in line with the postulated quenching mechanism.

At present we are exploring the non-radiative decay processes of the postulated twisted intramolecular charge-transfer state by examination of triplet state yields and properties.

We thank the S.R.C. for a research assistantship (to I. P.).

[0/1840 *Received*, 1*st December*, 1980]

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[*] For Et_2O solutions of TA at 293 K solvent relaxation is rapid and essentially complete ($\tau_{DR} \sim 5$ ps, $\tau_F \sim 1$ ns). In the case of EtOH at 293 K the pure solvent dielectric relaxation time [24] is 270 ps and much longer than the anticipated fluorescence lifetime of TA in EtOH of *ca.* 10 ps. The latter is estimated from the ϕ_F value assuming (i) that k_F is the same as for TA in cyclohexane and (ii) that the TICT state formed in the quenching process does not revert in part to the original planar emitting state, *i.e.* irreversible quenching. These assumptions may not be strictly valid and hence the estimate of τ_F is only an approximate order of magnitude. Picosecond laser studies [25] of the relaxation of alcohols around Coumarin 102 dye reveal faster relaxation times (*ca.* 90 ps for EtOH at 293 K) than dielectric studies on the pure solvents [24] would indicate.

Thus the extent of the disparity between τ_F for TA in alcohols and τ_{DR} for the alcohols is difficult to estimate in other than a qualitative manner.

It is of note that fluorescence rise times of *NN*-dimethylaminobenzonitrile have been reported [26] as being retarded in methanol and ethanol as solvents.

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