The Fluorescence of Some Dipolar *NN*-Dialkyl-4-(dichloro-1,3,5-triazinyl)anilines. Part 3.† Intersystem Crossing Yields from Intramolecular Charge-transfer Excited States and Triplet State Properties

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The phosphorescence and triplet–triplet optical absorption characteristics of *NN*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline have been examined in rigid and fluid media. A value of 31 000 ± 5 000 $dm^3 mol^{-1} cm^{-1}$ has been determined for the molar extinction coefficient of the triplet–triplet absorption maxima at 490 nm of the compound dissolved in ether–pentane–alcohol (5:5:2) glass at 77 K and in poly(methyl methacrylate) at 293 K. Intersystem crossing yields in toluene (0.10), tetrahydrofuran (0.15), n-butanol (0.14), ethanol (0.07), and acetonitrile (0.05) have been related to the quenching of fluoresence induced by polar solvent, and rationalised on the basis of a previously proposed 'twisted intramolecular charge-transfer state' model.

The spectral properties of other related *NN*-disubstituted anilines possessing an electron acceptor substituent [CO_2H, CO_2Me, CN, CHO, $C_3N_3Cl(NMe_2)$, and NO_2] in the *para*-position have also been investigated.

Recent interest in the photophysics of intramolecular charge-transfer systems D–A, where D and A are π-electron donors and acceptors respectively, has focused on the roles played by internal conformational changes and solvent media dynamics in determining the rates of formation and decay of dipolar excited states.[1-15] A twisted intramolecular charge-transfer (t.i.c.t.) state model has been proposed and tested in relation to the dual luminescence phenomena shown by *NN*-dimethylaminobenzonitrile and related molecules in solution.[3,5] It has been extended to other D–A systems,[1,2,5-7,9] especially those having a strong donor group D, *e.g.* a dialkyl/aryl amino-group.

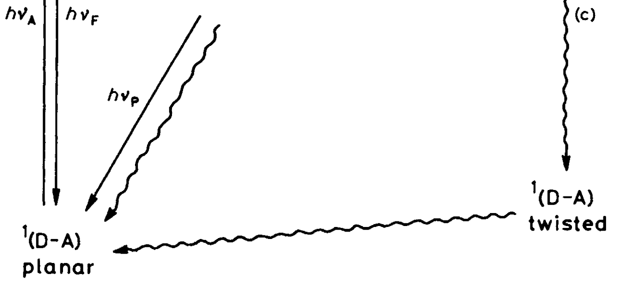
Important photophysical pathways relevant to the model are given in the Scheme.

The essential feature is the possible evolution (path a) of an initially conjugated and moderately dipolar excited singlet state into a highly dipolar excited state. The transfer of one electron from D to A is judged to be almost complete in the latter state on the basis of theoretical calculations.[3,9,15] Formation of the zwitterionic excited state is believed to arise *via* a solvent viscosity [5] and solvent polarity [2] dependent internal rotation of the donor component D relative to the acceptor component A, which effectively removes their mutual conjugation. The feasibility of such a rotation demands certain requirements in the electronic properties of D and A.[3,9] The process of t.i.c.t. state formation is analogous to the separation of cation and anion radical species in intermolecular c.t. exciplexes, except that the D and A moieties remain directly σ-bonded.

An unexplored and interesting possibility is suggested by the t.i.c.t. state model. The postulated twisted biradicaloid singlet state [1] $(^{+\cdot}D—A^{\cdot -})^*$ should be quasi-degenerate with the corresponding triplet species, the $^{+\cdot}D$ and $A^{\cdot -}$ components being almost orthogonal. Thus, intersystem crossing (i.s.c.) might be highly favoured from the twisted singlet state (path d, e) on energetic and electronic grounds (since ultrafast i.s.c. has been reported [13] in 1-pyrenyl-$[CH_2]_n$-NMe_2 and related heteroexcimers, and related to the orthogonality of donor and acceptor moieties).

We report here measurements of the triplet yield of the dye *NN*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline, (TA) in fluid media of various polarities for which the dye fluorescence characteristics are known in detail [1,2] and interpretable on the basis of the t.i.c.t. state model. No dramatic enhancements of triplet yield were found and we discuss the likely reasons for this.

We report the phosphorescence spectra, lifetimes, and triplet–triplet absorption characteristics of the triazine dye TA obtained by both steady-state and pulsed methods. Triplet-state properties of related triazine dyes, and also of *NN*-dialkylanilines *para*-substituted by the electron acceptor groups CN, CHO, CO_2H, CO_2Me, and NO_2, have been investigated in part, for purposes of comparison and because published data are lacking or incomplete for these ICT compounds.



t.i.c.t. state model

Wavy lines correspond to non-radiative routes. Straight lines correspond to radiative routes. Internal conversion of $^1(^{\delta+}D–A^{\delta-})^*$ into ground state, and possible fluorescence from $^1(^{+\cdot}D–A^{\cdot -})$ have been omitted for clarity since they are normally of low efficiency

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† Part 2, ref. 2.

Experimental

The compounds *NN*-diethyl- and *NN*-diphenyl-4-(dichloro-1,3,5-triazinyl)aniline, and *NN*-diethyl-4-(2-dimethylamino-4-chloro-1,3,5-triazinyl)aniline were prepared and purified as described by Shaw and Ward;[16,17] 4-*NN*-diethylaminobenzonitrile (Fluka), 4-*NN*-dimethylaminobenzaldehyde (Koch–Light), and 4-*NN*-dimethylaminobenzoic acid (Aldrich) were used as received. The methyl ester of the latter acid was prepared and purified as described elsewhere.[18] Merck UVASOL grade solvents were used as received, and showed negligible fluorescence and phosphorescence under the excitation conditions.

Poly(methyl methacrylate) (PMMA) solutions were prepared by thermal polymerisation at 70 °C in the dark of freshly distilled methyl methacrylate containing the desired compound, in the absence of added initiator.[19] PMMA samples were cut into rectangular blocks, polished, and stored under nitrogen.

Phosphorescence spectra (uncorrected) and decay curves were measured using the rotating-can accessory of a Perkin-Elmer MPF-2A spectrofluorimeter for clear glasses formed on cooling 10^{-3}—10^{-4}M solutions to 77 K in 2 mm internal diameter Spectrosil tubes.

Pulsed-laser photolysis of nitrogen-flushed fluid solutions at room temperature was conducted with a conventional optical layout. Light from a frequency-doubled ruby laser (System 2000, J. K. Lasers Ltd.; *ca.* 4×10^{15} photons of 347.2 nm wavelength per pulse, pulse half-width *ca.* 30 ns) impinged *via* an aperture (8 mm × 8 mm) on a 10 mm optical cuvette. Pulse energies were constant to $\pm 5\%$ as measured by a power meter. The optical density (1 cm path) of the sample solution at 347 nm was always adjusted to 1.0. A monitoring beam from a 150 W xenon arc, of cross-section 6 mm height ×2.5 mm width at the cuvette, had its central propagation axis at right angles to the laser beam and 1.3 mm to the rear of the irradiated inner front face of the cuvette. The detection system consisted of a short wavelength cut-off filter, a Bausch and Lamb monochromator (*ca.* 5 nm band pass), and an IP28 photomultiplier whose output was displayed on a Tetronix 564B storage oscilloscope.

Fresh nitrogen-flushed solutions of benzophenone in benzene were used as reference standards for calibrating the pulse energy delivered to the monitored irradiation volume. The molar extinction coefficient of benzophenone triplets in benzene at the absorption maximum was taken to be 8 000 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, a mean of relevant reported values.[20]

Triplet–triplet absorption spectra of PMMA and rigid glass samples were obtained with an apparatus and methodology similar to that described previously.[21] Sample solutions were contained in rectangular 10 mm silica cuvettes embedded in a copper block cooled by liquid nitrogen. Radiation from a filtered compact 125 W Hanovia high-pressure mercury arc impinged on the glassy sample *via* a slit 1.5 mm wide and 13 mm deep. A monitor beam of parallel rays at the sample and of dimensions 2 mm wide and 10 mm deep was provided by a 30 W tungsten lamp fed by a low-ripple stabilised 12 DC power supply (Farnell ' S ' series). The monitor beam passed through a short wavelength cut-off filter and a Glen–Creston Minimate 1650 monochromator (5 nm band pass usually) to an EMI 9786QB photomultiplier tube operated at 450—700 V. The electrical signal was either monitored directly by a Phillips PM2422A digital voltmeter in steady state studies, or fed into a slightly modified Northern Scientific NS-544 digital memory oscilloscope when accumulation of transient absorption rise and decay curves was required. A manually operated shutter on the irradiation beam, with associated trigger pulse contacts, allowed opening–closing times of under 5 ms and was suitable therefore for the determination of the triplet lifetimes of 0.5 s or greater reported here. Irradiation beam intensity was adjustable *via* the insertion of wire mesh screens of known transmittance. Intersystem crossing yields were determined in two ways.

(i) From the observed maximum changes in optical density immediately following a laser pulse in relation to that of benzophenone in benzene as a reference system, as outlined in the Results section.

(ii) The sensitised triplet dimerization of cyclohexa-1,3-diene was employed as a triplet counter following the method of Vesley and Hammond.[22]

Solutions *ca.* 10^{-3}—10^{-4}M in the compound, 1.0M in cyclohexa-1,3-diene, and containing a known amount of n-hexadecane as an internal standard appropriate to the dimer production expected (usually 5—15% conversion) were purged with nitrogen gas presaturated with solvent.

Irradiations were conducted at 320 and/or 366 nm wavelength, with 20 and 10 nm band passes respectively. The light flux was monitored regularly by a u.v. meter. The optical density of the solution was always greater than 2.0 at the wavelength of irradiation. Samples withdrawn at various time intervals were analysed by g.l.c. on a 2 m SE-30 column with temperature programming from 40—200 °C at 10 °C $\mathrm{min^{-1}}$. Benzophenone in benzene ($\varphi_{\mathrm{i.s.c.}}$ 1.0) served as a reference system.

Results

(a) *Phosphorescence.*—Table 1 summarises the phosphorescence emission maxima and first-order decay constants of various *para*-substituted *NN*-dialkylanilines in rigid glasses. The spectra of ethanol glasses at 77 K were very similar in form and bandwidth to spectra obtained for EPA glasses but the former were red-shifted by up to 10 nm relative to the latter. Spectra obtained for PMMA glasses at room temperature were appreciably broader and structureless.

Strong phosphorescence emission was detectable from DEABN, DMAB, DMABA, and DMABAE but only very weak emissions were found for TAN and DPTA. The long-lived lime-green emission from triplet TA molecules was weak but distinct from the intense blue fluorescence ($\varphi_F = 0.74$; PMMA; 293 K). The phosphorescence quantum yield of TA in PMMA at 293 K was reckoned to be *ca.* 0.01 from studies of the total luminescence. Assuming $\varphi_{\mathrm{i.s.c.}} = 0.09$ (see Table 2) for this system the radiative and non-radiative rate constants of the $S_0 \longleftarrow T_1$ process are 0.2 and 1.6 $\mathrm{s^{-1}}$, respectively.

The phosphorescence decays of all the compounds were found to follow strict first-order kinetics for over three half-lives. Good reproducibility of the decay rate constant, k_d, was obtainable with individual PMMA samples but the k_d values varied a little from sample to sample, as is often noted with PMMA matrices. For reasonably dilute solutions k_d was independent of the concentration of compound in the PMMA matrix. The spectra and lifetimes reported here for DMANB agree closely with those given by Kimura *et al.*,[23] and the values for DEABN and DMABA are in good correspondence with those reported by McGlynn *et al.*[24] for EPA glass at 77 K.

(b) *Triplet–Triplet Absorption.*—(i) *Spectra in rigid media.* Figure 1 displays spectral curves obtained by the steady irradiation method for TA, DMAB, and DMABAE in EPA glass at 77 K. Other compounds exhibited absorption changes on irradiation that were very weak (Δ O.D. $\leqslant 10^{-2}$) owing to low i.s.c. yield (TAN, DPTA) and/or low intrinsic triplet absorption coupled with the fall-off in irradiation source intensity for compounds with $S_1 \longleftarrow S_0$ absorption lying towards the shorter wavelength u.v. region.

Table 1. Summary of phosphorescence wavelength maxima and decay constants for ethanol (77 K), EPA (77 K), and PMMA (293 K) glasses[a]

	PMMA (293 K)		EPA (77 K)			Ethanol (77 K)	
Compound	λ_p/nm	k_d/s^{-1}	λ_p/nm	k_d/s^{-1}	k_{TT}/s^{-1}	λ_p/nm	k_d/s^{-1}
TA	530	0.5—0.6[b]	535	0.20	0.23	540	0.21
DPTA			532	0.44	0.39	540	0.47
DMANB			524	1.52	1.2	530	1.77
TAN	425	1.1[b]	438	0.33	0.24	445[c]	0.35
DMAB	465	1.2[b]	453	2.1		458[d]	2.0
DEABN	435	0.70[b]	419[e]	0.36	0.39	428[f]	0.29
DMABAE			419[g]	0.34		430[h]	0.33
DMABA			420[g]	0.36		422[h]	0.40

[a] Abbreviations: EPA = ether–pentane–alcohol (5 : 5 : 2); TA = *NN*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline; DPTA = *NN*-diphenyl-4-(dichloro-1,3,5-triazinyl)aniline; TAN = *NN*-diethyl-4-(2-dimethylamino-4-chloro-1,3,5-triazinyl)aniline; DMANB = 4-*NN*-dimethylaminonitrobenzene; DMAB = 4-*NN*-dimethylaminobenzaldehyde; DEABN = 4-*NN*-diethylaminobenzonitrile; DMABA and DMABAE = 4-*NN*-dimethylaminobenzoic acid and its methyl ester. [b] Dependent on sample preparation; reproducible for a given sample. [c] Prominent shoulder at 465 nm. [d] Shoulder at 485 nm. [e] Minor peaks at *ca.* 432 and 445 nm. [f] Shoulder in region 440—460 nm. [g] Shoulder *ca.* 438 nm. [h] Shoulder *ca.* 445 nm.

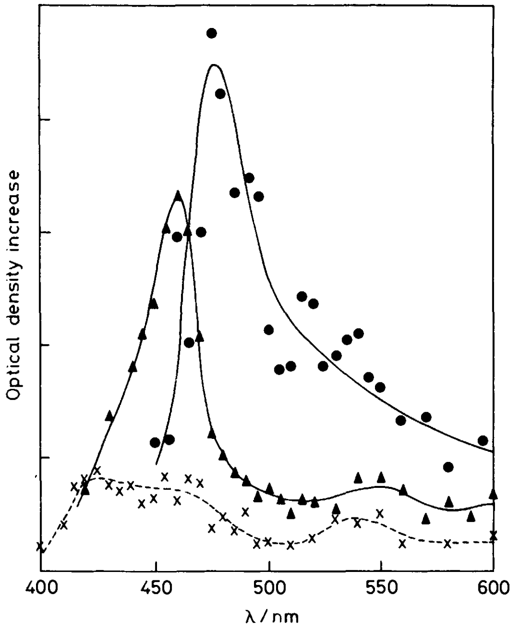


Figure 1. Induced increase in optical density (arbitrary scales) on steady irradiation of TA (●), DMAB (▲), and DMABAE (×) in EPA glass at 77 K. Maximum optical density increases are: TA (0.11); DMAB (0.017); DMABAE (0.006)

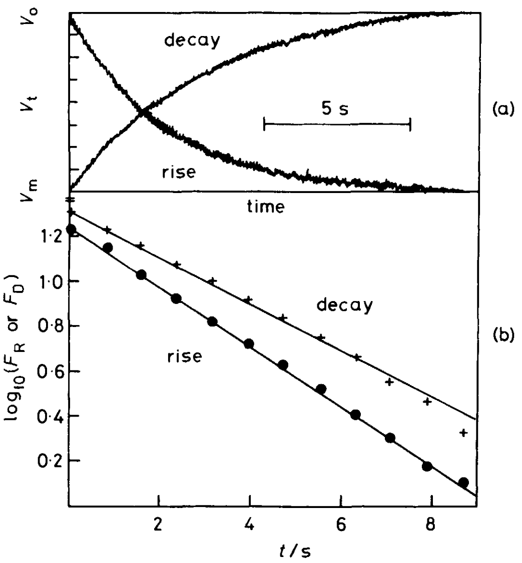


Figure 2. Rise and decay of triplet transient absorption at 490 nm of triazine dye TA in EPA glass at 77 K. (a) Experimental rise–decay in monitor beam photomultiplier output, V_t, *vs.* time after opening–closing steady irradiation beam shutter. (b) First-order kinetics are obeyed during the rise–decay of the triplet transient $F_R = \log_{10}(V_0/V_m) - \log_{10}(V_0/V_t)$; $F_D = \log_{10}(V_0/V_t)$

In EPA glass at 77 K, DMABA showed a broad absorption centred around 440 nm similar to that of DMABAE (Figure 1). DMANB gave transient absorption peaks around 450 and 550 nm; DEABN showed a low overall absorption in the visible region with the possibility of a small peak at 465 nm. DPTA in EPA at 77 K gave a spectral curve almost identical in form and position to that shown in Figure 3 (TA, PMMA; 293 K) where S_0 state depletion is apparent. TAN in EPA at 77 K exhibited a definite peak at 485 nm with a shoulder to longer wavelengths; in PMMA at 293 K a prominent peak centred on 490 nm was found. In PMMA at room temperature DMAB exhibited a broad peak, maximum *ca.* 470 nm, and TA similarly, peak maximum 490 nm, with a long tail absorption to the red.

(ii) *Rise-decay in rigid media.* For the compound of major interest to this study, TA, it was possible to determine the molar extinction coefficient of the triplet–triplet (T–T) absorption maximum (490 nm) in both PMMA at 293 K and EPA glass at 77 K. Owing to the long triplet-state lifetime a high steady-state concentration of triplets, C_T^∞, could be generated, which was an appreciable fraction, x, of the initial singlet ground-state concentration C_0. In our experiments x was in the range 0.07—0.40. Ground-state depletion leads to a considerable shortening of the triplet absorption rise-time constant, k_r, compared to its decay constant, k_d. If decay and rise processes are exponential, as was found experimentally here (Figure 2), then a simple kinetic analysis shows that[25,26] equation (1) applies. Since C_0 is known and the optical density

$$C_T^\infty/C_0 = x = (k_r - k_d)/k_d \qquad (1)$$

increase on steady illumination can be measured, together with the known optical pathlength (1 to 2 mm in our case), $\varepsilon_m(T\text{-}T)$ can be calculated.

For TA in EPA glass at 77 K we found $\varepsilon_m = 31\,000 \pm$

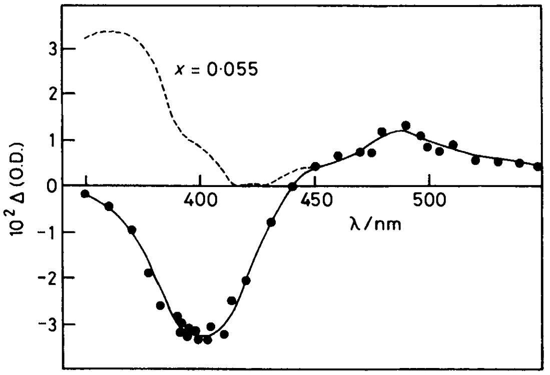


Figure 3. Observed changes in optical density, Δ O.D., on irradiation of a 2.63 × 10^{-3}M solution of TA in PMMA at 293 K. The decrease in optical density centred on 400 nm is due to singlet ground state depletion. The dotted curve shows the computed triplet–triplet absorption for a fractional population x of the triplet state of 0.055. This represents the minimum value of x which leads to Δ(O.D.) $\geqslant 0$ at all wavelengths and enables an upper limit of 66 000 dm^3 mol^{-1} cm^{-1} for the triplet–triplet molar extinction coefficient at 490 nm to be set (the effective optical path length being 0.125 cm in this experiment)

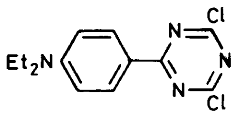
5 000 dm^3 mol^{-1} cm^{-1} (490 nm) on the basis of eight independent determinations, each utilising an accumulation of at least five decay–rise curves. The average k_d value was 0.23 ± 0.02 s^{-1}, which compares favourably with the phosphorescence decay constant (Table 1) and confirms the identity of the absorbing species with the triplet state. Similar studies on TA dissolved in PMMA at 293 K also yielded a value for ε_m(T—T) at 490 nm of 31 000 dm^3 mol^{-1} cm^{-1}, and a mean decay constant of 0.60 ± 0.05 s^{-1}.

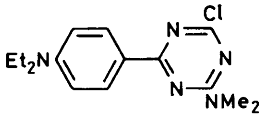
On irradiation of TA in PMMA at 293 K an obvious ground-state depletion, resulting in an increase in light transmittance by the sample, was observed (Figure 3). Knowing the $S_1 \longleftarrow S_0$ absorption spectrum it is possible to calculate the minimum value for the fractional depletion x[27] (equivalent to the fractional population of the triplet state) which ensures a positive or at least zero change in optical density (dotted curve, Figure 3). An upper limit to ε_m(T–T) of 66 000 dm^3 mol^{-1} cm^{-1} at 490 nm was thus obtained.

Attempts to apply the irradiation-intensity-variation method[28] were only partially successful owing to photodecomposition ($\varphi \leqslant 0.001$) during the much longer irradiation times required as compared with the kinetic method. Values of ε_m approaching 31 000 dm^3 mol^{-1} cm^{-1} were obtainable using higher concentrations of TA in PMMA.

(iii) *Laser photolysis in fluid media* (293 K). Transient absorption spectra are shown in Figure 4(a)—(f) with qualifying remarks in the footnotes.

The presence of molecular oxygen in solution led to a strong quenching of the transient absorption in all cases.


TA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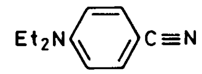
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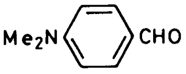
DMAB


DMANB

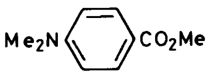
DMABAE

Table 2. Intersystem crossing yields at 293 K

Compound	Solvent	$\varphi_{i.s.c.}$ (LP)[a]	$\varphi_{i.s.c.}$ (CH)[b]
TA	Benzene	0.11	
	Toluene	0.10	0.09
	Tetrahydrofuran	0.15	0.15
	n-Butanol	0.14	
	Ethanol	0.07	
	Acetonitrile	0.05	
	PMMA	0.09	
TAN	Toluene		0.027
	Tetrahydrofuran		0.017

[a] $\varphi_{i.s.c.}$ (LP): yield determined by pulsed-laser photolysis. [b] $\varphi_{i.s.c.}$ (CH): yield determined by sensitised dimerization of cyclohexa-1,3-diene.

The decays of the transient absorptions obeyed first-order kinetics fairly well in most systems, the half-lives being in the range 10—40 μs. No change in spectral curve shape with time was found except in the cases of *NN*-dimethylaminonitrobenzene (DMANB) in n-butanol or in ethanol. In this case a longer lived ($\tau_{\frac{1}{2}} > 100$ μs) transient appeared to be generated from the triplet species which had an absorption spectrum similar to that of the triplet species [see curve y, Figure 4(e)]. Characterisation of this intermediate requires further evidence. The species could be a nitro anion radical or its protonated form, formed by an electron transfer reaction, *e.g.* equation (2). Alternatively, the species may be a radical such as $\cdot CH_2\text{–}N(Me)C_6H_4NO_2$ or $Me\text{–}\dot{N}\text{–}C_6H_4NO_2$.[29]

$$^3ArNO_2 + ROH \longrightarrow ArNO_2^{\cdot -} + RO\cdot + H^+ \quad (2)$$

(c) *Intersystem Crossing Yields*.—Table 2 gives the i.s.c. values determined for TA and TAN in various solvents which can be related to the known fluorescence quantum yields.

The method of triplet counting using the sensitized dimerization of cyclohexadiene could not be applied in some solvents because of solubility problems and suspected side-reactions.

Intersystem crossing yields were estimated from the pulsed laser photolysis data using benzophenone in benzene as a reference system to calibrate the 347 nm laser pulse input under standard optical and geometric conditions (see Experimental section). In equation (3), S = sample, R = reference,

$$\frac{\Delta\ \mathrm{O.D.}_{\mathrm{max.}}\ (S, \lambda_S)}{\Delta\ \mathrm{O.D.}_{\mathrm{max.}}\ (R, \lambda_R)} = \frac{\varepsilon_T(\lambda_S)\ \varphi_{i.s.c.}(S)}{\varepsilon_T(\lambda_R)\ \varphi_{i.s.c.}(R)} \qquad (3)$$

and Δ O.D.$_{\mathrm{max.}}$ is the observed optical density change at the appropriate wavelength λ_S and λ_R immediately following the laser pulse. The pulse is assumed to be short in duration relative to the triplet lifetimes. Under our conditions the decay of benzophenone triplets followed good first-order kinetics, as did that of the triazine dye TA also, thus providing some confidence in the use of the equation (3). The reported values for $\varphi_{i.s.c.}$ (LP) in Table 2 assume that the triplet–triplet molar extinction coefficient for TA at the absorption maxima

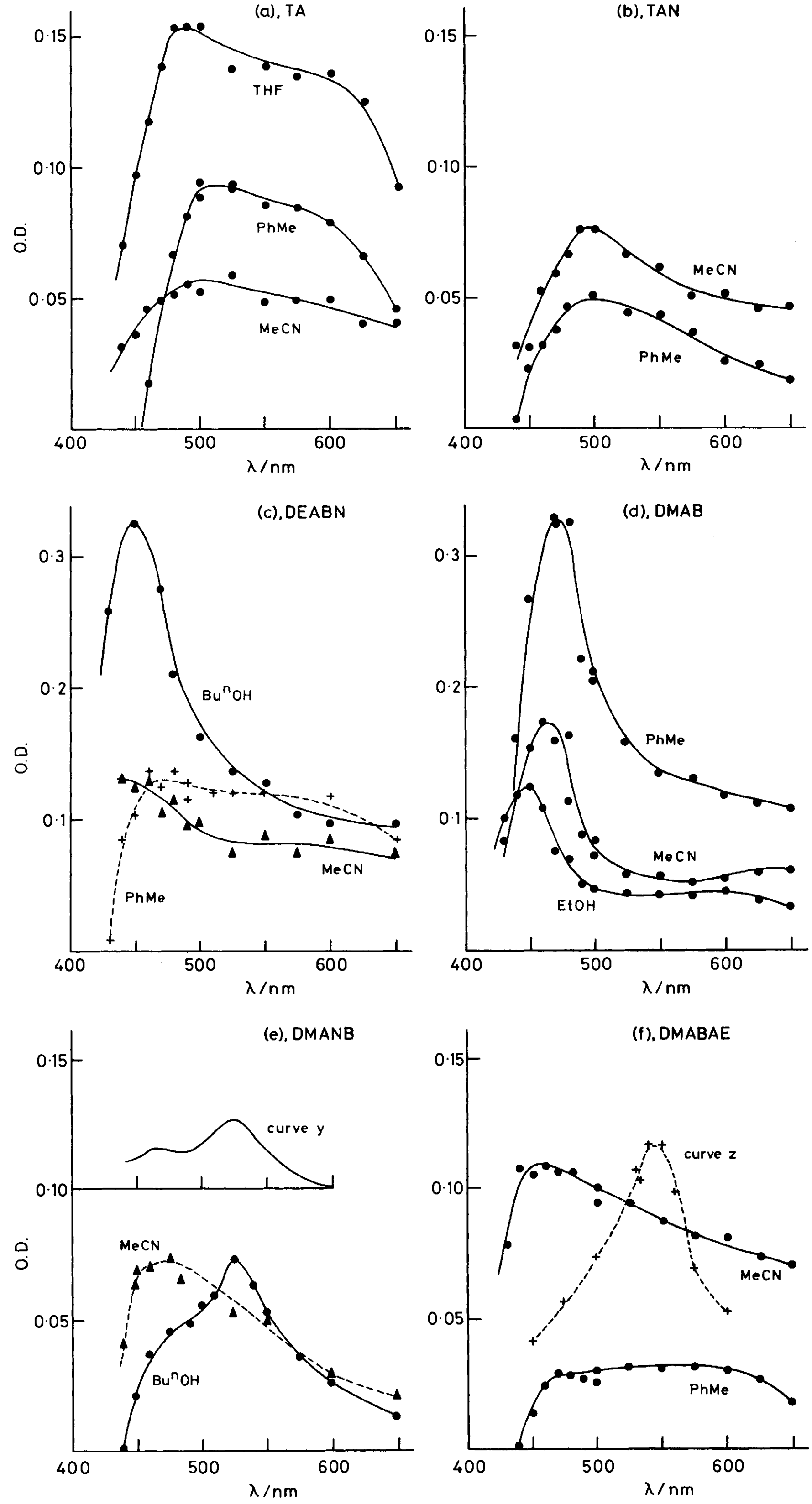

Figure 4. Triplet absorption spectra of p-$R_2NC_6H_4A$ compounds obtained on laser photolysis (347 nm) of fluid solutions at 293 K. All spectra, except curve ' y ' in (e), correspond to the maximum optical densities observed shortly after (*ca.* 1 μs) the laser pulse. Curve ' y ' was obtained for DMANB in Bu^{n}OH 100 μs after the laser pulse. Curve ' z ' (+, – – – –) is the absorption spectrum of benzophenone triplets in benzene determined under conditions identical to those pertaining to the other spectra. Ground-state depletion may be distorting the transient absorption spectra at wavelengths shorter than *ca.* 440 nm in the following cases: (a) tetrahydrofuran (THF) and MeCN; (b) MeCN. Some distortions of the triplet–triplet absorption spectra at shorter wavelengths are likely to be present for strongly fluorescent toluene solutions (<460 nm), owing to the tail of the laser pulse, in the cases of (a), (b), (c), and (f)

Table 3. Triplet transient absorption of TA in toluene–acetonitrile mixtures at 293 K on pulsed laser photolysis at 347 nm

% v/v Acetonitrile	Maximum O.D. change [a]	φ_F [b]
0 (PhMe)	0.052	0.54
0.5	0.067	0.45
5	0.086	0.12
10	0.082	0.037
15	0.057	0.017
100 (MeCN)	0.018	0.0006

[a] Observed maximum change in optical density at the triplet–triplet absorption maximum (range 500—540 nm) following the laser pulse. [b] Fluorescence quantum yield, as determined in separate experiments using optically dilute solutions of TA in toluene–acetonitrile mixtures.

(*ca.* 490 nm in all solvents) is constant from solvent to solvent at 31 000 dm^3 mol^{-1} cm^{-1}, the value determined for EPA glass at 77 K and for PMMA at 293 K. In the cases where comparison is possible good agreement was found for $\varphi_{\rm i.s.c.}$ values determined by the two methods.

The trend in $\varphi_{\rm i.s.c.}$ on increasing solvent polarity using neat solvents (see Table 2) was substantiated by measurements of the yield of TA triplet transient generated in toluene–acetonitrile solvent mixtures (Table 3) for which (i) the polarity could be smoothly adjusted and (ii) the fluorescence quantum yields were also known.[1,2]

Discussion

The identification of the transient absorbing species with the phosphorescent triplet state is clear from the good correspondence of the respective decay rate constants for the dye TA dissolved in EPA glass at 77 K and in PMMA at 293 K. The great similarity of the transient optical absorptions detected on irradiation of TA in fluid and in rigid media suggests that the species generated and detected on laser photolysis of the fluid media is also the triplet. The strong quenching by molecular oxygen in the fluid media supports this inference.

Since the transient optical density changes obtained for the other compounds were low (<0.02) even in EPA glass at 77 K, the decay curves were noisy. Thus, the extracted first-order decay constants are not very precise and the agreement of the triplet–triplet absorption and phosphorescence decay constants (Table 1), while satisfactory, is not conclusive.

The long phosphorescence lifetimes (0.3—5 s) of the *NN*-dialkylaniline derivatives in low-temperature glasses indicate a π,π^* character for the lowest triplet state. The electron-acceptor substituent does not appear to introduce a large perturbation (*NN*-dimethylaniline[30] in EtOH–Et$_2$O glass at 77 K shows a phosphorescence, $\lambda_{\rm max.}$ 417 nm, and lifetime 2.4 s). The exceptions possess NO$_2$ and CHO substituents, for which the non-radiative decay ($S_0 \longleftarrow T_1$) is nearly an order of magnitude faster than for the other substituents (CN, C$_3$N$_3$Cl$_2$, CO$_2$H, CO$_2$Me), and whose origin may lie in the greater opportunity for spin–orbit coupling *via* vibronic mixing of the $^3(\pi,\pi^*)$ state with a relatively low-lying $^3(n,\pi^*)$ state.

The triplet-state energies, as gauged from phosphorescence wavelength maxima, tend to decrease with increase in substituent electron-acceptor character [where CO$_2$R $<$ CN $<$ C=O $<$ C$_3$N$_2$Cl (NMe$_2$) $<$ C$_3$N$_2$Cl$_2$ $<$ NO$_2$ as judged from n.m.r. chemical shift and optical absorption correlations[16]]. However, increasing conjugation must also depress the triplet energy, as is seen on comparison of TA with DMANB.

The triplet–triplet absorption spectra of this series of compounds consist of two major absorptions in the 400—700 nm region akin to the 340 and 460 nm bands observed in the spectrum of triplet *NN*-dimethylaniline.[23,31,32] Increasing rigidity of the solvent medium favours the prominence of the shorter wavelength band whose position is altered by the electron-acceptor substituent A (for which increase in conjugative size is more important than the π-electron withdrawal ability). In fluid media, an increase in solvent polarity changes the absorption band envelope only slightly with the shorter wavelength band undergoing a hypsochromic shift.

A prime target of our investigations was to measure the intersystem crossing yield, $\varphi_{\rm i.s.c.}$, for the triazine dye, TA, in various solvent environments for which the fluorescence behaviour has been documented.[1,2] Briefly, the fluorescence of TA is progressively and strongly quenched with increase in the polarity of low-viscosity solvents. The quenching is ascribed to an internal conversion process transforming the planar i.c.t. excited singlet state into a twisted, highly dipolar (t.i.c.t.) excited singlet state (path a in the Scheme).

The low values of $\varphi_{\rm i.s.c.}$ obtained in all solvents (Table 2) eliminate enhanced intersystem crossing as the reason for the strong quenching of the initial fluorescent excited singlet state.

The variation in $\varphi_{\rm i.s.c.}$ with solvent polarity for neat solvents (Table 2) parallels the variation in the extent of triplet–triplet absorption for toluene–acetonitrile binary solutions of the dye TA (Table 3).

A direct internal conversion process to the ground state from planar $^1(^{\delta+}\text{D–A}^{\delta-})^*$ is not eliminated by the $\varphi_{\rm i.s.c.}$ data as the dominant fluorescence quenching mode. However, this appears unlikely since it requires a concomitant large increase in the rate of intersystem crossing and it is difficult to explain such large solvent-induced enhancements of *both* i.c. and i.s.c. without recourse to changes in the conformation of the donor dialkylamino moiety. The latter idea is the basis, however, of the t.i.c.t. approach! The intermediacy of a second, essentially non-fluorescent, highly dipolar excited singlet state $^1(^{+\bullet}\text{D–A}^{\bullet-})^*$ enables the present results to be rationalised. It is significant that $\varphi_{\rm i.s.c.}$ attains a maximum in the solvent polarity region in which the postulated twisted i.c.t. singlet state is also approaching its maximum yield, *i.e.*, when fluorescence is very strongly reduced (tetrahydrofuran, $\varphi_F = 0.033$, or *ca.* 10% v/v acetonitrile in toluene solutions, for example).

On the basis of the t.i.c.t. model, we propose that $\varphi_{\rm i.s.c.}$ for the twisted singlet state is *ca.* 0.15 in solvents of low to medium polarity, not much higher than that of the planar excited singlet state for which $\varphi_{\rm i.s.c.} =$ *ca.* 0.10. Thus, while the rate of intersystem crossing from the twisted $^1(^{+\bullet}\text{D–A}^{\bullet-})^*$ state *may be* enhanced relative to that of the planar $^1(^{\delta+}\text{D–A}^{\delta-})^*$ state (*i.e.*, path d of the Scheme) this is compensated by enhanced internal conversion into the twisted ground state (path c of the Scheme). The energy gap between the twisted Franck–Condon ground state and the twisted excited singlet state will be reduced appreciably (40 kJ mol^{-1}) compared to the corresponding energy gap of the planar species. Decrease of this energy gap by the differential interaction of polar solvent with the highly dipolar twisted excited singlet species and the twisted ground state (which is expected to be even less dipolar than the planar ground state) can account for the gradual decrease in $\varphi_{\rm i.s.c.}$ from the twisted excited singlet state in moving from medium to high polarity solvents. The intersystem crossing rate, being dependent probably on nuclear hyperfine coupling perturbations, should be approximately independent of solvent whereas the internal conversion rate can be enhanced *via* decreasing energy gap between the two potential surfaces.

In conclusion, dramatic enhancements of $\varphi_{\rm i.s.c.}$ with changes in solvent polarity have not been observed but the results are conveniently and adequately rationalised on the basis of the t.i.c.t. model.

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References

1 D. J. Cowley and P. J. Healy, *J. Chem. Soc., Perkin Trans. 2*, 1979, 484.
2 D. J. Cowley and I. Pasha, *J. Chem. Soc., Perkin Trans. 2*, 1981, 918.
3 Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann, *Nouv. J. Chim.*, 1979, **3**, 443, and references therein.
4 D. Huppert, S. D. Rand, P. M. Rentzepis, P. F. Barbara, W. S. Struve, and Z. R. Grabowski, *J. Photochem.*, 1982, **18**, 89.
5 W. Rettig, *J. Phys. Chem.*, 1982, **86**, 1970.
6 W. Rettig and M. Zander, *Chem. Phys. Lett.*, 1982, **87**, 229.
7 A. A. Ayuk, W. Rettig, and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 553.
8 Y. Wang, M. McAuliffe, F. Nouak, and K. B. Eisenthal, *J. Phys. Chem.*, 1981, **85**, 3736.
9 D. J. Cowley and A. H. Peoples, *J. Chem. Soc., Chem. Commun.*, 1977, 352.
10 R. A. Auerbach, G. W. Robinson, and R. W. Zwanzig, *J. Chem. Phys.*, 1980, **72**, 3528.
11 D. Huppert, H. Kanety, and E. M. Kosower, *Chem. Phys. Lett.*, 1981, **84**, 48.
12 M. Migita, T. Okada, N. Mataga, N. Nakashima, K. Yoshihara, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, 1980, **72**, 229.
13 T. Okada, I. Karaki, E. Matsuzawa, N. Mataga, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, 1981, **85**, 3957.
14 M. Van der Auweraer, A. Gilbert, and F. C. De Schryver, *J. Phys. Chem.*, 1981, **85**, 3198.
15 J. Lipinski, H. Chojnacki, Z. R. Grabowski, and K. Rotkiewicz, *Chem. Phys. Lett.*, 1980, **70**, 449.
16 R. A. Shaw and P. Ward, *J. Chem. Soc. B*, 1967, 123.
17 R. A. Shaw and P. Ward, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2075.
18 D. J. Cowley and P. J. Healy, *Proc. R. Irish Acad.*, 1977, 397.
19 M. A. West, K. J. McCallum, R. J. Woods, and S. J. Formosinho, *Trans. Faraday Soc.*, 1970, **66**, 2135.
20 H. Labhart and W. Heinzelmann, 'Organic Molecular Photophysics,' ed. J. B. Birks, Wiley–Interscience, New York, vol. 1, 1973, p. 326.
21 D. J. Cowley, *Helv. Chim. Acta*, 1977, **61**, 184.
22 G. F. Vesley and G. S. Hammond, *Mol. Photochem.*, 1973, **5**, 367.
23 K. Kimura, S. Arimitsu, N. Yamamoto, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1274.
24 T. P. Carsey, G. L. Findley, and S. P. McGlynn, *J. Am. Chem. Soc.*, 1979, **101**, 4502.
25 D. Lavalette and A. Kastler, *C. R. Acad. Sci., Ser. B*, 1968, **266**, 279; D. Lavalette, *J. Chim. Phys.*, 1969, **66**, 1853.
26 M. V. Alfimov, I. G. Batekha, Y. B. Sheck, and V. I. Gerke, *Spectrochim. Acta, Part A*, 1971, **27**, 329.
27 See ref. 20, p. 302, for full references to this approach.
28 D. S. McClure, *J. Chem. Phys.*, 1951, **19**, 670.
29 J. Wolleben and A. C. Testa, *J. Phys. Chem.*, 1977, **81**, 429.
30 V. L. Ermolaev, *Opt. Spectrosc.*, 1961, **11**, 266.
31 K. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, 1968, **73**, 1868.
32 E. Zador, J. M. Warman, and A. Hummel, *J. Chem. Soc., Faraday Trans. 1*, 1976, 1368.

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