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Intramolecular Charge Transfer in Rigidly Linked Naphthalene–Trialkylamine Compounds

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The photophysical properties of two rigidly linked naphthalene–trialkylamine compounds have been examined in a series of solvents using transient absorption spectroscopy and time-resolved spectrofluorimetry. In alkane solvents, excitation of either compound populates a locally excited (naphthalene-like) singlet state (LESS) which fluoresces strongly and which retains a relatively long lifetime. In polar aprotic solvents, the lifetime of the LESS is substantially reduced owing to formation of an intramolecular charge-transfer state (CTS), which corresponds to full electron transfer across the molecule. The rate of formation of the CTS, under such conditions, is extremely fast and comparable to the reorientation time of the solvent. Deactivation of the CTS, which occurs on the nanosecond timescale, involves fluorescence, population of a locally excited triplet state, and charge recombination to restore the ground state. The rate of formation of the CTS is markedly slower in alkanol solvents that can hydrogen bond to the N atom on the donor and, in such cases, charge transfer involves an additional activation energy of *ca.* 0.12 eV. Under these conditions, it appears that the controlling feature involved in formation of the CTS concerns breakage of a hydrogen bond, whereas in aprotic solvents the intrinsic barrier is likely to be associated with the modest structural changes that might accompany charge transfer. The rates of formation and deactivation of the CTS are discussed briefly in terms of current electron-transfer theory.

The nature of the solvent can exert a pronounced influence on the rates of photochemical reactions, especially those involving electron transfer[1] and/or conformational exchange.[2] Indeed, the solvent can affect the dynamics of electron-transfer reactions by modifying thermodynamic properties of the system,[3] by perturbing frictional forces between chromophore and solvent bath,[4] and by modulating the rate of solvent realignment to the change in charge distribution.[5] Numerous studies have addressed various aspects of solvent-controlled electron transfer[6–12] over the past 20 years or so and a good theoretical understanding of such processes has been attained.[13–16] However, for meaningful evaluation of how the nature of the solvent modifies kinetic parameters it is necessary to employ molecular systems having donor and acceptor moieties held in well defined positions so that electron transfer can be separated from diffusion and/or rotation. A second requisite for detailed investigation of such systems in that the product of the intramolecular electron-transfer step must be readily detectable by time-resolved spectroscopic methods. This is most easily accomplished with compounds that exhibit fluorescence from a charge-transfer state formed *via* intramolecular electron redistribution following initial population of a non-polar excited singlet state. Often, formation of the charge-transfer state requires a modest structural change in order to optimise the geometry for charge transfer, giving rise to the so-called twisted intramolecular charge transfer (TICT) phenomenon,[17–20] and it should be noted that the compounds described herein can undergo an important conformational change associated with inversion of the amine. This process has the effect of orienting the non-bonding pair on the N atom(s) essentially perpendicular to or parallel with the plane of the naphthyl ring, although it is unlikely that the N atom changes its state of hybridization[21] during the charge-transfer step. In principle, therefore, inversion of the amine could play a key role in controlling the extent of electronic coupling between donor and acceptor but we have no information regarding the rate or activation energy for this process.

Here, we report the photophysical properties of two naphthalene–trialkylamine compounds in which the redox-active moieties are separated by two rigid σ bonds. The luminescence spectra of structurally similar compounds have been described previously[22] and used to estimate the extent of Coulombic stabilization of the charge-transfer state. A closely-related compound has been studied by Wasielewski *et al.*,[23] who reported exciplex-type emission in slightly polar solvents. It was further shown that formation of the exciplex was extremely fast in polar solvents (*i.e.* <20 ps) but the exciplex itself survived for many nanoseconds. For our systems, we have used both time-resolved fluorescence spectroscopy and transient absorption spectrometry in order to elicit rates of formation and deactivation of the charge-transfer state in different solvents. The advantage of using transient absorption spectroscopy to monitor the course of reaction is that it is possible to demonstrate unequivocally that decay of the charge-transfer state results in population of an excited triplet state and to ascertain that the charge-transfer state corresponds to net electron transfer. By using rigidly linked donor–acceptor systems of this type, it becomes possible to establish kinetic data for intramolecular charge transfer and subsequent charge recombination, and thereby estimate the levels of electronic communication between the reactants in their various states.

Experimental

2-Methyl-1,3-dihydrobenz[*d*,*e*]isoquinoline (DHBIQ) and 2,7-dimethyl-1,3,6,8-tetrahydrobenzo[*m*,*n*][3,8]phenanthroline (THBP) were prepared following the method of Hünig *et al.*[24] and were recrystallised from chlorobenzene. Their structures are shown in Fig. 1. Thus, naphthalene-1,8-dicarboxylic acid (21.6 g, 0.10 mol) was mixed with 40% aqueous methylamine (150 ml) and excess methylamine was evaporated at

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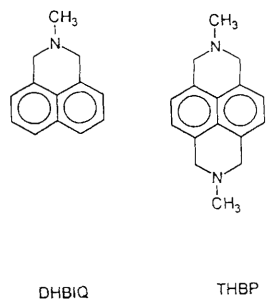

Fig. 1 Structures of the two compounds used in this study

40 °C under reduced pressure. The solid material was filtered, washed with diethyl ether, and dried at 50 °C under reduced pressure. The resultant solid (24.7 g) was dissolved in nitrobenzene (250 ml) and refluxed in a Dean and Stark apparatus until dehydration was complete. On cooling to room temperature, a solid deposited. This was isolated by filtration, washed with cold diethyl ether, and dried at 70 °C under reduced pressure. The powdered solid (19.0 g, 0.09 mol) was added slowly to a stirred suspension of $AlCl_3$ (14.6 g, 0.11 mol) and $LiAlH_4$ (11.8 g, 0.31 mol) in anhydrous tetrahydrofuran (250 ml) maintained under N_2 in an icebath. The mixture was stirred for 30 min at room temperature before being refluxed for 3 h, cooled to 4 °C, and added cautiously to a mixture of tetrahydrofuran (250 ml) and ice (100 g). The solid material was filtered and extracted with 5 × 1 l of boiling $CHCl_3$. The $CHCl_3$ extracts were combined, dried with $MgSO_4$, and evaporated to dryness to give the required compound. After recrystallization from chlorobenzene, the final yield of DHBIQ was 11.4 g. Found (calc.) for $C_{13}H_{13}N$ ($M = 183.25$): C, 85.41 (85.20); H, 7.09 (7.15); N, 7.50% (7.65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.84 (s, 3); 4.16 (d, 4 H); 7.43 (d, 2 H); 7.64 (t, 2 H); 7.93 (d, 2 H). CIMS: $m/z = 183$ (54.8%); 182 (100%). Calc. for $C_{13}H_{13}N$: 183.1048. Found: 183.1039. Samples of THBP were prepared as above but starting from naphthalene-1,4,5,8-tetracarboxylic acid. Found (calc.) for $C_{16}H_{18}N_2$ ($M = 238.33$): C, 80.68 (80.63); H, 7.42 (7.61); N, 11.90% (11.76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.55 (s, 6 H); 3.86 (d, 8 H); 7.10 (d, 4 H). CIMS: $m/z = 238$ (71.6%); 237 (100%). Calc. for $C_{16}H_{18}N_2$: 238.1470. Found: 238.1463.

Solvents were spectroscopic grade materials and were redistilled as necessary. UV–VIS absorption spectra were recorded on a Hitachi U3210 spectrophotometer. Fluorescence measurements were recorded on a Perkin-Elmer LS5 spectrofluorimeter and were corrected for the spectral responses of the instrument. Both spectrometers were interfaced to a microcomputer for data storage and manipulation. Fluorescence spectra were standardised against naphthalene in the same solvent using optically dilute solutions and an excitation wavelength of 265 nm. The fluorescence quantum yields at room temperature were calculated from integration of the appropriate spectra by comparison to naphthalene in cyclohexane ($\phi_f = 0.29$)[25] and were corrected for differences in solvent refractive index.[26] Temperature variations were made with a thermostatted sample cell connected to a VWR Model 1140 circulating fluid bath, the temperature being monitored by a thermocouple in direct contact with the solution. Low-temperature emission spectra were recorded at 77 K with a Spex Fluorolog spectrofluorimeter using a mechanical chopper to isolate phosphorescence. All emission studies were made in deoxygenated media.

Electrochemical measurements were made by cyclic voltammetry using a glassy carbon working electrode and a Pt wire as counter-electrode. A saturated calomel electrode was used as reference. The voltammograms were recorded in deoxygenated acetonitrile containing tetra-*N*-butyl ammonium tetrafluoroborate (0.2 mol l^{-1}) as background electrolyte. The quoted redox potentials were reproducible to within 15 mV.

Time-resolved fluorescence studies were made with an Antares 76S Nd-YAG laser mode-locked at 76 MHz. The second harmonic ($\lambda = 532$ nm) was used to pump a Spectra Physics model 375B dye laser operated with Rhodamine 6G. The 590 nm output from the dye laser was cavity-dumped at 45 kHz and frequency-doubled to 295 nm in order to serve as excitation source. Part of the cavity-dumped output was used as the start pulse for single-photon counting studies. Emitted photons were collected at 90° to excitation and focussed onto the entrance slit of a Spex monochromator interfaced to a Hamamatsu microchannel plate detector operated at 3.5 kV. Data analysis was made by computer iterative procedures using scattering solutions for deconvolution of the instrumental response (FWHM *ca.* 70 ps).

Conventional laser flash photolysis studies were made with a frequency-quadrupled, Q-switched Quantel YG481 Nd-YAG laser, used in conjunction with a pulsed Xe arc lamp as monitoring beam. The 10 ns pulses ($\lambda = 266$ nm) from the laser were attenuated as necessary with metal screen filters and defocussed onto the sample cell. The solution was adjusted to possess an absorbance at 266 nm of *ca.* 0.2 and was purged continuously with N_2. Transient differential absorption spectra were recorded point-by-point with five individual records being averaged at each wavelength. Kinetic studies were made at fixed wavelength with *ca.* 30 individual records being averaged at each time delay, baseline-corrected and analysed by computer non-linear least-squares iteration. The laser intensity was calibrated using naphthalene in cyclohexane as a standard, for which the triplet quantum yield[27] is 0.71 and the molar differential absorption coefficient[28] at 415 nm is 24 500 l mol^{-1} cm^{-1}.

Experiments requiring improved time resolution were made with either of two instruments, both of which have been described before.[29,30] The spectrometers used a frequency-doubled, mode-locked cw Nd-YAG laser (76 or 82 MHz) to pump synchronously a Rhodamine 6G dye laser. The amplified output from the dye laser was frequency doubled to provide sub-ps excitation pulses at 295 nm. Residual fundamental output was used to generate a white light continuum for use as the probe beam by focussing into D_2O. The excitation and probe pulses were directed almost collinearly onto the sample cuvette and transient absorption measurements were made with a multichannel photodiode detector after dispersion of the optical signal with a spectrograph. Where necessary, band shapes were corrected for non-linear spectral dispersion (spectral chirp). Kinetic studies were made by overlaying spectra collected at different delay times and data analysis was made by computer, non-linear least-squares iteration. The time resolution of these instruments is better than 1 ps but the small signals observed, together with their appearance at either end of the measurable spectral range, limit the precision of experimental data collected with these samples.

Results and Discussion

Photophysical Properties in Non-polar Solvents

In alkane solvents, both DHBIQ and THBP exhibit photophysical properties that resemble those of naphthalene. Thus, absorption spectra recorded for the two compounds in an alkane solvent exhibit a series of highly structured absorption transitions in the 200–300 nm region (Fig. 2A). Three series of bands can be resolved, each being red-shifted with respect to naphthalene in accordance with well documented substituent

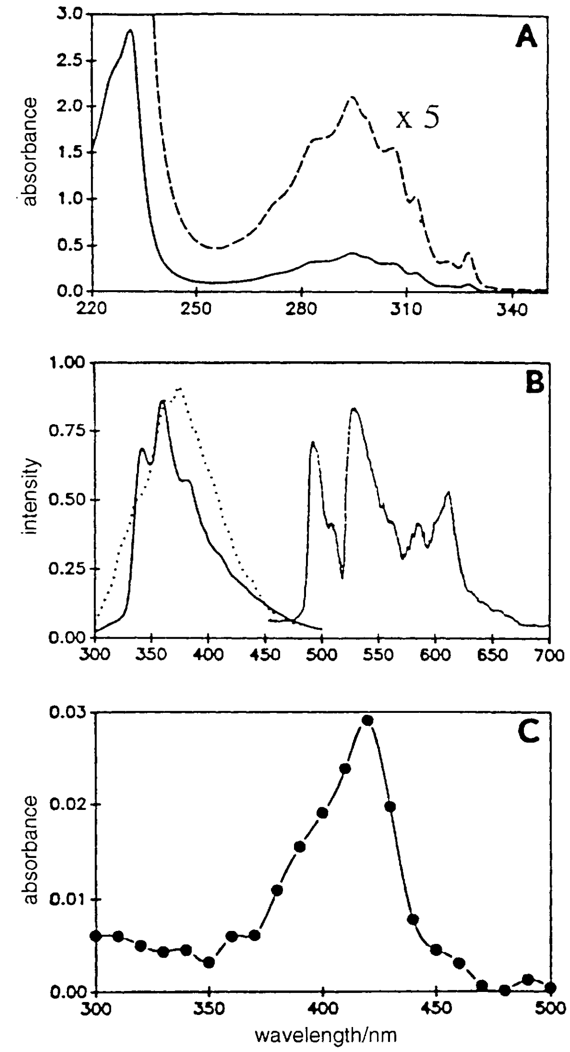

Fig. 2 A, UV-VIS absorption; B, fluorescence and phosphorescence, and C, triplet–triplet absorption spectra recorded for THBP in pentane. The fluorescence spectrum recorded for DHBIQ is also shown on panel B as a dashed line.

effects,[31] that can be attributed to π–π^* transitions. The positions of the band maxima are essentially independent of solvent polarity, even in polar solvents. For DHBIQ, the lowest energy absorption transition is very weak ($\varepsilon \approx 300$ l mol^{-1} cm^{-1}) and corresponds to promotion to the ^1L_b state; the energy of this excited state (E_s), as calculated from the (0, 0) absorption band located at 322 nm, is given in Table 1. A more intense transition ($\varepsilon \approx 6725$ l mol^{-1} cm^{-1}) is centred at 285 nm and corresponds to population of the ^1L_a state. A much more intense transition ($\varepsilon = 123000$ l mol^{-1} cm^{-1}), which corresponds to promotion to the ^1B_b state, is centred at 222 nm. For THBP, the $^1A \rightarrow {}^1B_b$ band ($\varepsilon \approx 59300$ l mol^{-1} cm^{-1}) is centred at 232 nm while the $^1A \rightarrow {}^1L_a$ band is red-shifted, the maximum occurring at 295 nm ($\varepsilon \approx 8700$ l mol^{-1} cm^{-1}), so that it overlaps the $^1A \rightarrow {}^1L_b$ band. Consequently, the (0,0) band, which is located at 328 nm, appears more intense ($\varepsilon \rightarrow 1720$ l mol^{-1} cm^{-1}) than expected for promotion to a pure ^1L_b state.

Table 1 Comparison of the photophysical properties of the various compounds as studied in deoxygenated pentane

compound	E_s[a] /kJ mol^{-1}	SS[b] /cm^{-1}	ϕ_f[c]	τ_s[d] /ns	E_t[a] /kJ mol^{-1}	τ_t[e] /μs
naphthalene	385	310	0.19	70	255	200
DHBIQ	370	290	0.07	2.6	245	250
THBP	365	280	0.30	5.3	240	280

[a] ±2 kJ mol^{-1}. [b] Stokes' shift, ±30 cm^{-1}. [c] ±10%. [d] ±0.1 ns. [e] ±50 μs.

The fluorescence spectrum recorded for THBP in pentane is well structured (Fig. 2B) with a small Stokes' shift (SS) (Table 1) and for which the excitation spectrum matches the absorption spectrum across the entire UV region. The fluorescence spectral profile shows reasonable mirror symmetry with the lowest-energy absorption transition but, in view of the low oscillator strengths of these absorption bands, the relationship is far from ideal.[32] For DHBIQ in pentane, the fluorescence spectrum is less well resolved (Fig. 2B), while the fluorescence quantum yield (ϕ_f) was found to be somewhat lower than that of naphthalene under the same experimental conditions (Table 1). In contrast, THBP shows a slightly higher fluorescence quantum yield, possibly owing to the more pronounced mixing within the π–π^* manifold and because of the increased molar absorption coefficient for the lowest-energy absorption transition. The lifetimes of the excited singlet states (τ_s) were measured in pentane solution and are listed in Table 1. The fluorescence decay profiles recorded for both compounds could be analysed satisfactorily in terms of a single exponential with the derived τ_s values being much shorter than that measured for naphthalene.

At 77 K in a pentane glass, both fluorescence and phosphorescence could be observed (Fig. 2B), the latter being assigned to π–π^* emission in view of its characteristic spectral profile. The (0,0) bands for the phosphorescence transitions were located at 485 and 495 nm, respectively, for DHBIQ and THBP and these values were used to calculate the triplet energy levels (E_t) collected in Table 1. In deoxygenated pentane at room temperature the triplet state is readily observed by laser flash photolysis methods, following excitation at 266 nm, and the derived transient differential absorption spectra are similar to that recorded[27,28] for naphthalene (Fig. 2C). In each case, the spectrum consists of a strong transition ($\varepsilon \approx 25000$ l mol^{-1} cm^{-1}) centred around 420 nm. Decay of the triplet state followed first-order kinetics at low laser intensity but involved bimolecular triplet–triplet annihilation at higher laser power. The rate of deactivation of the triplet excited state was also found to increase with increasing concentration of the compound. Triplet state lifetimes (τ_t), extrapolated to zero concentration and zero laser power, remain similar to the value found for naphthalene (Table 1). Minor variations in the apparent triplet lifetimes most probably reflect small differences in the concentration of dissolved oxygen and the error involved in the various extrapolations.

Picosecond laser flash photolysis studies carried out with THBP and DHBIQ in hexane indicate that, immediately after the excitation pulse, the excited singlet state is present (Fig. 3). This species is characterised by a fairly broad absorption transition centred around 450 nm; the broadness of the transient absorption spectrum with respect to that of naphthalene may be due to the alkyl substitution and to vibronic mixing with the ^1L_a state and/or a charge-transfer state. The excited singlet state decays over several ns to generate the corresponding excited triplet state, the latter species appearing as a sharper absorption transition centred around 420 nm (Fig. 3).

On the basis of the noted similarity to naphthalene, excitation of DHBIQ or THBP in nonpolar solvents is believed to populate a π–π^* locally excited (*i.e.* naphthalene-like) singlet state (LESS). Fluorescence from the LESS is readily observed for both compounds and, from the small Stokes' shift, it appears that the LESS is of similar polarity and geometry to the corresponding ground state. Intersystem crossing, which

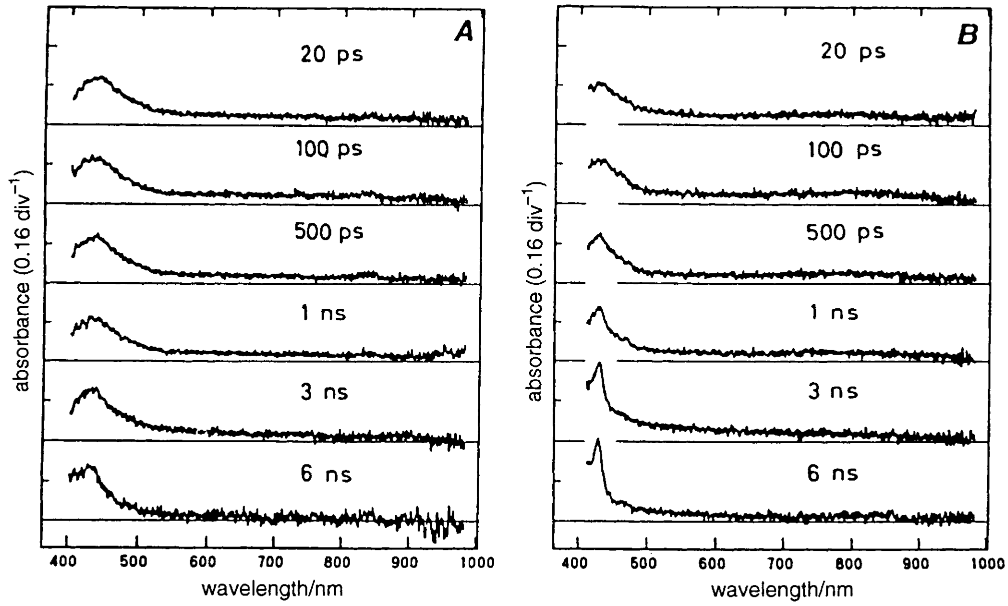

Fig. 3 Picosecond time-resolved transient absorption spectra recorded in hexane solution for *A*, DHBIQ and *B*, THBP showing conversion of the LESS into the locally excited triplet state

populates a π–π^* locally excited triplet state, does not involve a significant change in molecular geometry, as evidenced by examination of the phosphorescence spectra. The higher ϕ_f and τ_s found for THBP relative to DHBIQ may be a consequence of the mixing of ^1L_a and ^1L_b states that occurs for this compound. This effect serves to increase the radiative rate constant and to decrease the rate of non-radiative transitions, owing to the change in symmetry. The shortness of the lifetimes noted for the LESS of the amino-substituted compounds relative to naphthalene is attributed to a small extent of mixing of the π–π^* LESS with a low-lying charge-transfer state, as discussed below for the compounds in polar media.

Photophysical Properties in Polar Aprotic Solvents

For both DHBIQ and THBP, a slight increase in the polarity of the solvent, as expressed in terms of the static relative permittivity (ε_s), results in a dramatic decrease in fluorescence from the LESS and in the concomitant appearance of a fluorescence band situated at lower energy (Fig. 4). For the same solvents, the ground-state absorption spectra remain essentially insensitive to changes in ε_s and, in particular, there is no indication of a new (charge-transfer) absorption band. The long-wavelength fluorescence band observed in polar solvents (Fig. 4) is structureless, fairly broad, and fits reasonably well to a Gaussian profile. Fluorescence quantum yields measured for this new band were <0.005 in all solvents; ϕ_f values estimated for the LESS in polar aprotic solvents were <0.001. Furthermore, the peak maximum of the long-wavelength fluorescence band (λ_{CTS}) moved to longer wavelength with increasing polarity of the solvent (Tables 2 and 3). The decrease in energy, and consequent increase in Stokes' shift, with increasing solvent polarity indicates to us that this excited state is significantly more polar than is the corresponding ground state. This behaviour is consistent with the observed fluorescence emanating from an intramolecular charge-transfer state (CTS) arising *via* charge transfer from the amine donor to the excited singlet state of the naphthalene-like chromophore.[33] As such, the position of the emission maximum reflects the extent of solvent stabilization of the dipolar species (or exciplex).[34] Despite good correlations between the CTS emission maximum and the solvent Pekar polarity function,[35,36] uncertainties about the size of the solvent cavity prevent precise calculation of the change in dipole moment that accompanies charge transfer,[37] this latter value being estimated as being *ca.* 25 D.†

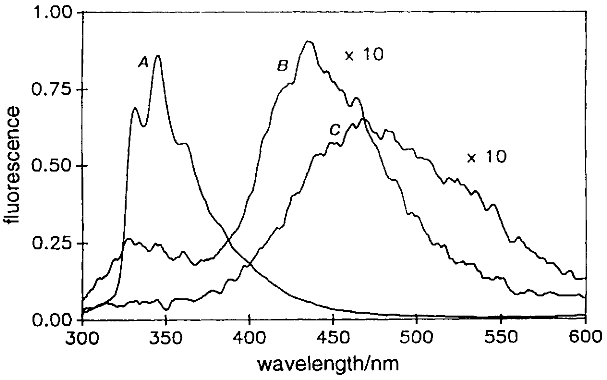

Fig. 4 Fluorescence spectra recorded for THBP at room temperature in *A*, pentane; *B*, methanol and *C*, acetonitrile

Time-resolved fluorescence studies were carried out with both compounds in a series of polar aprotic solvents in an attempt to measure fluorescence lifetimes for the LESS (τ_s) and CTS (τ_{CTS}) as a function of solvent polarity. In such solvents, however, it was not possible to resolve LESS fluorescence clearly from the instrumental response at the expected emission maximum around 340 nm so that, under these conditions, $\tau_s < 20$ ps. Monitoring at longer wavelengths, corresponding to fluorescence from the CTS, allowed determination of τ_{CTS} and the derived values are collected in Tables 2 and 3. In each case, the fluorescence decay profile could be analysed satisfactorily in terms of a single exponential, as assessed by the reduced chi-squares parameter and by the quality of the weighted residuals. It was observed that the lifetime of the CTS remained similar for both compounds and essentially independent of solvent polarity, despite the fact that the CTS emission maximum changes significantly over the range of ε_s studied (Tables 2 and 3). This behaviour, which was not expected, contrasts with that reported by Wasielewski *et al.*[23] for a related anthracene-*N*,*N*-dimethyl-

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† 1 D ≈ 3.33564×10^{-30} C m.

Table 2 Fluorescence spectral data recorded for DHBIQ in a range of solvents at 20 °C

solvent	F^a	SS^b /cm^{-1}	$\lambda_{CTS}{}^c$ /nm	$\tau_s{}^d$ /ps	$\tau_{CTS}{}^d$ /ns
CCl_4	0.011	5400	405	30	0.90
CCl_3CF_3	0.062	6230	419	<20	0.90
$CHCl_3$	0.148	6790	429	<20	0.87
diethyl ether	0.162	7180	437	<20	0.97
THF^e	0.211	7730	447	<20	1.00
CH_2Cl_2	0.219	7460	442	<20	0.98
$C_2H_4Cl_2$	0.221	7580	444	<20	1.00
$(CH_3)_2SO$	0.264	8220	457	<20	1.05
DMF^f	0.276	8450	462	<20	1.12
PC^g	0.286	8920	473	<20	1.10
CH_3CN	0.305	9210	479	<20	1.15
hexan-1-ol	0.240	8100	455	200	0.91
pentan-1-ol	0.250	8340	460	200	1.10
tert-butyl alcohol	0.267	8380	461	170	1.14
propan-2-ol	0.273	8610	466	160	1.18
propan-1-ol	0.274	8700	468	190	1.15
ethanol	0.290	9020	475	180	1.10
methanol	0.307	9240	480	190	1.10

[a] Pekar solvent polarity function. [b] Stokes' shift, ±40 cm^{-1}. [c] ±2 nm. [d] ±10%. [e] Tetrahydrofuran. [f] *N*,*N*-Dimethylformamide. [g] Propylene carbonate.

aniline compound where the lifetime of the exciplex was found to decrease as the emission maximum moved progressively to longer wavelength. This latter situation is common[38–40] and can be explained, at least qualitatively, in terms of the energy-gap law.[41]

In order to define this system better, ps laser flash photolysis studies were made in several polar aprotic solvents (Fig. 5). Under such conditions, laser excitation results in immediate (*i.e.* <20 ps) formation of a species displaying absorption bands centred around 430 and 750 nm. This species, which is clearly not the LESS, is attributed to the CTS in view of the similarity of the transient absorption spectrum with that recorded for the π-radical anion of 1,8-dimethylnaphthalene.[42] (This latter species was generated by laser flash photolysis of the compound in the presence of a large excess of triethylamine.) The lifetime (τ_d) of the CTS, as measured by monitoring the decay of the transient absorbance at 750 nm (Tables 4 and 5), agrees satisfactorily with the CTS fluorescence decay time measured by single-photon counting (Tables 2 and 3). This finding confirms that the 750 nm absorption band is related to the CTS and, because of its assignment as the naphthalene π-radical anion, the results are consistent with the CTS evolving by way of net electron transfer from amine to naphthalene subunits within the excited state.

Deactivation of the CTS results in formation of the corresponding excited triplet state, which is responsible for the sharp absorption band centred at 420 nm that can be seen in the flash photolysis records at long delay times (Fig. 5). Consequently, by monitoring kinetic changes occurring at 420 nm it was possible to measure the rate of formation of the triplet excited state (τ_r). The derived values, which are collected in Tables 4 and 5, confirm that the triplet state is populated *via* the CTS and not directly from the shorter-lived LESS. From the laser flash photolysis records, it is also possible to estimate the quantum yield (ϕ_t) for formation of the triplet state, as formed from the CTS, on the basis of known molar absorption coefficients for the triplet state at 420 nm

Table 3 Fluorescence spectral data recorded for THBP in a range of solvents at 20°C

solvent	F^a	SS^b /cm^{-1}	$\lambda_{CTS}{}^c$ /nm	$\tau_s{}^d$ /ps	$\tau_{CTS}{}^d$ /ns
CCl_4	0.011	4900	397	45	0.90
CCl_3CF_3	0.062	6100	417	<20	1.00
$CHCl_3$	0.148	6790	429	<20	1.02
diethyl ether	0.162	7230	438	<20	1.04
THF^e	0.211	7600	445	<20	1.06
CH_2Cl_2	0.219	7650	446	<20	1.08
$C_2H_4Cl_2$	0.221	7550	444	<20	1.02
$(CH_3)_2SO$	0.264	8150	456	<20	1.09
DMF^f	0.276	8200	457	<20	1.10
PC^g	0.286	8850	471	<20	1.12
CH_3CN	0.305	9210	479	<20	1.14
hexan-1-ol	0.240	8100	455	170	1.05
pentan-1-ol	0.250	8170	456	160	1.09
tert-butyl alcohol	0.267	8220	457	140	1.08
propan-2-ol	0.273	8460	463	180	1.18
propan-1-ol	0.274	8480	463	190	1.11
ethanol	0.290	8750	469	190	1.12
methanol	0.307	9240	478	190	1.12

[a] Pekar solvent polarity function. [b] Stokes' shift, ±40 cm^{-1}. [c] ±2 nm. [d] ±10%. [e] Tetrahydrofuran. [f] *N*,*N*-Diemthylformamide. [g] Propylene carbonate.

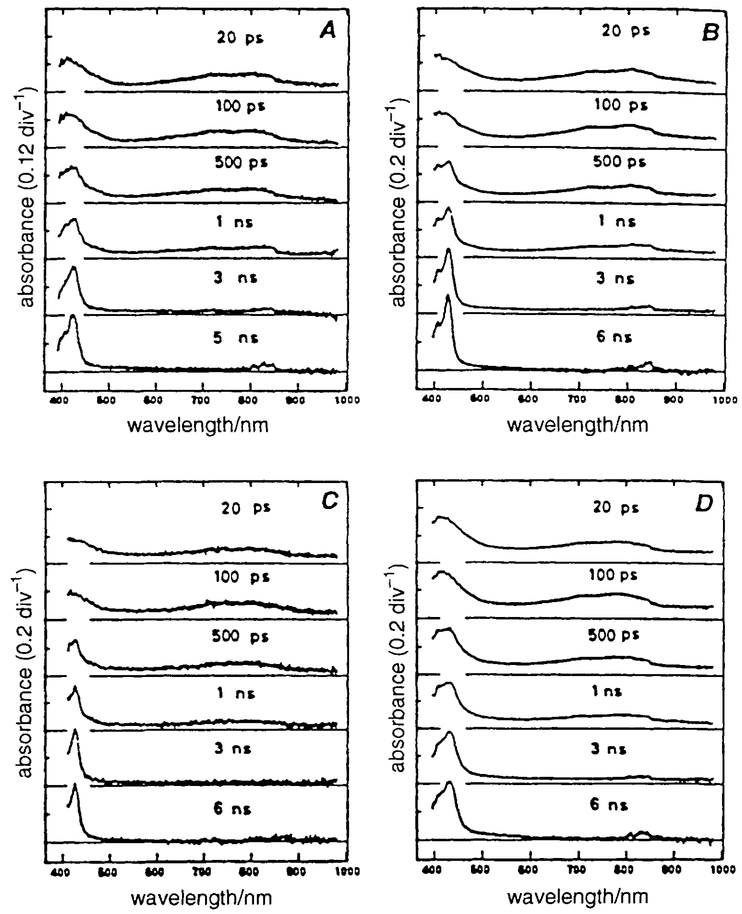

Fig. 5 Picosecond time-resolved transient absorption spectra recorded for DHBIQ in *A*, acetonitrile, *B*, tetrahydrofuran and *C*, diethyl ether. Panel *D* shows the corresponding spectra recorded for THBP in tetrahydrofuran. The CTS is present immediately after the laser pulse (FWHM ≈ 30 ps) and decays to form, in part, the locally excited triplet state.

($\varepsilon \approx 25000$ l mol^{-1} cm^{-1}) and for the naphthalene π-radical anion[42] at 750 nm ($\varepsilon \approx 3000$ l mol^{-1} cm^{-1}). The derived quantum yields are given in Tables 4 and 5 but, because of experimental uncertainties, they should be regarded as approximate. It is clear, however, that intersystem-crossing to the triplet state competes effectively with charge recombination to restore the ground state for both compounds.

Thus, charge recombination within the CTS may result in fluorescence, restoration of the ground state of the molecule, or population of the locally excited triplet state (Fig. 6), as has been observed with related fixed-distance[23] and flexibly linked[43–45] donor–acceptor systems. That these processes occur in competition is clear from the observed charge-recombination fluorescence and from formation of the triplet state, as observed by flash photolysis (Fig. 5). Restoration of

Table 4 Kinetic parameters and triplet quantum yields measured for DHBIQ in polar aprotic solvents by femtosecond laser flash photolysis techniques

solvent	τ_s[a] /ps	τ_d[b] /ns	τ_r[c] /ns	ϕ_t[d]	k_{isc}[e] /10^8 s^{-1}	k_{cr}[f] /10^8 s^{-1}
CH_3CN	4	1.0	1.1	0.34	3.2	6.3
$C_6H_{13}CN$	4	1.1	1.2	0.26	2.3	6.4
CH_2Cl_2	2	1.0	1.0	0.26	2.6	7.4
$CHCl_3$	8	0.9	1.1	0.42	4.2	5.8
$(CH_2Cl)_2$	3	1.0	1.0	0.36	3.6	6.4
THF[g]	2	1.5	1.7	0.28	1.7	4.5
$(C_2H_5)_2O$	6	1.6	1.4	0.37	2.5	4.2

[a] Lifetime of the LESS measured at 450 nm by transient absorption spectroscopy, ±1 ps. [b] Lifetime of the naphthalene π-radical anion measured at 750 nm by transient absorption spectroscopy, ±0.1 ns. [c] Reciprocal of the first-order rate constant for appearance of the triplet state measured at 420 nm by transient absorption spectroscopy, ±0.1 ns. [d] Quantum yield for formation of the triplet state, ±25%. [e] Rate constant for formation of the locally excited triplet state from the CTS, ±25%. [f] Rate constant for charge recombination within the CTS restoring the ground state, ±25%. [g] Tetrahydrofuran.

Table 5 Kinetic parameters and triplet quantum yields measured for THBP in polar aprotic solvents by femtosecond laser flash photolysis techniques

solvent	τ_s[a] /ps	τ_d[b] /ns	τ_r[c] /ns	ϕ_t[d]	k_{isc}[e] /10^8 s^{-1}	k_{cr}[f] /10^8 s^{-1}
CH_3CN	4	1.0	1.0	0.37	3.7	6.3
$C_6H_{13}CN$	6	1.1	1.2	0.37	3.2	5.5
CH_2Cl_2	6	1.1	1.0	0.37	2.7	6.3
$CHCl_3$	3	1.0	0.9	0.41	4.3	4.3
$(CH_2Cl)_2$	7	1.0	1.2	0.41	3.7	3.7
THF[g]	2	1.5	1.7	0.39	2.4	2.4
$(C_2H_5)_2O$	2	1.1	1.0	0.44	4.2	4.2

[a] Lifetime of the LESS measured at 450 nm by transient absorption spectroscopy, ± 1 ps. [b] Lifetime of the naphthalene π-radical anion measured at 750 nm by transient absorption spectroscopy, ±0.1 ns. [c] Reciprocal of the first-order rate constant for appearance of the triplet state measured at 420 nm by transient absorption spectroscopy, ±0.1 ns. [d] Quantum yield for formation of the triplet state, ±25%. [e] Rate constant for formation of the locally excited triplet state from the CTS, ±25%. [f] Rate constant for charge recombination within the CTS restoring the ground state, ±25%. [g] Tetrahydrofuran.

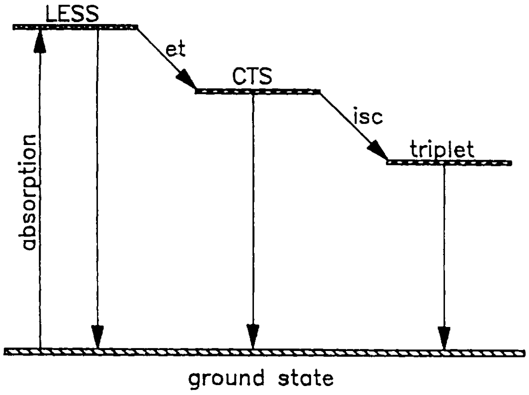

Fig. 6 Simplified energy-level diagram proposed for the compounds studied here. The energy levels for the locally excited singlet and triplet states are independent of solvent polarity while that of the CTS moves to lower energy with increasing polarity of the solvent. In alkane solvents, the CTS is situated above the LESS such that deactivation of the LESS may involve direct population of the triplet state.

the ground state requires dissipation of a large amount of vibrational energy; the CTS emission maxima vary between 3.1 and 2.6 eV, such that charge recombination might be expected to fall well within the Marcus 'inverted' region.[46] From our analysis of the ps laser flash photolysis records, it appears that the rate constant for charge recombination (k_{cr}) falls within the range 10^8–10^9 s^{-1} for all the solvents studied here (Tables 4 and 5):

$$k_{cr} = [1 - \phi_t]/\tau_{CTS} \qquad (1)$$

Conversely, charge recombination to form the triplet state (k_{isc}) involves a spin-forbidden process for which the energy gap will be smaller than that for charge recombination by the magnitude of the triplet energy ($E_t \approx 2.5$ eV):

$$k_{isc} = \phi_t/\tau_{CTS}$$

This latter process is less likely to fall within the Marcus 'inverted' region such that the rate constant might be expected to increase with increasing energy of the CTS. Since the two rate constants are of comparable magnitude and tend to offset each other (Tables 4 and 5), the lifetime of the CTS remains essentially unaffected by changes in solvent polarity. This situation is unusual, and probably coincidental, but it should be recalled that the relevant kinetic parameters remain self-consistent and they have been measured by (i) charge-recombination fluorescence, (ii) monitoring growth of the triplet state, and (iii) monitoring decay of the naphthalene π-radical anion. The large experimental uncertainty and possible specific solvent effects associated with the derived rates, however, prevent more detailed exploration of their energy-gap dependence. It should also be noted that relatively high rates of triplet state formation *via* CTS intermediacy have been observed previously.[23,43–45]

The absence of delayed fluorescence from the LESS may be considered as an indication that charge transfer is irreversible in these systems. However, because of the similarity between the transient absorption spectra characteristic of the LESS and CTS around 380–450 nm, together with the fact that the signal observed around 750 nm is weak, determination of the rate of formation of the CTS by fs laser flash spectroscopy is rather unreliable. For both DHBIQ and THBP in polar aprotic solvents, the fs laser flash photolysis records exhibit an increase in absorbance around 380 nm and a concomitant decrease in absorbance around 450 nm occurring over a few ps. This process is attributed to conversion of the LESS into the CTS and the derived lifetimes (τ_s) are compiled in Tables 4 and 5. By comparison with the corresponding values measured in alkane solvents, it appears that intramolecular charge transfer to form the CTS is quantitative in polar aprotic solvents. Indeed, it is clear that charge transfer is rapid under these conditions and occurs on a timescale comparable to that needed for solvent rearrangement around the new dipole (*i.e.* a few ps).[47] However, the limited precision of the experimental data does not permit a quantitative investigation of whether or not the process is controlled by solvent reorientation dynamics or by some other barrier.

The restricted precision attainable with the fs laser spectroscopic measurements also prevents direct determination of the activation energy for charge transfer in these systems by measuring the rate as a function of temperature. However, the reaction exergonicity ($\Delta_{CT}G^\circ$) for charge transfer can be calculated from electrochemical measurements

$$\Delta_{CT}G^\circ = (E_{ox} - E_{red} - E_s) - (e^2/4\pi\varepsilon_0\varepsilon_s d) \qquad (3)$$

where e is the electronic charge, ε_0 is the permittivity of free space, E_{ox} (= 0.97 V *vs.* SCE) refers to the half-wave potential for one-electron oxidation of the amine donor in acetonitrile solution, E_{red} (= −2.50 V *vs.* SCE) refers to the half-wave potential for one-electron reduction of the naphthalene ring in acetonitrile and d (= 3.4 Å) is the distance between the reactants. The derived value ($\Delta_{CT}G^\circ \approx -0.35$ eV) indicates that there is only a small thermodynamic driving force for charge transfer, despite the high singlet-state energy. The reaction exergonicity for subsequent charge recombination to restore the ground state ($\Delta_{CR}G^\circ \approx -3.5$ eV) and total reorganization energy ($\lambda \approx 0.9$ eV) accompanying charge transfer in acetonitrile solution can be estimated[48] from spectroscopic and electrochemical measurements as follows:

$$\Delta_{CR}G^\circ = (E_{red} - E_{ox}) + (e^2/4\pi\varepsilon_0\varepsilon_s d) \qquad (4)$$

$$hc/\lambda_{CTS} = \lambda - \Delta_{CR}G^\circ \qquad (5)$$

Here, hc/λ_{CTS} refers to the energy of the maximum of the CTS fluorescence peak as observed in acetonitrile solution. Assuming both charge transfer from the LESS and charge recombination within the CTS involve a reorganization energy of 0.9 eV, the activation energy (E_A) for the charge-transfer process in acetonitrile is estimated[46] from Marcus theory to be *ca.* 0.08 eV.

$$E_A = [\lambda + \Delta_{CT}G^\circ]/4\lambda \qquad (6)$$

If correct, these various thermodynamic values require that charge transfer occurs within the Marcus 'normal' region (*i.e.* $-\Delta_{CT}G^\circ < \lambda$). As such, by application of conventional Marcus theory [eqn. (7)] the electronic coupling matrix element (V_{DA}) for this process can be estimated as being *ca.* 140 cm^{-1}. This is a relatively high value, indicative of strong electronic coupling within the LESS in acetonitrile, and corresponds to an activationless (*i.e.* $E_A = 0$) rate constant for charge transfer of *ca.* 5×10^{12} s^{-1}.

$$k = (1/\tau_s) = (4\pi^2 V_{DA}^2/h)(4\pi\lambda RT)^{-1/2} \exp(-E_A/RT) \qquad (7)$$

The total reorganization energy can be partitioned into terms associated with restructuring of the surrounding solvent molecules (λ_s) and with any changes in the nuclear coordinates (λ_v).[46]

$$\lambda = \lambda_s + \lambda_v \qquad (8)$$

The magnitude of the solvent reorganization energy can be estimated from dielectric continuum theory[49]

$$\lambda_s = (e^2/4\pi\varepsilon_0)[(2r_A)^{-1} + (2r_B)^{-1} - (1/d)][(1/n^2) - (1/\varepsilon_s)] \qquad (9)$$

where n is the solvent refractive index, r_A ($= 2.8$ Å) is the radius of the naphthalene π-radical anion and r_B ($= 2.5$ Å) is the radius of the amine cation. On this basis, λ_s is estimated to be *ca.* 0.6 eV and, consequently, λ_v should be in the region of 0.3 eV. This latter term, as derived in this rather indirect manner, appears to be small but perhaps consistent with the restricted structural changes that can occur in these rigid molecules. In particular, the amine N atom is not free to rotate, nor is it likely to change its state of hybridization, although it can undergo inversion. Similarly, the negative charge should be delocalized over the naphthalene ring without causing significant structural distortion.[50] It is also pertinent to note that studies made with aryl hydrocarbons linked to *N,N*-dimethylaniline *via* a single (rotatable) bond have concluded that λ_v is small in such systems.[51,52]

Given these various thermodynamic parameters, but bearing in mind the assumptions used in their estimation, it is instructive to calculate the expected rate constant for charge transfer (k_{ct}) in the event that the process is controlled by solvent dynamics.[53]

$$k_{ct} = \langle 1/\tau_L \rangle (\lambda_s/16\pi RT)^{1/2} \exp[-(\lambda_s + \Delta G^\circ)^2/4\lambda_s RT] \tag{10}$$

In this relationship, which corresponds to the solvent-controlled adiabatic limit[53] and would apply to the present systems if $V_{DA} \gg 60$ cm^{-1}, τ_L(≈ 0.5 ps) refers to the solvent longitudinal dielectric relaxation time.[54] The derived value for the rate constant is *ca.* 5×10^{11} s^{-1} which, under the circumstances, seems to be in exact accord with the measured rate. On this basis, we cannot exclude the possibility that charge transfer is controlled by solvent dynamics.

Our results are consistent with strong electronic coupling between the reactants within the LESS, perhaps sufficient for charge transfer to fall within the solvent-controlled adiabatic limit.[53] Although the thermodynamic driving force for charge transfer is limited, the rate of this process in polar aprotic solvents is extremely fast owing, in part, to the effective overlap of the relevant orbitals localized on donor and acceptor species. The total reorganization energy that accompanies charge transfer is kept modest by the close proximity of the reactants and by the rigid structure. As such, there is only a small activation energy for the charge-transfer process. It is clear that there is a large disparity between rates of formation and decay of the CTS in these solvents and, indeed, the CTS survives long enough for intersystem crossing to a locally excited triplet state to compete with charge recombination to restore the ground state. Such behaviour has been observed previously for both flexibly linked[43–45] and fixed-distance[23] donor–acceptor systems and it is necessary to enquire as to why restoration of the ground state is so slow in these systems. It is also interesting to explore what role, if any, inversion of the amine plays in controlling the relative rates of charge transfer and recombination. To some degree, this latter process might be affected by attachment of a solvent molecule to the amine donor *via* hydrogen bonding to the N atom, and this possibility is explored below.

Photophysical Properties in Alkanols

In polar aprotic solvents it appears that formation of the CTS competes favourably with the inherent non-radiative and radiative processes that result in deactivation of the LESS and which involve intersystem crossing to the triplet manifold, internal conversion and fluorescence. In most cases studied, growth of the CTS occurred over a few ps and might be controlled by solvent dynamics. However, in alkanol solvents at 20 °C, where hydrogen bonding to the N atom of the donor is expected to occur, the lifetime of the LESS (τ_s) was found to be surprisingly long (Tables 2 and 3). For example, the lifetime of the LESS for THBP was found to be *ca.* 4 ps in acetonitrile but *ca.* 200 ps in methanol, despite the fact that these two solvents demonstrate similar polarity and viscosity. In alkanol solvents, the appearance of fluorescence from the CTS was well resolved from the instrumental response and the rate of formation of the CTS was observed to match the rate of decay of the LESS. As in aprotic solvents, charge transfer to form the CTS is the dominant process leading to deactivation of the LESS. Time-resolved fluorescence decay profiles recorded for DHBIQ in hexanol are shown in Fig. 7 so as to illustrate this effect. Comparison of the kinetic data collected in various alkanols (Tables 2 and 3) shows that the rate of decay of the LESS, and the rate of formation of the CTS, appear to be relatively insensitive to the nature of the solvent. In particular, there is no obvious correlation between the rate of charge transfer and solvent viscosity, static relative permittivity or longitudinal reorientation time. Furthermore, rates of charge transfer derived for the two compounds remain similar.

The fluorescence spectral profiles recorded for these compounds is alkanol solvents were markedly dependent upon temperature. Thus, upon lowering the temperature it was observed that fluorescence from the CTS decreased in intensity while there was a concomitant escalation in fluorescence from the LESS. There was also a small change in the maximum of the CTS emission band with varying temperature, presumably owing to the change in relative permittivity. This behaviour can be used to infer that, unlike the situation in polar aprotic solvents, there must be a considerable barrier to formation of the CTS in protic solvents. Indeed, from time-resolved fluorescence studies made with DHBIQ in hexanol as a function of temperature, it was clear that the rate of formation of the CTS exhibits a pronounced temperature dependence (Fig. 8). It should be noted that over this temperature range there was good agreement between the rate of deactivation of the LESS and the rate of formation of the CTS. Expressing the kinetic data in the form of an Arrhenius plot allowed determination of the activation energy for formation of the CTS as *ca.* 0.20 eV. The same value was found for THBP in hexanol.

Similar activation energies were found for DHBIQ in other alkanol solvents and it is clear to us that there is a further barrier to charge transfer in protic solvents that is not apparent in polar aprotic media. The magnitude of this additional barrier, relative to the activation energy estimated for acetonitrile solution, is *ca.* 0.12 eV and it is most likely associated with hydrogen bonding of a solvent molecule to the N atom

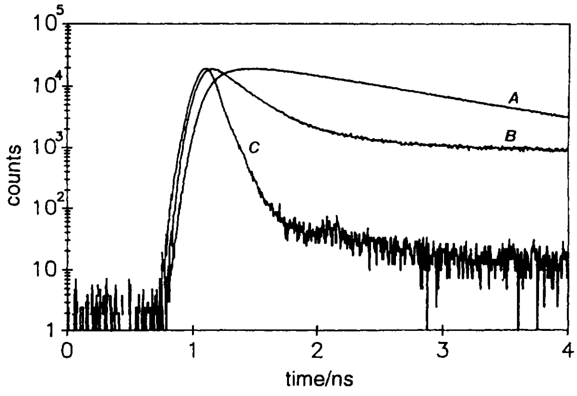

Fig. 7 Fluorescence decay profiles recorded for DHBIQ in hexanol at room temperature showing *A*, growth and decay of the CTS; *B* decay of the LESS; and *C* the instrumental response function

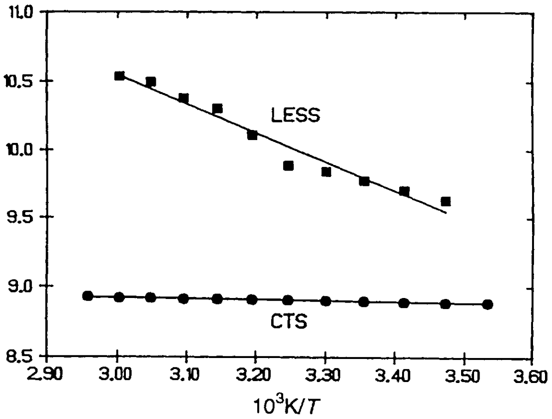

Fig. 8 Effect of temperature on the rate constants for formation ($k = 1/\tau_s$) and deactivation ($k = 1/\tau_{CTS}$) of the CTS for DHBIQ in hexanol solution. The solid lines drawn through the data points are computer least-squares best fits to the Arrhenius equation, giving rise to the activation energies and barrierless rate constants quoted in the text.

of the electron donor in the ground state. The activation energy, however, remains essentially insensitive to the nature of the alkanol and shows no clear correlation with the molar volume of the solvent. This finding, together with the absence of a viscosity dependence for the rate of charge transfer, may indicate that electron transfer is accompanied by breakage of the hydrogen bond. This hypothesis demands that the ground-state hydrogen-bonded complex survives for at least several hundred ps[55] but we have no experimental support for this contention.

Interestingly, deactivation of the CTS was found to be almost activationless ($E_A \approx 0.006$ eV) in alkanol solvents and its lifetime remained similar in protic and aprotic media. Thus, deactivation of the CTS does not involve formation or breakage of a hydrogen bond in the rate-limiting step and, as in aprotic media, results in population of the locally excited triplet state. From the Arrhenius plots made in alkanol solvents, the barrierless rate constant for charge recombination within the CTS was determined to be *ca.* 1×10^9 s^{-1}, whereas that calculated for charge transfer is *ca.* 1×10^{13} s^{-1}. This latter value, which is comparable to that found in acetonitrile, illustrates that formation and decay of the CTS occur on very disparate timescales. At first glance, therefore, it is tempting to suggest that the reactants are electronically decoupled in the CTS but strongly coupled in the LESS, possibly owing to precise orientation of the non-bonding orbital.

Concluding Remarks

Bimolecular quenching of the fluorescence from aryl hydrocarbons by amines in fluid solution is a very well studied phenomenon and, in addition, considerable attention has been given to the investigation of exciplex formation between such reactants when linked together by a flexible chain.[56] In particular, Davidson,[57] De Schryver[58] and Mataga,[59] and their co-workers, have made significant contributions to our understanding of this subject. In more recent years, interest has focussed on rigid structures[22,23,51,52] where the effects of charge transfer can be separated from those associated with diffusion or rotation. In such cases, charge transfer might be expected to take place through orbitals localized on the connecting spacer moiety.[60] The rigidly linked naphthalene–alkylamine compounds described here undergo light-induced charge transfer only in polar solvents since in non-polar media the CTS lies at higher energy than the naphthalene-like LESS. Formation of the CTS in acetonitrile solution, where the thermodynamic driving force is *ca.* 0.35 eV and where reaction occurs within the Marcus 'normal' region, is extremely fast and occurs on a timescale comparable to that of solvent reorientation. The reactants are strongly coupled such that charge transfer might be under adiabatic solvent control, although the experimental uncertainty does not permit detailed exploration of this point. The CTS appears to be made up of the respective radical ions, as evidenced by transient absorption spectroscopy, and its formation involves only a small nuclear reorganization energy (*i.e. ca.* 0.3 eV). This latter finding, taken together with the fast rates of charge transfer, suggests to us that charge transfer is not dependent on a substantial structural change. No obvious differences are observed between THBP and DHBIQ, despite the somewhat different character of their LESSs.

The rate of formation of the CTS, but not its subsequent decay, it slower in alcohol solvents that can associate with the N donor *via* hydrogen bonding. This association serves to render the amino group a weaker electron donor but the experimental results have been interpreted in terms of a concerted process in which breakage of the hydrogen bond occurs simultaneously with electron transfer. It is important to realise that in these systems, which appear to correspond to full electron transfer, CTS fluorescence is not quenched by alcohols. Hydrogen bonding serves only to increase the activation energy for charge transfer and the magnitude of this increase is consistent with the overall electron-transfer process involving breakage of the hydrogen bond. There is no indication of hydrogen bonding in acetonitrile or dichloromethane although these solvents are weakly acidic.

Charge recombination to restore the ground state falls within the Marcus inverted region (*i.e.* $-\Delta G^\circ > \lambda$) but, even so, it occurs on a relatively slow timescale that permits both fluorescence and intersystem crossing to the triplet manifold to compete. In acetonitrile solution, the energy gaps for charge recombination to restore the ground state and intersystem crossing to the triplet manifold within the CTS, respectively, are calculated from electrochemical and luminescence measurements to be *ca.* 3.5 and 1.0 eV. The respective rate constants are 7×10^8 and 3×10^8 s^{-1}. According to Marcus theory [*i.e.* eqn. (7)] with $\lambda = 0.9$ eV, the electronic coupling matrix element (V_{DA}) appropriate for conversion of the CTS into the locally excited triplet state has a value of *ca.* 1 cm^{-1}. This level of coupling, which is very much lower than that estimated for the corresponding charge-transfer step ($V_{DA} \approx 140$ cm^{-1}), might be considered to reflect the spin-forbidden nature of the process. Of course, rapid intersystem crossing within a CTS has been observed for many other systems, including fixed distance aryl hydrocarbon–amine systems.[23] It has been recognized that the level of spin–orbital interaction in such systems is very sensitive to the configuration of donating and accepting orbitals. In particular, interaction is enhanced in the case where the non-bonding orbital on the amine is held perpendicular to 2pπ orbitals on the aryl hydrocarbon.[45] The rigidly linked systems studied here can acquire the appropriate configuration needed to maximize spin–orbital interaction during amine inversion. It is not unreasonable, therefore, to expect high rates of intersystem crossing in such systems.

The same procedure cannot be applied to estimate V_{DA} for direct charge recombination since it is necessary, in this case, to allow for the possible effects of quantum mechanical tunnelling.[61] However, taking the activationless rate constant for charge recombination, as measured in alkanol solvents ($k \approx 10^9$ s^{-1}), as being an upper limit for the direct process and allowing for the electron–vibrational coupling constant[62]

($S_c \approx \lambda_v/hc\nu \approx 1.6$, where the average vibrational frequency $hc\nu \approx 1500$ cm^{-1}), it can be shown that $V_{DA} < 3$ cm^{-1}. Given the close proximity of the reactants, this seems to be a surprisingly low level of electronic coupling that would indicate poor overlap of relevant orbitals on the donor and acceptor species. Such a concept is consistent with localization of the positive charge at the N atom, perhaps with the non-bonding orbital being held parallel with the plane of the naphthalene ring. However, in cases where $-\Delta_{CR}G^\circ \gg \lambda$ it is questionable if Marcus theory, even with corrections for quantum mechanical tunnelling,[61] is applicable and, instead, the rates of charge recombination may be better explained in terms of an (almost) exponential energy-gap law.[41] According to this latter treatment, the apparent weak dependence of k_{cr} on the energy of the CTS (expressed in terms of the emission maximum, ν_{max}) demands a substantial displacement of the vibrational mode that is coupled to the electron-transfer event.[63] This could well apply to the skeletal motion responsible for inversion of the N atom.

The energy-gap law, with its weak dependence on temperature,[64] can also be invoked to explain the negligible activation energy observed for deactivation of the CTS in alkanol solvents. Furthermore, the concept of very weak electronic coupling between the reactants in the CTS, as implied from our analysis of the kinetic data in terms of Marcus theory, is inconsistent with the appearance of charge-recombination fluorescence, since this latter process demands extensive coupling.[65] Thus, taking the radiative rate constant (k_{rad}) for charge-recombination in acetonitrile solution as *ca.* 5×10^5 s^{-1} ($k_{rad} = \phi_f/\tau_{CTS}$) the transition dipole moment[66] (M) can be estimated as being *ca.* 0.25 D.

$$k_{rad} = (64\pi^4/3h)(n\nu_{max})^3 M^2 \qquad (11)$$

Furthermore, the transition dipole moment can be related to the extent of electronic coupling between the reactants[67]

$$M \approx V_{DA}\,\mu_{CTS}/\nu_{max} \qquad (12)$$

where μ_{CTS} ($\approx$25 D) is the dipole moment of the CTS. On this basis, it is possible to estimate that the electronic coupling matrix element must be *ca.* 200 cm^{-1}. Such a value requires extensive coupling between the redox-active sites within the CTS.

It seems likely, therefore, that the redox-active subunits remain in strong electronic communication in both the LESS and the CTS. The difference in rates of charge transfer from the LESS and charge recombination within the CTS to restore the ground state can be explained, at least qualitatively, in terms of the relevant ratio of the thermodynamic driving force ($\Delta_{CT}G^\circ$ or $\Delta_{CR}G^\circ$) and the reorganization energy (λ) appropriate to that process. Charge transfer ($-\Delta_{CT}G^\circ \approx 0.4\lambda$) is likely to occur within the Marcus 'normal region' and, because of the high electronic coupling matrix element, is a rapid process. The magnitude of V_{DA} may be sufficient for charge transfer to be adiabatic, the adiabaticity parameter defined by Jortner and Bixon[14] being *ca.* 10, and controlled by solvent dynamics.[53] Charge recombination within the CTS to form the locally excited triplet state ($-\Delta_{CR}G^\circ \approx \lambda$) may occur near to the apex of a Marcus-type rate *vs.* energy gap profile.[46] This situation would account for the high rate with which this spin-forbidden process takes place, despite the apparently weak coupling between the reactants. Charge recombination to restore the ground state ($-\Delta_{CR}G^\circ \approx 4\lambda$) involves dissipation of a large amount of vibrational energy. The rate is relatively slow and seemingly insensitive to the energy gap, although the appearance of fluorescence from the CTS is consistent with the redox-active subunits being strongly coupled. The rate is well described in terms of the energy-gap law as formulated by Englman and Jortner[41] but the limited precision with which the rates of charge recombination can be extracted from the laser flash photolysis records precludes a more quantitative investigation along these lines.

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