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Synthesis and photophysical studies of donor-acceptor substituted tetrahydropyrenes†‡

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The tetrahydropyrene derivatives 2-*N*,*N*-dimethylamino-7-nitro-4,5,9,10-tetrahydropyrene (**1**) and 2-*N*,*N*-dimethylamino-7-acetyl-4,5,9,10-tetrahydropyrene (**2**) were synthesized and characterized. Photophysical properties of these molecules were investigated in several solvents. The absorption spectrum of **1** shows a slight red shift with solvent polarity, whereas that of **2** remains more or less unchanged. Fluorescence spectra of these compounds exhibit large, solvent-polarity-dependent Stokes shifts. The Stokes shifts are correlated to $E_T(30)$ and E_T^N parameters and were quantitatively analyzed by the Mataga–Liptay equation. Both compounds show low fluorescence quantum yields in cyclohexane. Nanosecond flash photolysis studies suggested that the low quantum yield in cyclohexane is due to intersystem crossing to a triplet state. In the case of **2**, the fluorescence quantum yields are high in all other solvents. In the case of **1** fluorescence quantum yields are very low in polar solvents and this is explained by invoking a twisted intramolecular charge transfer state.

1. Introduction

Excited state processes taking place in donor (D)-acceptor (A) substituted biphenyl systems have been studied in great detail by several groups.[1–19] The most prominent photoprocess taking place in D-A biphenyls is an intramolecular charge transfer (ICT) from the donor to the acceptor fragment.[4] Other important issues related to the photophysics of these systems are: (1) the relative energies of the Franck–Condon (FC) and CT excited states, (2) the electronic structure and conformation of the FC and CT excited states, (3) the intramolecular and environmental factors controlling the radiative and non-radiative charge recombination ($^1CT \rightarrow S_0$) process and (4) the nature and role of triplet states, if any. Rettig and co-workers have recently investigated the excited state ICT processes in a series of differently twisted 4-*N*,*N*-dimethylamino-4′-cyanobiphenyl systems in great detail. The dipole moments, radiative rates and torsional relaxations in the excited states were analyzed by comparison with absorption spectra and CNDO/S calculations. The electronic nature of these molecules could be explained in terms of a composite molecular model with the dimethylaminophenyl moiety acting as the donor unit and the cyanophenyl moiety acting as the acceptor unit. In the case of 4-*N*,*N*-dimethylamino-4′-cyanobiphenyl, in which the two phenyl rings are twisted by 39° in the ground state, the first excited state is shown to be a planar, emissive ICT state, irrespective of solvent polarity. For 2,6-dimethyl-4-*N*,*N*-dimethylamino-4′-cyanobiphenyl, which is twisted by 78° in the ground state, the first excited state is shown to be a planar, ICT state only in non-polar solvents. Upon increasing solvent polarity, a highly twisted, relaxed conformation is populated for this compound, and this results in a strong decrease in the radiative rates.

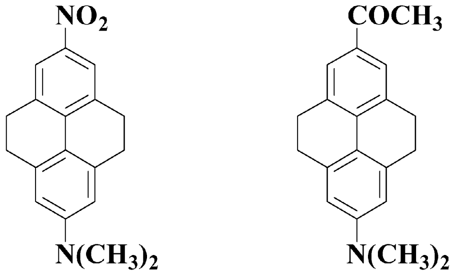
In view of the general interest in D-A biphenyls and their potential applications, we have investigated the photophysical properties of a few D-A substituted tetrahydropyrene (THP) derivatives.[20] THPs are bridged biphenyl derivatives where the rotation about the C_1–$C_{1'}$ bond is restricted. The phenyl rings in the THP system are twisted by 14° (from AM1 calculations): this value is in-between those reported for D-A fluorenes and D-A biphenyls studied earlier by Rettig and others.[2–8] Our studies showed that the photophysical properties of D-A THP systems are very similar to those of D-A biphenyl systems studied earlier.

Herein we report the synthesis and photophysical properties of two new THP systems, namely, 2-*N*,*N*-dimethylamino-7-nitro-4,5,9,10-tetrahydropyrene (**1**) and 2-*N*,*N*-dimethylamino-7-acetyl-4,5,9,10-tetrahydropyrene (**2**), shown in Chart 1. Compared to the D-A THP and D-A biphenyl systems studied earlier, these compounds exhibit several differences in their photophysical behavior. Hence, a detailed study was undertaken and the results are presented here.

2. Experimental

2.1. General techniques

The melting points are uncorrected and were determined using a Mel-Temp melting point apparatus. The ^1H and ^{13}C NMR



1 **2**

Chart 1

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‡ Electronic supplementary information (ESI) available: details of the synthesis and characterization of compounds **1**, **2**, **4** and **5**. See http://www.rsc.org/suppdata/nj/b4/b409411e/

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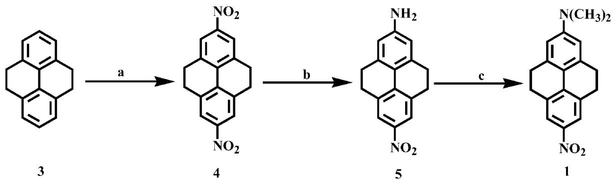


Scheme 1

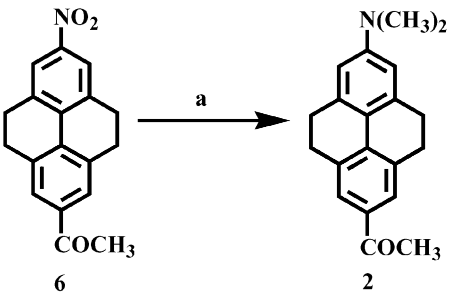
spectra were obtained using a 300 MHz Bruker Avance DPX spectrometer. FT-IR spectra were recorded on a Nicolet Impact 400 D infrared spectrometer. Elemental analyses were done using a Perkin Elmer Series II 2400 CHN analyzer. The absorption spectra were recorded on a Shimadzu 3101PC UV-vis-NIR scanning spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog F112X spectrofluorometer. The fluorescence spectra were corrected for detector response. Fluorescence quantum yields (Φ_f) were determined relative to quinine sulfate in 0.5 M sulfuric acid ($\Phi_f = 0.546$)[21] or triphenylpyrylium perchlorate in acetonitrile ($\Phi_f = 0.52$)[22] or cresyl violet perchlorate in ethanol ($\Phi_f = 0.56$)[23] as reference materials. Fluorescence lifetimes were determined using a Edinburgh FL900CD single photon counting system and decay analysis were carried out using Edinburgh software. Laser flash photolysis experiments were carried out in an Applied Photophysics model LKS–20 laser kinetic spectrometer using a Quanta Ray GCR–12 series Nd-YAG laser. The excitation wavelength was 355 nm. Spectroscopic grade solvents were used throughout.

2.2. Syntheses

Tetrahydropyrene derivatives **1** and **2** were prepared as shown in Schemes 1 and 2. For the synthesis of **1**, tetrahydropyrene (**3**) was nitrated to give the 2,7-dinitro derivative **4**, which was partially reduced followed by methylation using iodomethane (see the ESI for details). The preparation of **2** was achieved by the reductive methylation of the previously known 2-nitro-7-acetyltetrahydropyrene (see ESI for details).

Data for **1**: mp 219–220 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.85–2.89 (m, 8 H, benzylic), 3.03 [s, 6 H, $N(CH_3)_2$], 6.46 (s, 2 H, ArH), 7.9 (s, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 28.29, 28.56, 40.24, 109.55, 118.06, 121.17, 134.2, 137.86, 138.03, 144.5, 151.09; IR (KBr): 2934, 2831, 1615, 1506, 1434, 1310, 1191, 1082, 881, 725 cm^{-1}; anal. calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.5; found: C, 73.28; H, 6.22; N, 9.08.

Data for **2**: mp 174–175 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.5 (s, 3 H, $COCH_3$), 2.89 (s, 8 H, benzylic), 3.0 [s, 6 H, $N(CH_3)_2$], 6.46 (s, 2 H, ArH), 7.64 (s, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 26.3, 28.4, 28.9, 40.4, 109.9, 126.1, 133.6, 134.1, 136.2, 137.6, 150.7, 197.6; IR (KBr): 2925, 2365, 1672, 1590, 1480, 1430, 1340, 1280, 1190, 1150, 1080, 950, 870 cm^{-1}; anal. calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81; found: C, 82.5; H, 7.03; N, 5.17.



Scheme 2

3. Results and discussion

3.1. Absorption spectra

Absorption spectra of **1** and **2** in cyclohexane, benzene and acetonitrile are shown in Fig. 1. The spectrum in cyclohexane exhibits vibrational structure. In other solvents the absorption band is somewhat broadened and the fine structure is lost. In the case of **1** the absorption maximum exhibits a moderate red shift with solvent polarity. It can be noted that the onset of absorption exhibited significant red shifts with increase in solvent polarity. In the case of **2** the absorption maxima exhibits only slight changes with solvent polarity. In both cases, the integrated absorption intensity $\int \varepsilon d\nu_a$, which is proportional to the oscillator strength f, changes only slightly with solvent polarity (Table 1). This suggests that the electronic and structural nature of the ground and FC excited states responsible for these absorptions do not vary much with solvent polarity. The absorption bands of **1** and **2** are analogous to the lowest energy bands in D-A biphenyls[4] and the D-A THP systems[20] studied earlier. Hence we assign this band as arising from an ICT transition, which involves transfer of charge from the dimethylaminophenyl donor moiety to the nitrophenyl (or acetylphenyl) acceptor moiety. This assignment is confirmed by the changes observed in the absorption spectra upon addition of trifluoroacetic acid (TFA).

Fig. 2 shows the effect of TFA on the absorption spectrum of **1** in cyclohexane. The band due to **1** decreases with simultaneous formation of a new band at ~325 nm. This new absorption band is similar to the absorption band of 2-nitro-4,5,9,10-tetrahydropyrene. Compound **2** also exhibits a similar behavior. TFA protonates the dimethylamino group in **1** or **2** and prevents the ICT process, leading to the observed changes in the absorption spectrum.

3.2. Fluorescence properties

The fluorescence properties of **1** and **2** were investigated in solvents of varying polarity. The emission spectra in a few solvents are shown in Fig. 3. The fluorescence spectra in cyclohexane exhibit vibrational structure for both compounds. Spectra in other solvents are structure-less and exhibit solvatochromic red shifts with increase in solvent polarity. The emission maxima observed in different solvents and the corresponding Stokes shift values ($\nu_{abs}^{max} - \nu_{em}^{max}$) are presented in Table 1. It can be seen from Table 1 that the Stokes shifts for **1** and **2** are very large in polar solvents.

Solvent-dependent shifts in the fluorescence spectra can be attributed to factors such as: (1) dipole-dipole interactions between solvent and solute, (2) changes in the nature of emitting state induced by the solvent and (3) specific solvent-solute interactions such as hydrogen bonding. In order to have a better understanding of the excited states of **1** and **2** we have tried to correlate the observed Stokes shifts to the Dimroth $E_T(30)$ and E_T^N solvent parameters.[24] The results are plotted in Fig. 4. In both cases the plots were linear with correlation coefficients $r = 0.92$. The linearity of these plots suggests that dipole-dipole interactions between the solute and solvent are responsible for the large solvent-dependent shifts observed in the fluorescence spectra of **1** and **2**.

The solvatochromic shifts in the fluorescence maxima were further analyzed to obtain quantitative information about the dipole moments of the fluorophores. The Mataga–Liptay equation was used:[25]

$$\nu_f = -2\mu_e(\mu_e - \mu_g)\Delta f/hca^3 + \text{constant} \qquad (1)$$

where

$$\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - 0.5[(n^2 - 1)/(2n^2 + 1)] \qquad (2)$$

In the equations μ_e and μ_g are the excited and ground state dipole moments, respectively, h is Planck's constant, c is the

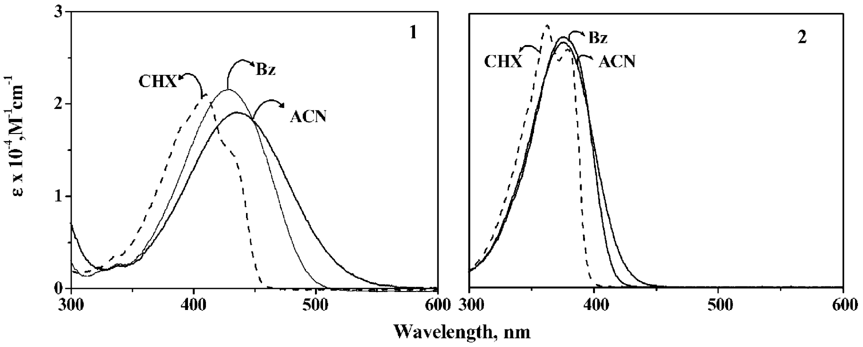
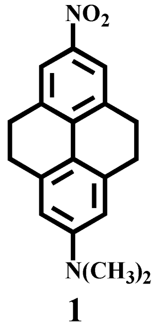
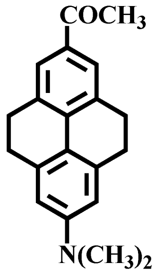


Fig. 1 Absorption spectra of **1** and **2** in cyclohexane (CHX), benzene (Bz) and acetonitrile (ACN).

Table 1 Spectroscopic data for **1** and **2** in different solvents

Compound	Solvent	λ_a^{max}/nm	$\int \varepsilon d\nu_a/10^8$ M^{-1} cm^{-2}	λ_f^{max}/nm	ν_{St}/cm^{-1}
 **1**	Cyclohexane	410, 431	0.92	450, 477	3425
	Benzene	429	0.98	568	5700
	Toluene	426	0.92	563	5700
	Diisopropyl ether	420	1.0	588	6800
	Tetrahydrofuran	431	1.0	619	7000
	Chloroform	438	0.92	667	7800
	Dichloromethane	439	1.0	677	8000
	Ethyl acetate	428	0.97	639	7700
	Acetonitrile	436	0.98	722	9100
	Methanol	431	0.99	748	9800
 **2**	Cyclohexane	363, 379	1.2	399, 411	1322
	Benzene	376	1.2	440	3900
	Toluene	376	1.3	440	3900
	Diisopropyl ether	369	1.3	446	4700
	Chloroform	382	1.2	485	5600
	Dichloromethane	380	1.3	495	6100
	Ethyl acetate	373	1.3	488	6300
	Acetonitrile	376	1.3	518	7300
	Methanol	380	1.2	589	9300

velocity of light, a is the radius of the cavity in which the fluorophore resides (Onsager radius), Δf is known as the solvent polarity parameter and ε and n are the dielectric constant and refractive index, respectively, of the medium. Δf values for the various solvents were calculated from known values of ε and n. The fluorescence maxima for **1** and **2** were then plotted against Δf and straight line plots were obtained (Fig. 5).

From the slopes of theses plots, the dipole moments of the compounds in the excited state can be calculated if the values of a and μ_g are known. μ_g for **1** and **2**, obtained from AM1 calculations, is 8.27 and 4.63 D, respectively. Using a value of 6.0×10^{-10} m for a,[10] we calculated μ_e for **1** and **2**; the values obtained were 23.7 and 21.6 D, respectively. The very large values of μ_e indicate significant charge transfer in the excited state of both the compounds. We thus conclude that fluorescence of **1** and **2** occurs from a ^{1}CT state.

3.3. Fluorescence quantum yield and lifetimes

The fluorescence quantum yields (Φ_f) and lifetimes (τ_f) for the compounds were measured in different solvents. The radiative

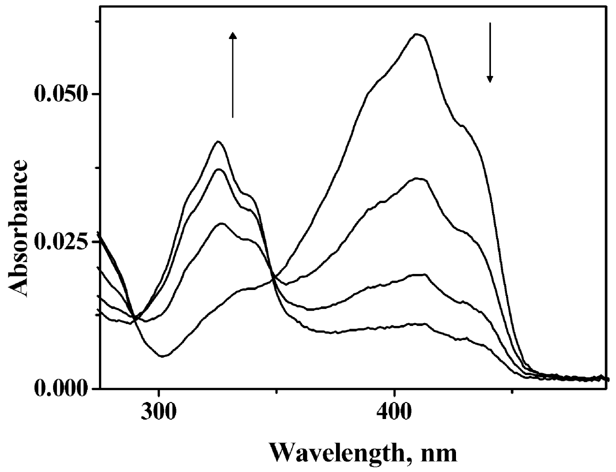


Fig. 2 Effect of addition of TFA on the absorption spectrum of **1** in cyclohexane.

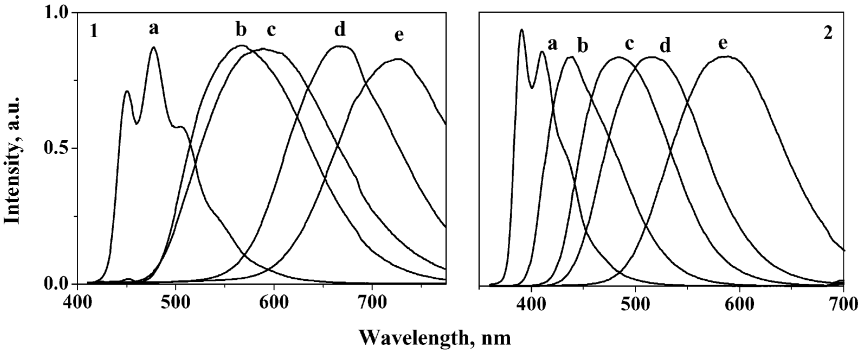


Fig. 3 Normalized fluorescence spectra at 298 K of **1** in (a) cyclohexane, (b) benzene, (c) diisopropyl ether, (d) chloroform and (e) acetonitrile and **2** in (a) cyclohexane, (b) benzene, (c) chloroform, (d) acetonitrile and (e) methanol.

($k_r = \Phi_f/\tau_f$) and nonradiative [$k_{nr} = (1 - \Phi_f)/\tau_f$] rate constants were calculated using the Φ_f and τ_f values. The values of Φ_f, τ_f, k_r and k_{nr} obtained are given in Table 2. As can be seen, the fluorescence quantum yields exhibit variations with solvent polarity.

In order to see if these quantum yield variations are due to a solvent-dependent change in the nature of the excited state, the following procedure was adopted. The natural fluorescence rate constant (also known as the Strickler–Berg rate constant, $k_r^{(SB)}$) for a fluorophore can be calculated using eqn. (3):[26,27]

$$k_r^{(SB)} = \frac{8\pi \boldsymbol{c} 10^3 \ln 10}{N_L} n^2 \nu_f^3 \int \varepsilon(\nu_a) \mathrm{d} \ln \nu_a \qquad (3)$$

In eqn. (3), **c** is the velocity of light, N_L is Loschmidt's constant (Avogadro's number), n is the refractive index of the solvent used, ν_f is the fluorescence maximum, and $\int \varepsilon(\nu_a)\mathrm{d}(\ln\nu_a)$ is the area under the $\varepsilon(\nu_a)$ *vs.* $\ln\nu_a$ curve. The Strickler–Berg relation is applicable only when the fluorescence occurs from the state (FC state) populated by the absorption. It can be shown that the ratio of the radiative rate constant k_r to the Strickler–Berg rate constant $k_r^{(SB)}$ is given by:[20]

$$k_r/k_r^{(SB)} = M_f^2/M_a^2 \qquad (4)$$

If the fluorescence spectrum arises from the same state as that populated by the absorption process, then $M_a = M_f$ and $k_r/k_r^{(SB)} = 1$ for such systems. In order to see if the fluorescence takes place from the FC state or from a slightly different state, we have calculated values of $k_r/k_r^{(SB)}$ for compounds **1** and **2** in the various solvents; the values obtained are given in Table 2. Notice that $k_r/k_r^{(SB)}$ is not equal to 1 in all solvents, indicating that the emissions do not arise from the FC states.

An inspection of Table 2 shows that the photophysical data for the compounds exhibit several differences with those of the D-A biphenyls[2–4] and D-A THP systems[20] studied earlier. For example, the fluorescence quantum yields of **1** and **2** are very low in CHX. The fluorescence decays in this solvent are biexponential. We have observed that the values of the two lifetimes are independent of emission wavelength, but their relative contributions change with wavelength. For example, in the case of **1**, with λ_{exc} = 410 nm and λ_{em} = 477 nm, the contributions due to the short and long components are 92% and 8%, respectively. When λ_{em} was changed to 540 nm, the contributions change to 75% and 25%, respectively. Similar results were obtained in the case of **2** (λ_{exc} = 377 nm, λ_{em} = 411 nm, τ_1 85% and τ_2 15%; λ_{exc} = 377 nm, λ_{em} = 475 nm, τ_1 65% and τ_2 35%). This suggests that the fluorescence band observed in CHX is a composite of two emission bands, namely the FC and ^{1}CT states. We tentatively assign the component with the short lifetime to the FC state. Since there are two emitting states with different lifetimes, it is meaningless to calculate $k_r/k_r^{(SB)}$ values. Hence these calculations were not carried out for **1** and **2** in CHX.

In solvents more polar than CHX, **2** exhibits high fluorescence quantum yields. As the polarity increases from benzene to acetonitrile, Φ_f remains constant. The fluorescence decays are single exponential and the lifetime shows a slight enhancement with solvent polarity. The $k_r/k_r^{(SB)}$ values for **2** are similar in all solvents. These values are slightly greater than 1, indicating that the molecular structure of the FC is only slightly different from that of the emitting state. The behavior of **2** in this respect is similar to that of the D-A biphenyl systems[2–4] and D-A THP systems[20] studied earlier. Accordingly, the dimethylaminophenyl moiety can be considered as the donor fragment and the acetylphenyl moiety can be labelled as the acceptor fragment in **2**. In the ground state, the donor and acceptor fragments are twisted by 14°. Upon excitation in polar solvents the FC state undergoes relaxation to a planar ^{1}CT state, which is responsible for the observed emission. The ^{1}CT state is stabilized in polar solvents, leading to an increase in the lifetime and a decrease of the radiative and non-radiative rates. It is to be noted that the lifetimes of the ^{1}CT state in

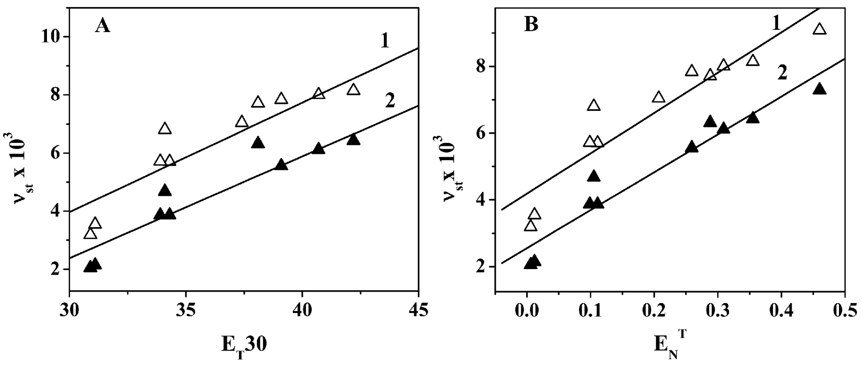


Fig. 4 Plots of Stokes shift values of **1** (△) and **2** (▲) *vs.* (A) $E_T(30)$ and (B) E_T^N.

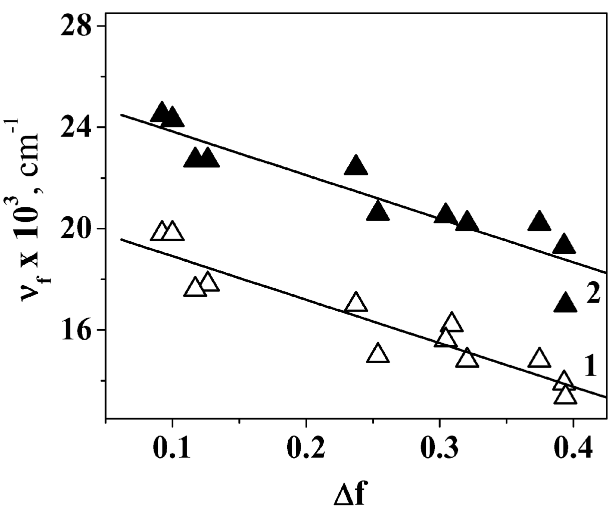


Fig. 5 Plots of ν_f *vs.* Δf for **1** (△) and **2** (▲).

benzene and toluene are comparable to the long-lifetime component in CHX. This lends support to our assignment of the long-lived state in CHX to a ^{1}CT state.

For **1**, the fluorescence quantum yields are high in benzene and toluene. In these solvents **1** follows the same photophysical pathway exhibited by **2**. Further increase in solvent polarity leads to a decrease in Φ_f values. This is associated with a decrease of fluorescence lifetimes and an increase in radiative and non-radiative rates. Our results suggest that a very strong deactivation pathway is open to **1** in polar solvents. The $k_r/k_r^{(SB)}$ values differ considerably in the different solvents, indicating that the excited state structure varies with the solvent used for **1**.

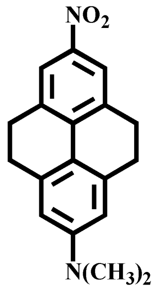
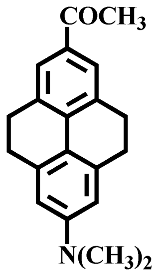
3.4. Laser flash photolysis experiments

The very low Φ_f values in CHX suggest a facile non-radiative pathway for **1** and **2** operating only in this solvent. In order to see if this is due to an intersystem crossing (ISC), we have carried out laser flash photolysis of **1** and **2**. In cyclohexane **1** gives a very strong transient characterized by bleaching in the 300–400 nm region and strong absorption in the 500–700 nm region (Fig. 6). In the case of **2** the transient exhibits strong bleaching below 400 nm and strong absorption above 450 nm with a maximum around 550 nm. The transient spectrum was assigned to the triplet-triplet absorption based on the following two observations: (1) the lifetime of the transients decrease very strongly in the presence of oxygen and (2) the transients are quenched by β-carotene, leading to the formation of a β-carotene triplet (λ_{max} = 540 nm in benzene). Flash photolysis of these compounds in other solvents listed in Table 2 gave extremely weak transients on the nanosecond time scale. This suggests that ISC to the triplets does not contribute significantly to excited state deactivation in these solvents.

The quantum yield of triplet formation (Φ_t) for **1** was determined by the energy transfer method, using β-carotene as the acceptor. For this experiment, solutions of benzophenone in benzene (10 ml) and **1** in cyclohexane (10 ml) were optically matched at 355 nm and mixed with 0.1 ml of a 1.0 mM solution of β-carotene in benzene. The solutions were flash photolyzed and the triplet absorptions due to β-carotene at 540 nm were monitored. Comparison of plateau absorbances (ΔA^S for **1** and ΔA^R for benzophenone) following the completion of sensitized triplet formation, properly corrected for the decay of the donor triplets in competition with energy transfer to β-carotene, enabled us to determine Φ_T for **1**. The following equation was used:[28]

$$\Phi_T = \Phi_R \frac{\Delta A^S}{\Delta A^R} \left(\frac{k_{S+\beta}}{k_{S+\beta} - k_S} \right) \left(\frac{k_{R+\beta} - k_R}{k_{R+\beta}} \right) \qquad (5)$$

Table 2 Photophysical data for **1** and **2** in different solvents

Compound	Solvent[a]	Φ_f	τ_f/ns	$k_r/10^8\ s^{-1}$	$k_{nr}/10^8\ s^{-1}$	$k_r^{(SB)}/10^8\ s^{-1}$	$k_r/k_r^{(SB)}$
 **1**	CHX	0.03	0.28, 1.96	0.27	8.7	2.8	—
	Bz	0.72	2.38	3.0	1.2	1.6	1.9
	Tol	0.69	2.79	2.5	1.1	1.5	1.6
	DIE	0.34	1.13	3.0	5.8	1.2	2.5
	EA	0.16	0.66	2.4	12.7	0.9	2.7
	ACN	0.01	0.32	0.31	30.9	0.6	0.5
 **2**	CHX	0.049	0.23, 1.46	0.057	1.1	3.8	—
	Bz	0.74	1.85	4	1.4	3.2	1.2
	Tol	0.74	1.77	4.2	1.4	3.8	1.1
	DIE	0.72	2.4	3.0	1.2	2.7	1.1
	EA	0.74	2.5	2.9	1.0	2.2	1.3
	ACN	0.72	2.9	2.5	0.9	1.8	1.4

[a] CHX = cyclohexane, Bz = benzene, Tol = toluene, DIE = diisopropyl ether, EA = ethyl acetate, ACN = acetonitrile.

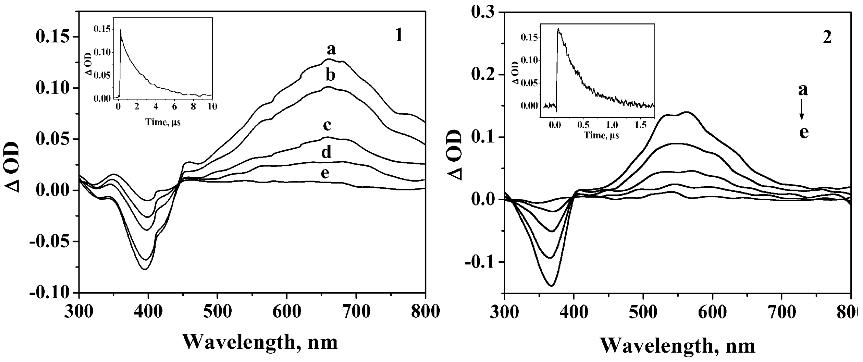


Fig. 6 Transient absorption spectra of **1** and **2** in cyclohexane at 298 K at different time intervals following the laser excitation. Inset shows the decay trace at 650 nm for **1** and 550 nm for **2**. Spectra a, b, c, d and e were taken at 0.34, 0.84, 4.0, 10.0 and 25.0 μs after excitation.

In eqn. (5), Φ_R is the triplet quantum yield of the reference compound benzophenone, $k_{S+\beta}$ and $k_{R+\beta}$ refer to the observed rate constants for the growth of β-carotene triplet in the presence of **1** and benzophenone, respectively, and k_R and k_S refer to observed decay rate constants, respectively, of the triplets of **1** and benzophenone in the absence of quenchers. Using this method, we obtained $\Phi_T = 0.97$ for **1**. Thus $\Phi_f + \Phi_t = 1$ in cyclohexane, indicating that no other deactivation process takes place for **1** in this solvent. Transient absorptions due to **2** and β-carotene triplets occurred at the same wavelength. Because of this the growth kinetics of β-carotene could not be measured properly. Thus, we could not measure Φ_T of **2**. Since **1** and **2** exhibit similar photophysical properties in cyclohexane (Table 1), we propose that triplet quantum yields of **1** and **2** will also be similar in this solvent. Since no triplet was observed in polar solvents, the low fluorescence quantum yields observed for **1** in polar solvents cannot be attributed to ISC.

3.5. Excited state processes in 1 and 2

As is clear from the results, excited state processes taking place in **1** and **2** are solvent-dependent. In cyclohexane, excitation leads to population of an FC state that seems to decay by three competing pathways: (1) fluorescence to the ground state, (2) cross-over to a closely lying ^{1}CT state and (3) ISC to a triplet state (Fig. 7). ISC to the triplet is the major pathway in this solvent. The existence of the ^{1}CT state is inferred from the biexponential nature of the fluorescence decay. Since the ^{1}CT state is not stabilized in non-polar solvents, this state is formed only in very small amounts in CHX.

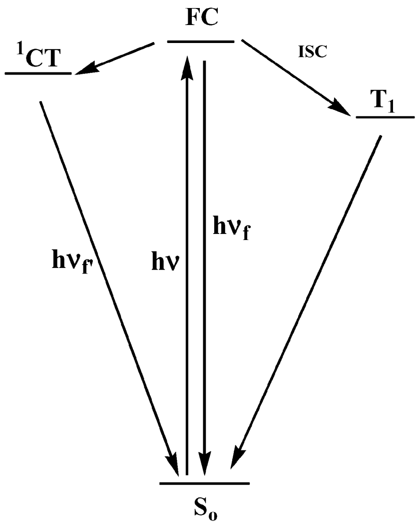
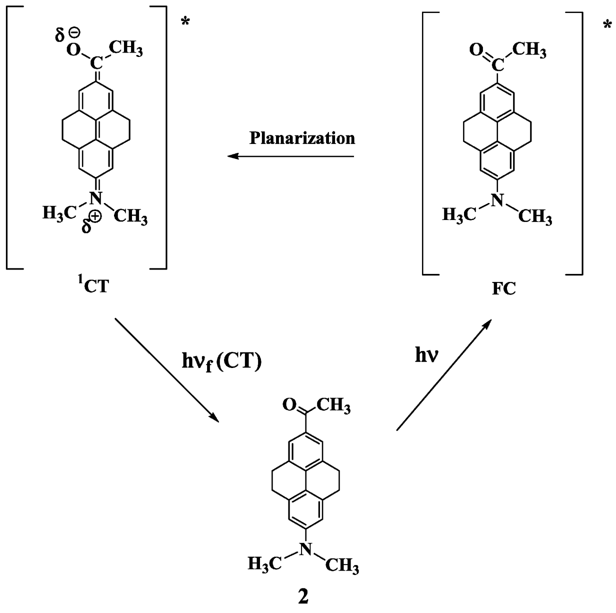


Fig. 7 Energy level diagram for **1** and **2** in cyclohexane.

In the case of **2**, in solvents other than CHX, the predominant species present in the excited state is the planar ^{1}CT state (*vide supra*), as observed in the case of D-A biphenyls. This is shown in Scheme 3. The molecule in the ground state is twisted by 14°. The FC state formed upon excitation also has the same geometry. $k_r/k_r^{(SB)}$ values are not equal to 1, suggesting that the emission is not from the FC state. Steady-state fluorescence spectra and nanosecond lifetime data did not give direct evidence for the FC state in polar solvents, suggesting that the FC state has a sub-nanosecond lifetime in polar solvents. The FC state undergoes planarization and delocalization to give the ^{1}CT state as observed in the case of D-A biphenyls (Scheme 3). Since the ^{1}CT state is stabilized in polar solvents, the quantum yield and lifetime values are higher in polar solvents.

For **1**, photoprocesses taking place in solvents such as benzene and toluene are similar to those shown in Scheme 3. The ^{1}CT state is formed in high yield in these solvents. With further increase in solvent polarity fluorescence quantum yields and lifetimes decrease drastically. The behavior of **1** in polar solvents is similar to that of 4-*N*,*N*-(dimethylamino)-2,6-dimethyl-4′-cyanobiphenyl studied by Rettig and co-workers. A fast equilibrium between a more planar and a more twisted rotamer distribution in the ^{1}CT state is invoked to explain the photophysics in this case. In the case of **1** also we attribute the low Φ_f value in polar solvents to a twisted ^{1}CT state. The twisting can be either at the dimethylamino group as suggested for 4-*N*,*N*-dimethylaminobenzonitrile (DMABN) and other



Scheme 3

compounds exhibiting dual emission, or at the nitro group. A third possibility is twisting about the single bond connecting the two phenyl groups. It must be mentioned here that rotation about the central C–C bond is restricted in THP systems. Hence twisting to high angles is not physically possible. Twisting of the dimethylamino or nitro group is more probable. Since a nitro group can stabilize a negative charge better (compared to the stabilization afforded to a positive charge by a dimethylamino group), the nitro group may be the twisting moiety. Twisting reduces delocalization, leading to localization of the charges. Localized charges are stabilized better in polar solvents and this reduces the energy of the ^{1}CT states further.

In the case of D-π-A systems such as DMABN, the ground state is planar. The TICT model invokes a twisting of the dimethylamino group with respect to the plane of the phenyl ring in the excited state of DMABN. The D-A biphenyl systems, on the other hand, are twisted in the ground state and exhibit very different excited state pathways. D-A biphenyls, which are not sterically crowded, undergo intramolecular charge transfer and planarization in the excited state. In sterically crowded D-A biphenyls, ICT in the excited state is associated with twisting of the phenyl rings to a perpendicular geometry in polar solvents. Twisting of the D or A substituent is not an active deactivation pathway in the D-A biphenyl systems (including the D-A THP systems) studied earlier. The behavior of **1** suggests that twisting of the acceptor substituent can also contribute towards the deactivation of the excited states in these molecules.

4. Conclusion

We have investigated the excited state processes taking place in donor-acceptor substituted tetrahydropyrenes **1** and **2** in several solvents. **1** and **2** have very similar structures and differ only in the nature of the acceptor substituent in them. The absorption spectra of these compounds exhibit only minor changes with solvent polarity while the fluorescence maxima exhibit solvent-polarity-dependent red shifts. The solvent dependent shifts were analyzed quantitatively to get the excited state dipole moments. In the non-polar solvent cyclohexane, fluorescence quantum yields are very low because of the facile intersystem crossing to a triplet state. The triplet was characterized by transient absorption spectra. In the case of **2**, increase in solvent polarity favors the formation of an emitting planar ^{1}CT state. In the case of **1**, this planar ^{1}CT state is the predominant species only in medium polarity solvents. In highly polar solvents the fluorescence quantum yields are very low and this is attributed to a deactivation pathway involving the twisting of the nitro group with respect to the phenyl ring to which it is attached. Thus, the photophysics of the D-A THP systems depend very much on the nature of the acceptor substituent. A strong electron-accepting group such as nitro can stabilize a negative charge and in this case twisting involving the nitro group is a predominant excited state deactivation pathway in polar solvents. With weaker acceptor groups such as acetyl, this pathway is not at all important.

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References

1 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3899 and references cited therein.
2 F. Lahmani, E. Breheret, A. Zehnacker-Rentien, C. Amatore and A. Jutand, *J. Photochem. Photobiol. A: Chem.*, 1993, **70**, 39.
3 F. Lahmani, E. Breheret, O. Benoist d'Azy, A. Zehnacker-Rentien and J. F. Delouis, *J. Photochem. Photobiol. A: Chem.*, 1995 **89**, 191.
4 M. Maus, W. Rettig, D. Bonafoux and R. Lapouyade, *J. Phys. Chem. A*, 1999, **103**, 3388.
5 M. Maus and W. Rettig, *Chem. Phys.*, 1997, **218**, 151.
6 M. Maus, W. Rettig, G. Jonusauskas, R. Lapouyade and C. Rulliére, *J. Phys. Chem. A*, 1998, **102**, 7393.
7 M. Maus and W. Rettig, *Chem. Phys. Lett.*, 2000, **324**, 57.
8 W. Rettig, V. Kharlanov and M. Maus, *Chem. Phys. Lett.*, 2000, **318**, 173.
9 J. Herbich and J. Waluk, *Chem. Phys.*, 1994, **188**, 247.
10 A. M. Klock and W. Rettig, *Pol. J. Chem.*, 1993, **67**, 1375.
11 M. Maus, W. Rettig and R. Lapouyade, *J. Inf. Rec. Mater.*, 1996, **22**, 451.
12 W. Rettig and M. Maus, *Ber. Bunsen-Ges. Phys. Chem.*, 1996 **100**, 2091.
13 M. Maus and K. Rurack, *New J. Chem.*, 2000, **24**, 677.
14 M. J. Foley and L. A. Singer, *J. Phys. Chem.*, 1994, **98**, 6430.
15 H. Ephardt and P. Fromherz, *J. Phys. Chem.*, 1991, **95**, 6792.
16 P. Fromherz and A. Heilemann, *J. Phys. Chem.*, 1992, **96**, 6864.
17 C. Rocker, A. Heilemann and P. Fromherz, *J. Phys. Chem.*, 1996, **100**, 12172.
18 P. T. Chou, C. P. Chang, J. H. Clements and K. Meng-Shin, *J. Fluoresc.*, 1995, **5**, 369.
19 Y. Zhu and G. B. Schuster, *J. Am. Chem. Soc.*, 1990, **112**, 8583.
20 S. Sumalekshmy and K. R. Gopidas, *J. Phys. Chem. B*, 2004 **108**, 3705.
21 D. F. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107.
22 M. A. Miranda and H. Garcia, *Chem. Rev.*, 1994, **94**, 1063.
23 D. Magde, J. H. Brannon, T. L. Cremers and J. Olmsted III, *J. Phys. Chem.*, 1979, **83**, 696.
24 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
25 W. Liptay, *Z. Naturforsch., A: Astrophys. Phys. Phys. Chem.*, 1965, **20**, 1441.
26 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814.
27 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, 1970.
28 C. V. Kumar, L. Quin and P. K. Das, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 783.