

SPECTRAL AND PHOTOPHYSICAL PROPERTIES OF 9,10-DIPHENYLANTHRACENE IN PERFLUORO-*n*-HEXANE: THE INFLUENCE OF SOLUTE-SOLVENT INTERACTIONS

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Summary

The photophysical properties of 9,10-diphenylanthracene (DPA) are found to be unusual in perfluoro-*n*-hexane (PFH) compared with other solvents. Low values of the fluorescence quantum yield, $\phi_F = 0.58$, and S_1 lifetime, $\tau_{S_1} = 6.7$ ns, and relatively large shifts in the absorption and emission spectra in PFH are attributable to changes in the electronic energies of DPA which permit an enhancement of the rate of $S_1 \rightsquigarrow T_2$ relaxation in this solvent. A large value of the intersystem crossing quantum yield in PFH, $\phi_{ISC} = 0.35$, supports this conclusion.

1. Introduction

9,10-Diphenylanthracene (DPA) is one of the most commonly used standards for measuring emission quantum yields in solution [1, 2]. The fluorescence quantum yields ϕ_F and first excited singlet state lifetimes τ_{S_1} of this molecule have thus been measured in many different solvents over a wide temperature range. In a very thorough study, Meech and Phillips [3] recently showed that the absorption and emission spectra of DPA shifted slightly to lower energies with increasing solvent refractive index n . This was accompanied by the anticipated variation of the radiative rate constant k_R with n^2 , but no significant change in the S_1 excited state non-radiative decay constant k_{NR} . Although their measured values of ϕ_F varied slightly from solvent to solvent (*n*-hexane, cyclohexane, decalin and benzene), Meech and Phillips judged that to within an experimental error of 3% the fluorescence quantum yield could be regarded as essentially independent of the solvent, with an average value of 0.93.

Although the radiative decay of DPA in its S_1 state has been well characterized, the nature and rates of its non-radiative process(es) are still uncertain. The accumulated evidence from many measurements indicates

that ϕ_F for DPA in most solvents is less than 1.0 at room temperature [3 - 8]. The minor, non-radiative, decay channel has usually been identified as inter-system crossing (ISC) to the triplet manifold [2, 9, 10], with $\phi_F + \phi_{ISC} = 1.0$. Quantum yields of ISC of 0.12 [9], 0.08 [11] and 0.09 [12] have been measured in liquid paraffin, toluene and dinonylphthalate respectively. However, using nanosecond laser flash photolysis with T-T transient absorption, Darmanyan [12] recently obtained the very small value $\phi_{ISC} = (8 \pm 1.5) \times 10^{-3}$ for DPA in toluene. Assuming that $\phi_F = 0.95$ in both benzene and toluene [3, 7, 10], Darmanyan therefore suggested that internal conversion (IC), $S_1 \rightsquigarrow S_0$, is the major non-radiative decay process of excited DPA so that, at least in toluene, $\phi_{IC} \approx 0.04$. A definitive determination of the relative contributions of ISC and IC to the decay of DPA S_1 is difficult because $\phi_{NR} = \phi_{ISC} + \phi_{IC} = 1 - \phi_F \leq 0.10$ for all solvents employed to date, and because the rate (or quantum yield) of internal conversion has never been measured directly in this system. We have recently shown that both the excited state lifetimes and $S_2 \rightarrow S_0$ fluorescence quantum yields of aromatic thiones are greatly increased in perfluoroalkanes compared with other common photochemically inert non-polar solvents [13, 14], owing to the unusual weakness of the solvent-solute interactions of the former [15, 16]. Anticipating that the rate constant for non-radiative decay of DPA S_1 might decrease in perfluoroalkanes (so that ϕ_F might approach unity more closely), and that the use of perfluoroalkane solvents would provide a good additional test of the dependence of the S_1 radiative rate constant k_F on n^2 [2, 3, 7, 17], we measured the emission and absorption spectra, ϕ_F and τ_{S_1} , of DPA in perfluoro-*n*-hexane (PFH). The results were unexpected and led us to measure ϕ_{ISC} ; they reveal the potential sensitivity of the photophysical properties of polyatomic molecules to small changes in solute-solvent interaction.

2. Experimental details

DPA was either scintillation grade (Koch) or Gold Label (Aldrich) and was recrystallized twice from 95 vol.% ethanol. Quinine bisulfate (BDH) was recrystallized three times from water. Ethanol, *n*-hexane and cyclohexane (Merck, fluorescence grade) were used as received. 3-Methylpentane (3-MP) (Aldrich, puriss) and PFH (PCR and K and K) were purified as described previously [18]. Solvent purity (better than 99.8%) was determined by gas chromatography using an HP Model 5880A gas chromatograph with a 50 m SE-52 capillary column, a PYE-104 chromatograph with a 2.7 m silicone OV 17 column and by UV and IR spectrophotometry.

Solutions were deoxygenated by flushing with oxygen-free helium or N_2 or by repeated freeze-pump-thaw cycles. DPA is only sparingly soluble in PFH and about 10^{-6} M solutions were used for investigation. At these low concentrations self-quenching and reabsorption of fluorescence can be entirely neglected. All experiments were performed at $21 \pm 1^\circ \text{C}$.

Steady state fluorescence spectra were recorded using Perkin-Elmer MPF-3 or MPF-44 spectrofluorometers or a modified version of an instrument of our own construction [19]. Absorption spectra were measured on Cary 118 and Specord M-40 (Zeiss) spectrophotometers. Picosecond fluorescence lifetimes were measured with a synchronously pumped, cavity-dumped, frequency-doubled R6G dye laser excitation system with time-correlated single-photon counting detection [18, 20]. In order to avoid distortion of decay curves caused by rotational fluorescence depolarization, magic angle excitation and detection was employed [21]. Deconvolutions of the instrument response function from the observed decay were performed using the response function mimic technique [20], yielding a precision of about ± 10 ps in the subnanosecond lifetime domain.

Fluorescence quantum yields were measured relative to DPA in cyclohexane ($\phi_F = 0.91$ [3, 4]) and quinine bisulfate in 0.1 N H_2SO_4 ($\phi_F = 0.51$ [3, 22]). The DPA fluorescence quantum yield was then calculated from the equation

$$\phi_F = (\phi_F)_s \frac{\int J(\bar{\nu}) d\bar{\nu}}{\int J_s(\bar{\nu}) d\bar{\nu}} \frac{(J_a)_s n^2}{J_a n_s^2} \quad (1)$$

where the integrals are the areas under the corrected fluorescence spectra, J_a is the absorbed light intensity, n is the refractive index and the subscript s refers to the standard. In each case the geometry, excitation wavelength and spectral bandpasses were identical for the sample and the standard. Also, the same spectral bandpass was used in the absorption and the emission measurements. The optical density was always lower than 0.03 and was approximately the same for both the sample and the reference standard.

In view of the previous controversy connected with the measurement of ϕ_F in solutions of different refractive index [3, 7, 23] and recognizing that substantial differences exist in the values of n (at 293 K) for PFH ($n = 1.2515$), 3-MP ($n = 1.3765$), 0.1 N H_2SO_4 ($n = 1.341$) and cyclohexane ($n = 1.426$), the validity of the " $1/n^2$ correction" employed in relative quantum yield measurements in right-angle fluorometers was tested experimentally. For this purpose the intensities of the fluorescence of azulene in PFH and 3-MP were measured relative to that of DPA in 3-MP for various widths (0.3 - 8.0 mm) of the emission slits placed 7 mm from the center of the cell. Both $J_{em}(\text{azulene-3-MP})/J_{em}(\text{DPA-3-MP})$ and $J_{em}(\text{azulene-PFH})/J_{em}(\text{DPA-3-MP})$ were independent of slit width, supporting the use of the $1/n^2$ correction [3, 23].

A value of the ISC quantum yield ϕ_{ISC} was measured using a nanosecond laser flash photolysis system previously described [24]. Samples were excited at $\lambda = 347$ nm by the second harmonic of a ruby laser with $E \leq 50$ mJ and a pulse width of 15 ns. The transient absorption was monitored by means of a 500 W xenon arc lamp. Anthracene (10^{-4} M in ethanol) was used as a standard.

The value of ϕ_{ISC} for DPA was calculated from the relation [25]

$$\phi_{ISC} = \phi_{ISC}^A \frac{OD \epsilon_T^A I_a^A I_0^A}{OD^A \epsilon_T^A I_a^A I_0^A} \quad (2)$$

where A refers to anthracene, OD is the optical density for the $T_1 \rightarrow T_n$ transition, ϵ_T is the corresponding molar absorption coefficient, I_a is the absorbed intensity at the excitation wavelength and I_0 is the intensity of the incident laser radiation at 347 nm. The anthracene solution was irradiated under the same conditions as those used for DPA, except that a significantly lower I_0 was employed. The values $\phi_{ISC}^A = 0.71$ [25, 26] and $\epsilon_T^A = 64\,700 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 421 \text{ nm}$ [25, 27] were used.

3. Results and discussion

Absorption and emission spectra of DPA dissolved in PFH are presented in Fig. 1. The spectra of DPA in 3-MP, cyclohexane and ethanol are included for comparison. The corrected excitation spectra are identical with the absorption spectra in the region $\lambda > 300 \text{ nm}$. The relevant spectral data are summarized in Table 1.

Note that the positions and widths of the 0-0 bands in both the absorption and the emission spectra differ only slightly among the four hydrogen-containing solvents (despite the substantial differences in their polarities), but exhibit consistent trends. The spectra in PFH, however, exhibit 0-0 bands which are considerably blue shifted, have the smallest $\bar{\nu}_a^{(0-0)} - \bar{\nu}_e^{(0-0)}$ and are substantially narrower than those of the other solvents. The magnitude of $\bar{\nu}_a^{(0-0)} - \bar{\nu}_e^{(0-0)}$ is largely determined by the degree of structural rigidity of the absorbing or emitting molecule, and the value of 410 cm^{-1} for DPA in PFH appears to be quite characteristic of partially flexible molecules in perfluoroalkane solvents. (Rigid molecules in PFH exhibit $\bar{\nu}_a^{(0-0)} - \bar{\nu}_e^{(0-0)} < 100 \text{ cm}^{-1}$ [26].) Among the aliphatic solvents the bathochromic shift in band position with decreasing solvent polarity is consistent with a transition terminating in an excited state of $^1(\pi, \pi^*)$ character, as has already been well established for DPA's near-UV absorption [2, 5].

An approximately linear relationship between the frequency of the 0-0 absorption band and Bayliss-McRae refractive index function $(n^2 - 1)/(2n^2 + 1)$ is observed for the four non-polar solvents studied. Such a relationship is expected for solutions of a non-polar solute in a series of similar non-polar solvents in which dispersion interactions dominate [28], and demonstrates that perfluoroalkane solvents are only unusual in the sense that they exhibit very weak dispersive interactions. A quantitative analysis of the solvent spectral shifts would have been desirable. However, preliminary experiments [26] in which the solvent spectral shifts of a number of aromatic hydrocarbons were measured in several perfluoroalkanes and perhydroalkanes have revealed that neither the Bayliss-McRae expression above nor more complete treatments of Nicol and others [28] are universally applicable to a mixed set of perfluorocarbon and hydrocarbon solvents.

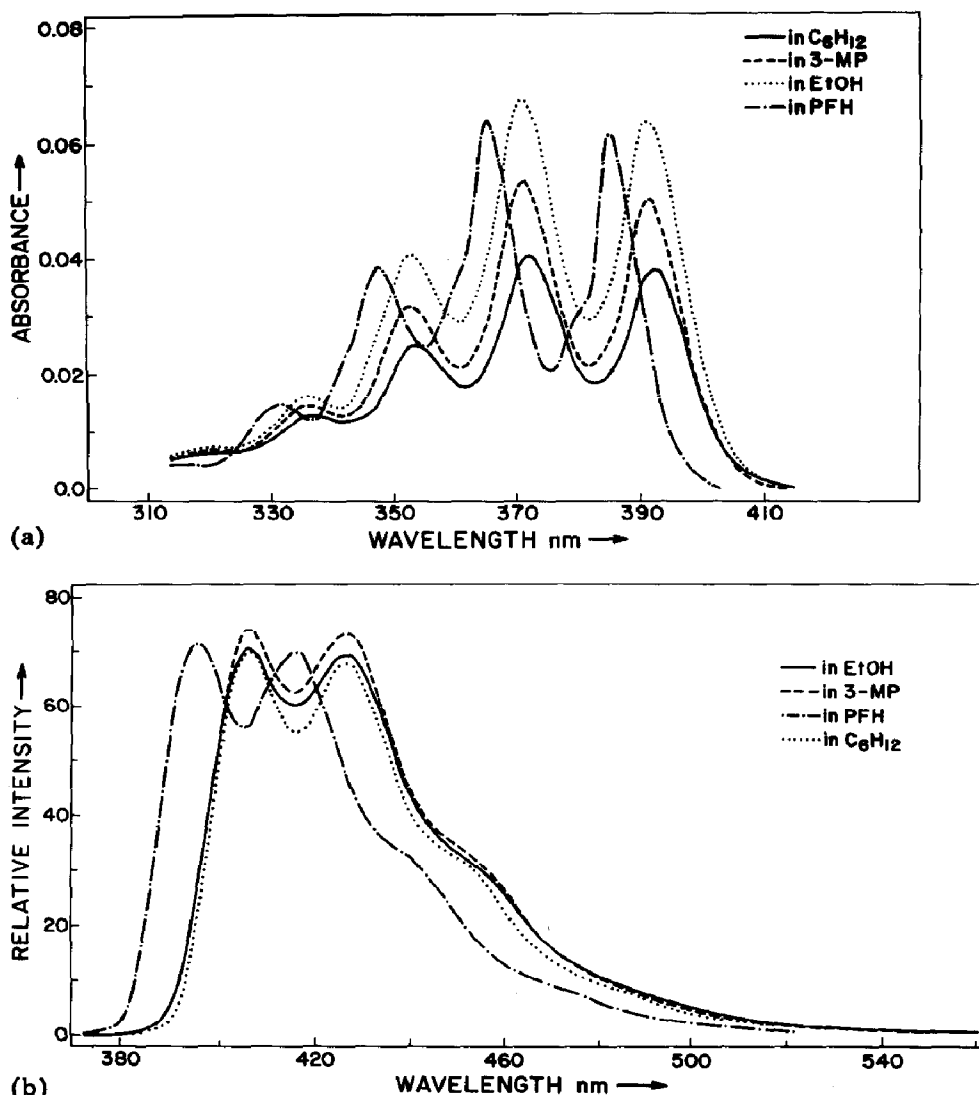


Fig. 1. (a) Absorption and (b) fluorescence spectra of DPA (about 2×10^{-6} M) in several different solvents at 293 K. Fluorescence spectra were excited at 365 nm.

The values of ϕ_F and τ_{S_1} obtained for DPA in PFH and 3-MP are given in Table 2. Previously determined values of these quantities in 3-MP and in several other solvents are also presented for comparison. The value $\phi_F = 0.91$ obtained for DPA in 3-MP is completely consistent with a previous measurement [7], but $\phi_F = 0.58$ for DPA in PFH is unexpectedly small. Similarly, the value $\tau_{S_1} = 7.79$ ns is in very close agreement with that reported earlier for DPA in 3-MP [7], whereas τ_{S_1} is significantly shorter in PFH than in all other solvents [3, 7, 10]. Results similar to those for DPA in PFH have also been obtained for DPA in perfluoromethylcyclohexane [26].

TABLE 1

Absorption and emission spectral data for DPA in several solvents at 293 K

Solvent	Absorption ^a		Emission ^a		$\bar{\nu}_a(0-0) - \bar{\nu}_e(0-0)$ (cm ⁻¹)	$\Delta\bar{\nu}(2/3)^b$ (cm ⁻¹)
	$\bar{\nu}_a(0-0)$ (cm ⁻¹)	E_{S_1} (kcal mol ⁻¹)	$\bar{\nu}_e(0-0)$ (cm ⁻¹)	E_{S_1} (kcal mol ⁻¹)		
PFH	25970	74.3	—	25300	72.4	410
3-MP ^c	25520	73.0	450	24610	70.4	590
Cyclohexane	25510	73.0	460	24600	70.4	620
Ethanol	25450	72.8	520	24550	70.3	610
C ₆ H ₆ ^d	25240	72.2	730	24260	69.4	—

^a Band positions measured to ± 10 cm⁻¹. E_{S_1} taken from the maximum of the 0-0 band.^b Width of the 0-0 band in absorption, measured at 2/3 height to facilitate comparison.^c Results in *n*-heptane are very similar.^d From ref. 3.

TABLE 2

Photophysical data for the first excited singlet state of DPA in various solvents

<i>Solvent</i>	ϕ_F	τ_{S_1} (ns)	$k_F \times 10^{-8}$ ^a (s ⁻¹)	$k_{NR} \times 10^{-8}$ ^a (s ⁻¹)	<i>n</i>	$10^{-8} k_F/n^2$ (s ⁻¹)	<i>Refer- ence</i>
PFH	0.58 ± 0.03	6.72	0.86	0.63	1.2515	0.55	This work
3-MP	0.91 ± 0.05	7.79					This work
	0.95	7.88					[7]
(average)	0.93	7.84	1.18	0.10	1.3765	0.62	
<i>n</i> -Hexane	0.90 ± 0.04	7.98	1.13	0.13	1.375	0.60	[3]
<i>n</i> -Heptane	0.89	8.0	1.11	0.14	1.387	0.58	[10]
Isopentane	0.91	8.8	1.03	0.10	1.351	0.58	[8]
Cyclohexane	0.91 ± 0.02	7.68					[3]
	0.90 ± 0.04	—					[4]
	0.95	7.58					[7]
	0.95 ± 0.03	—					[8]
(average)	0.925	7.61	1.22	0.10	1.426	0.60	
Decalin	0.94 ± 0.06	7.17	1.31	0.08	1.473	0.60	[3]
Ethanol	0.94	8.1					[10]
	0.95	8.19					[7]
(average)	0.945	8.14	1.15	0.07	1.359	0.62	
Benzene	0.955 ± 0.02	7.14					[3]
	0.96	6.8					[10]
	0.96	7.34					[7]
(average)	0.96	7.06	1.35	0.07	1.501	0.60	

^aCalculated from $k_F = \phi_F/\tau_{S_1}$ and $k_{NR} = (1 - \phi_F)/\tau_{S_1}$.

Measurements of τ_{S_1} in deoxygenated and in air-saturated solutions ($[O_2] = 3 \times 10^{-3}$ M in 3-MP [29] and $[O_2] = 5.7 \times 10^{-3}$ M in PFH [16, 30]) also permitted the rate constants k_{O_2} for the bimolecular quenching of S_1 by O_2 to be estimated. Assuming a simple competitive Stern–Volmer quenching mechanism, the values $k_{O_2} = 1.7 \times 10^{10}$ M⁻¹ s⁻¹ and $k_{O_2} = 2.9 \times 10^{10}$ M⁻¹ s⁻¹ were obtained for PFH and 3-MP respectively. The magnitude of k_{O_2} indicates that the oxygen quenching process is nearly diffusion controlled, in agreement with previous work [8, 11].

The values of ϕ_F and τ_{S_1} indicate that radiationless processes account for a much larger fraction of the decay of S_1 in perfluoroalkane solvents than in the hydrogen-containing solvents. These results are completely contrary to those anticipated solely on the basis of solvent effects observed in other systems. In previous studies, the use of perfluoroalkane solvents has, almost without exception, resulted in an increase in the excited state lifetime and emission quantum yield and a concomitant decrease in the rate constant for

overall radiationless decay and the quantum yield of intermolecular photochemical processes [13, 14, 31, 32]. Especially dramatic effects have been found for triplet ketones [32] and second excited singlet thiones [13, 14] for which τ_{T_1} and τ_{S_2} respectively are larger in perfluoroalkanes than in saturated hydrocarbons or benzene by more than a factor of 10.

Photochemical reactions of DPA can be entirely discounted as a possible explanation for these results because the quantum yield of disappearance of DPA is less than 10^{-3} in PFH. This result was obtained by measuring the change in absorbance of the DPA solutions during irradiation, and by measuring the absorbed radiation intensity by means of Reinecke salt actinometry [33]. DPA is also photochemically stable in other solvents.

Laser flash photolysis of about 1×10^{-6} M solutions of DPA in PFH resulted in the observation of a weak transient absorption with $\lambda_{\max} \approx 430$ nm. The transient absorber had a lifetime of 2×10^{-3} s. Both the lifetime and λ_{\max} are approximately the same as that of DPA T_1 in toluene [12]. We assign the transient in PFH to T_1 also and calculate an ISC quantum yield of 0.35 ± 0.10 using eqn. (2). Greater precision could not be obtained because DPA is only very sparingly soluble (less than 3×10^{-6} M) in PFH at room temperature. Thus I_a for the DPA-PFH system was necessarily small, as was the resulting $T_1 \rightarrow T_n$ absorption signal. Measurement of ϵ_T by the triplet-triplet energy transfer method [34] was impossible. Thus the value $\epsilon_T = 1.85 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, previously measured for DPA in toluene at 428 nm [12], had to be assumed. Despite these difficulties the magnitude of ϕ_{ISC} indicates that ISC from S_1 to the triplet manifold accounts for a large majority of the non-radiative decay of S_1 in the PFH solvent.

The explanation of the unusual results obtained for DPA in PFH compared with other solvents involves understanding the effect of solute-solvent interactions on the relative energies of the S_1 and T_2 states of DPA. Previous work has established that S_1 and T_2 lie within a few kilocalories per mole of one another in anthracene and its 9- and 9,10-substituted methyl and phenyl derivatives [35-37]. E_{T_2} assumes an approximately constant value of $74.3 \pm 0.8 \text{ kcal mol}^{-1}$ in these compounds and E_{S_1} varies between 71.5 and 76.3 kcal mol^{-1} in non-polar solvents. Accurate spectral measurements on anthracene in hydrogen-containing non-polar solvents have established that $\Delta E(S_1-T_2) = 2 \text{ kcal mol}^{-1}$ [35, 36]. Because $S_1 \rightsquigarrow T_2$ will be exothermic and because the Franck-Condon factor for this transition is expected to be relatively large for such a small electronic energy gap, the rate constant for the $S_1 \rightsquigarrow T_2$ process is expected to be relatively large, despite spin prohibition. In fact $\phi_{ISC} = 0.71$ [9, 25, 38] is measured for anthracene itself. 9-Methylantracene and 9-phenylantracene exhibit $\Delta E(S_1-T_2) \approx 0$, and for these compounds values of ϕ_{ISC} are smaller and ϕ_F are larger than for anthracene [9, 36, 37, 39], although this is due in part to the larger values of k_F for the derivatives. For the 9,10-dimethyl and 9,10-diphenyl derivatives, $\Delta E(S_1-T_2) = -2 \text{ kcal mol}^{-1}$ in hydrogen-containing non-polar solvents. Consequently the rate of radiationless decay is even smaller for these compounds, leading to $\phi_F \geq 0.9$ and small values of ϕ_{ISC} [2, 9, 11].

The crucial role played by the relative energies of S_1 and T_2 is supported by several experiments on anthracene itself. Kellogg [35] has shown that the increase in ϕ_F of anthracene from 0.27 in solution to about 1.0 in the pure crystalline solid is a direct result of a decrease in the energy of the S_1 state from 76.3 kcal mol⁻¹ in solution to 72.8 kcal mol⁻¹ in the crystal, thereby causing $S_1 \rightsquigarrow T_2$ to be endothermic in the latter case [35, 40]. An increase in τ_{S_1} from 6 ns under 1 atm pressure to 24 ns at pressures above 20 kbar has also been observed for anthracene in poly(methyl methacrylate) [41]. This "anomalous" pressure effect has been rationalized on the basis that the change in E_{T_2} with pressure is much less pronounced than the concomitant decrease in E_{S_1} , resulting in a reordering of the S_1 and T_2 levels with increasing pressure [42, 43]. This behavior is not observed in 9-methylanthracene and DPA, which exhibit normal lifetime shortening with increasing pressure [44]. For the latter molecules, $E_{T_2} \geq E_{S_1}$ at atmospheric pressure, so that the application of pressure only widens the energy difference between the two states.

Following these ideas, the unexpected values of ϕ_F , ϕ_{ISC} and τ_{S_1} can be attributed to a reordering of the energies of the S_1 and T_2 states brought about by solute-solvent interactions of different magnitudes. E_{S_1} is approximately constant in all solvents used in the present study, except PFH, and is consistently lower than E_{T_2} . Note that Jung and Heckner [36] place the value of $\Delta E(S_1-T_2)$ at -1.8 kcal mol⁻¹ for DPA in *n*-heptane. Because $S_1 \rightsquigarrow T_2$ is endothermic in such cases, and the competing radiative transition is electric-dipole allowed, radiationless decay is not favored and ϕ_F approaches unity. However, for DPA in PFH E_{S_1} is about 2 kcal mol⁻¹ higher than for DPA in 3-MP (Table 1). If one assumes that E_{T_2} is independent of the nature of the solvent, the $S_1 \rightsquigarrow T_2$ process should be approximately thermoneutral in PFH. The assumption appears to be reasonable in light of the evidence presented above.

The obvious consequence of an increase in E_{S_1} to approximately E_{T_2} would be an increase in k_{ISC} , which in turn would be responsible for the experimentally observed shortening of τ_{S_1} , decrease in ϕ_F and increase in ϕ_{ISC} . Substituting PFH for 3-MP would also have the effect of decreasing k_F slightly because of the difference in solution refractive index, but this effect is small compared with the almost fivefold change in k_{NR} . We conclude that the photophysical properties of DPA in PFH are similar to the properties of 9-phenylanthracene in non-polar hydrogen-containing solvents for which $E_{S_1} \approx E_{T_2}$ [9, 36, 39].

Whereas an increase in the rate of $S_1 \rightsquigarrow T_2$ ISC is responsible for the decrease in ϕ_F and τ_{S_1} and the increase in ϕ_{ISC} on substituting PFH for hydrogen-containing solvents, the relative importance of possible parallel competing processes, $S_1 \rightsquigarrow S_0$ and/or $S_1 \rightsquigarrow T_1$, remains unsettled. Darmanyan [12] has reported $\phi_{ISC} = 8 \times 10^{-3}$ for DPA in toluene (leading to $\phi_{IC} = 0.04$ by difference). However, Drews *et al.* [11] obtained $\phi_{ISC} = 0.08$ for the same system, and a value of 8×10^{-3} does not appear to be consistent with several other results obtained for DPA in other similar

solvents (cf. Table 2). However, DPA's behavior does appear to be consistent with that of anthracene and its 9- and 9,10-substituted methyl derivatives in which ISC to T_2 (and possibly T_1) is taken to be the major radiationless decay path. The possible involvement of $S_1 \rightsquigarrow T_1$ as a minor decay channel for DPA in PFH or as a major non-radiative decay channel for DPA in hydrogen-containing solvents cannot be ruled out unequivocally on the basis of the data presented here. However, internal conversion would appear not to be a significant mode of S_1 decay for DPA in any of the solvents examined to date.

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