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# Photophysical properties of an asymmetrical 2,5-diarylidene-cyclopentanone dye possessing electron donor and acceptor substituents

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#### 1. Introduction

Substituted 2,5-diarylidene-cyclopentanones have been the subject of numerous studies aimed at elucidating their nonlinear optical (NLO) properties [1-5]. Recently it has been reported that the asymmetric push-pull compound, (2E,5E)-2-(p-cyanobenzylidene)-5-(p-dimethylaminobenzylidene)-cyclopentanone (I). shown in Fig. 1, exhibits efficient two-photon absorption (TPA) when dissolved in chloroform (CHCl<sub>3</sub>) [5]. The TPA cross-section was determined by comparing the two-photon up-converted fluorescence of I to that of a reference compound. These measurements require knowledge of the one-photon absorption and fluorescence properties of the target molecule in the solvent used for the two-photon experiment. This paper reports the photophysical properties of I in a wide variety of solvent environments. The results demonstrate that these properties vary significantly with solvent. Other applications of 2,5-diarylidene-cyclopentanones include polarity probes [6,7] and fluoroionophores [8]. The work presented here is expected to be of importance to those interested in fundamental properties of dyes as well as those considering practical applications of I and related compounds.

#### 2. Experimental and computational methods

Compound I was synthesized by the two step procedure shown in Fig. 1. First, an equimolar mixture of cyclopentanone and p-

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#### ABSTRACT

Spectroscopic and photophysical properties have been measured in a variety of solvents for (2E,5E)-2-(p-cyanobenzylidene)-5-(p-dimethylaminobenzylidene)-cyclopentanone (I), an asymmetrically substituted 2,5-diarylidene-cyclopentanone known to have potential for applications utilizing two-photon absorption (TPA). Compound I was synthesized by a simple procedure utilizing DIMCARB catalyst. Absorption and fluorescence maxima have been correlated with the  $E_{\rm T}(30)$  solvent polarity scale. Theoretical TD-DFT calculations and Lippert–Mataga analysis demonstrate the internal charge transfer (ICT) nature of the  $S_0 \rightarrow S_1$  excitation. Radiative and nonradiative decay constants have been determined from fluorescence quantum yields and lifetimes. Substantial variation with solvent in the rate of nonradiative decay is interpreted in terms of a competition between internal conversion and intersystem crossing.

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dimethylaminobenzaldehyde were stirred at room temperature in the presence of N,N-dimethylammonium-N',N'-dimethylcarbamate (DIMCARB) catalyst [9,10] to produce (E)-2-(p-dimethylaminobenzylidene)-cyclopentanone (**1pdbma**). This was followed by the intermolecular base-catalyzed crossed aldol condensation of **1pdbma** with p-cyanobenzaldehyde to yield **I**. Both **1pdbma** and **I** were purified by silica gel column chromatography employing a gradient approach with a mixture of hexanes and ethyl acetate. Purity was confirmed by TLC. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz) of **1pdbma** and **I** agree with previously published data [5].

Absorption spectra were measured with a Shimadzu UV2100U spectrometer (2-nm band pass). Fluorescence emission spectra were obtained with a Perkin–Elmer LS 50B luminescence spectrometer equipped with a red sensitive R928 phototube. Fluorescence quantum yields ( $\Phi_f$ ) were determined by comparing the corrected integrated fluorescence spectrum of the sample with that of a standard (fluorescein in 0.1 N NaOH;  $\Phi_f$  = 0.95) according to [11]

$$\Phi_{\rm f} = \Phi_{\rm f,std} \left(\frac{A_{\rm std}}{A}\right) \left(\frac{n^2}{n_{\rm std}^2}\right) \left(\frac{D}{D_{\rm std}}\right) \tag{1}$$

where *A* is the absorbance at the excitation wavelength, *n* is the refractive index of the solvent, and *D* is the area under the corrected fluorescence spectrum. Solutions of both the standard and sample were prepared initially with the absorbance at  $\lambda_{max}$  approximately equal to 0.5, followed by an accurate tenfold dilution. Fluorescence spectra used to determine  $\Phi_{f}$  were corrected with correction factors that were obtained by measuring the spectra of compounds with known emission spectra [11]. Fluorescence lifetimes ( $\tau_{f}$ ) were



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Step 2



Fig. 1. Reaction scheme for the preparation of I.

obtained with a Photon Technology International TM-3 time resolved spectrofluorometer with pulsed nitrogen/dye laser excitation. All solutions were degassed with  $N_2$  to prevent excited state quenching by molecular oxygen. DFT and TD-DFT quantum chemical calculations were carried out using the Gaussian 03 program [12]. Solvent effects were computed using the Self-Consistent Reaction Field (SCRF) Polarizable Continuum Model (PCM) options. The DFT gas phase geometry was used in the solvent calculations without further optimization.



Fig. 2. Absorption spectrum and TD-DFT results for I in CHCl<sub>3</sub>.

#### 3. Results and discussion

#### 3.1. Geometry optimization and spectral calculations

Ground state DFT geometry optimization of **I** was carried out at the B3LYP/6-311 + G(d,p) level of theory. A minimum energy structure was confirmed by obtaining all positive frequencies for the calculated normal modes of vibration. The ground state structure obtained is nearly planar with ~6° rotation of the substituted phenyl rings. TD-DFT B3LYP/6-311 + G(d,p) spectral calculations were performed using the optimized ground state structure. The room temperature absorption spectrum of **I** in CHCl<sub>3</sub> along with the results of the TD-DFT (PCM = chloroform) calculations are shown in Fig. 2. Results for the first three computed excitations along with experimental data are summarized in Table 1. Examination of the orbitals that make the major contribution to the configuration interaction (CI) description of the excited state provides insight to the nature of these excitations. The  $S_0 \rightarrow S_1$  transition is

Table 1

Experimental spectral data and B3LYP/6-311 + G(d,p) TD-DFT calculated results for I.

S <sub>1</sub> (ICT, π, π*) λ <sub>max</sub> 473 nm 515 nm 468 nm f 0.73 0.94 0.61	
λ <sub>max</sub> 473 nm 515 nm 468 nm f 0.73 0.94 0.61	
f 0.73 0.94 0.61	
$\epsilon_{max}$ 3.20 × 10 <sup>4</sup> (M <sup>-1</sup> cm <sup>-1</sup>	)
$S_2(n, \pi^*)$	
$\lambda_{\rm max}$ 426 nm 403 nm Not observed	
f 0.00 0.00	
$S_{3}(\pi, \pi^{*})$	
$\lambda_{\rm max}$ 367 nm 376 nm 322 nm	
f 0.84 0.86 0.8 ± 0.2	
$\epsilon_{max}$ 2.27 × 10 <sup>4</sup> (M <sup>-1</sup> cm <sup>-1</sup>	)



Table 2			
Spectroscopic properties	of I in	various	solvents

Solvent	$\lambda_{abs}$ (nm)	$\lambda_{\rm f} ({\rm nm})$	$v_{\rm abs}~({\rm cm}^{-1})$	$v_{\rm f}({\rm cm}^{-1})$	$E_{\rm T}(30)$	$\Delta f$	$\Delta v (\text{cm}^{-1})$
Carbon tetrachloride	446	513	22,422	19,487	32.4	0.0119	2935
Carbon disulfide	464	535	21,552	18,688	32.8	-0.0007	2864
Toluene	455	558	21,978	17,923	33.9	0.0131	4055
Benzene	457	569	21,882	17,583	34.3	0.0031	4299
Diethyl ether	438	580	22,831	17,234	34.5	0.1669	5597
Tetrahydrofuran	458	651	21,834	15,360	37.4	0.2104	6474
o-Dichlorobenzene	465	625	21,505	16,000	38.0	0.1867	5505
Ethyl acetate	446	643	22,422	15,550	38.1	0.1996	6872
Ethyl benzoate	459	641	21,786	15,600	38.1	0.1581	6186
n-Butyl acetate	442	631	22,624	15,850	38.5	0.1709	6774
Chloroform	469	603	21,322	16,597	39.1	0.1491	4725
Cyclopentanone	460	678	21,739	14,760	39.4	0.2391	6979
Pyridine	467	673	21,413	14,863	40.5	0.2124	6550
Dichloromethane	464	643	21,552	15,560	40.7	0.2171	5992
Acetone	454	718	22,026	13,930	42.2	0.2843	8096
Dimethylformamide	464	740	21,552	13,520	43.2	0.2752	8032
Dimethyl sulfoxide	471	731	21,231	13,673	45.1	0.2637	7558
Acetonitrile	456	721	21,930	13,868	45.6	0.3054	8062
Isopropanol	471	647	21,231	15,450	48.4	0.2769	5781
n-Butanol	473	648	21,142	15,432	50.2	0.2642	5710
n-Propanol	473	644	21,142	15,530	50.7	0.2746	5612
Ethanol	472	659	21,186	15,177	51.9	0.2887	6009
Methanol	473	693	21,142	14,420	55.4	0.3093	6722

observed at 468 nm in CHCl<sub>3</sub> and is predicted by TD-DFT to be a strong transition appearing at 473 nm in the gas phase and 515 nm in CHCl<sub>3</sub>, arising from the HOMO  $\rightarrow$  LUMO orbital configuration. Examination of the HOMO and LUMO of I depicted in Fig. 3 reveals the internal charge transfer (ICT)  $\pi$ ,  $\pi^*$  nature of this absorption, in that  $\pi$  electron density is transferred from the electron donor side of the molecule in the HOMO to the electron acceptor side of the molecule in the LUMO. The  $S_0 \rightarrow S_2$  transition is computed to be a forbidden n,  $\pi^*$  excitation arising from HOMO- $2 \rightarrow$  LUMO where HOMO-2 is a nonbonding orbital localized on the carbonyl oxygen. The calculated wavelengths are 426 nm in



Fig. 4. Normalized absorption and fluorescence spectra of I in various solvents.

the gas phase and 403 nm in CHCl<sub>3</sub>. Absorption to this state has not been observed owing to its forbidden nature. Excitation to  $S_3$ is predicted to occur at 367 nm in the gas phase and 376 nm in CHCl<sub>3</sub> with major CI configurations HOMO-1  $\rightarrow$  LUMO, HOMO  $\rightarrow$  -LUMO + 1, corresponding to a  $\pi$ ,  $\pi^*$  transition delocalized over the entire molecule. The band observed at  $\lambda_{max}$  = 322 nm is assigned to this computed excitation.

Absorption and fluorescence properties of **I** were examined in 23 solvents and the results are presented in Table 2. A survey of absorption and fluorescence spectra of **I** in six of these solvents which vary in polarity and hydrogen bonding strength (nonpolar, polar aprotic, and protic) is shown in Fig. 4. The absorption and fluorescence maxima of **I** in wavenumbers are plotted against the  $E_{T}(30)$  empirical solvent polarity scale in Fig. 5. It is seen that with increasing polarity there is a small shift towards the red (bathochromic shift) in absorption and a much larger shift in fluorescence. Further, protic solvents do not appear to be anomalous in the absorption plot, but they clearly fall on a separate line in the fluorescence plot. Previous studies of molecules similar to **I** have



**Fig. 5.** Plot of (a) absorption and (b) fluorescence maxima of **I** in various solvents against  $E_{\rm T}(30)$ . Solid symbols represent aprotic solvents; open symbols represent protic solvents.

noted that there is a transfer of electron charge to the carbonyl oxygen following excitation from  $S_0$  to  $S_1$  causing the molecule to become a stronger base in the excited state. The increased basicity in  $S_1$  results in a stronger hydrogen bond with protic solvents [13,14] which is manifested in Fig. 5 by a shift of the fluorescence trend line for alcohols relative to other solvents.

Fig. 6 shows the Stokes shift, the difference in the absorption  $(\tilde{v}_A)$  and fluorescence  $(\tilde{v}_F)$  maxima, plotted against the solvent's orientation polarization function  $(\Delta f)$ . The orientation polarization function is given by

$$\Delta f = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$$
(2)

where  $\varepsilon$  is the dielectric constant and *n* is the index of refraction for the solvent. Again, separate lines are drawn for alcohols and nonalcohols. The positive slope is evidence that the dipole moment of I is larger in the excited electronic state than in the ground state. The change in dipole moment in going from  $S_0$  to  $S_1$  can be determined by application of the Lippert–Mataga equation

$$\tilde{v}_{\rm A} - \tilde{v}_{\rm F} = \frac{2\Delta\mu^2}{hca^3}\Delta f + \text{constant}$$
(3)

where  $\Delta \mu = \mu_e - \mu_g$  is the difference between the excited state and the ground state dipole moments, *h* is Planck's constant, *c* is the speed of light in vacuum, and *a* is the Onsager cavity radius for the spherical interaction of the dipole in a solvent [15,16]. The Onsager radius was computed by B3LYP/6-311 + G(d,p) to be 5.50 Å. Application of the Lippert–Mataga equation to the data for non-alcohols in Fig. 6 yields a  $\Delta \mu = 16.0$  D. Using the ground state dipole moment calculated by B3LYP/6-311 + G(d,p),  $\mu_g = 11.0$  D, an excited state dipole moment  $\mu_e = 27.0$  D is obtained. The large increase in dipole moment supports the ICT assignment for the  $S_0 \rightarrow S_1$  transition.

#### 3.2. Fluorescence quantum yields, lifetimes, and decay constants

Fluorescence quantum yields ( $\Phi_f$ ), lifetimes ( $\tau_f$ ), and radiative ( $k_f$ ) and nonradiative ( $k_{nr}$ ) decay constants are presented in Table 3. The decay constants were determined from

$$k_{\rm f} = \Phi_{\rm f} / \tau_{\rm f} \tag{4}$$

$$k_{\rm nr} = \left(\frac{1}{\Phi_{\rm f}} - 1\right) k_{\rm f} \tag{5}$$



Fig. 6. Lippert-Mataga plot for I in various solvents. Solid symbols represent aprotic solvents; open symbols represent protic solvents.

Fig. 7 displays a plot of  $\Phi_{\rm f}$  against the maximum frequency of fluorescence for I in the solvents listed. The appearance of the plot is reminiscent of Fig. 11 of our previous work [17] where a similar plot is shown for an unsubstituted 2,5-diarylidene-cylopentanone (2,5-bis-(5-phenyl-penta-2,4-dienylidene)-cyclopentanone). It is seen that  $\Phi_{\rm f}$  reaches a maximum (CHCl<sub>3</sub>,  $\Phi_{\rm f}$  = 0.30), approximately in the middle (16,597 cm<sup>-1</sup>) of the frequency range plotted (13,000–20,000 cm<sup>-1</sup>), then falls off towards higher frequencies (nonpolar solvents: CCl<sub>4</sub>,  $\Phi_f = 0.019$ ) and towards lower frequencies (polar protic: MeOH,  $\Phi_f$  = 0.003 and aprotic solvents: ACN,  $\Phi_{\rm f}$  = 0.004). Related to this result is the plot shown in Fig. 8 of  $k_{\rm nr}$ against the frequency of fluorescence. Here a minimum is observed for  $k_{nr}$  in the mid frequency range with an increase in  $k_{nr}$  towards higher and lower frequencies. The data for the aprotic solvents describes a trend in  $k_{nr}$  that is nearly parabolic over the frequency range of fluorescence emission. The  $k_{nr}$  rates for I in alcohols are higher than the rates for I in aprotic solvents that have similar

Table 3
Photophysical properties of I in various solvents.

Solvent		$\Phi_{ m f}$	$\tau_{\rm f}$ (ns)	$k_{\rm f}$ (s <sup>-1</sup> )	$k_{\mathrm{nr}}(\mathrm{s}^{-1})$
1	Carbon tetrachloride	0.019	0.17	$1.12\times10^{8}$	$5.77\times10^9$
2	Carbon disulfide	0.034	0.28	$1.21\times10^{8}$	$3.45\times10^9$
3	Toluene	0.05	0.56	$8.93\times10^7$	$1.70  imes 10^9$
4	Benzene	0.066	0.76	$8.68  imes 10^7$	$1.23  imes 10^9$
5	Diethyl ether	0.074	0.89	$8.31  imes 10^7$	$1.04  imes 10^9$
6	Tetrahydrofuran	0.027	0.18	$1.50  imes 10^8$	$5.41  imes 10^9$
7	o-Dichlorobenzene	0.29	2.18	$1.33\times10^{8}$	$\textbf{3.26}\times \textbf{10}^{\textbf{8}}$
8	Ethyl acetate	0.09	0.90	$1.00  imes 10^8$	$1.01 \times 10^9$
9	Ethyl benzoate	0.18	1.24	$1.45  imes 10^8$	$6.61  imes 10^8$
10	n-Butyl acetate	0.14	1.01	$1.39  imes 10^8$	$8.51  imes 10^8$
11	Chloroform	0.3	2.08	$1.44  imes 10^8$	$3.37  imes 10^8$
12	Cyclopentanone	0.034	0.31	$1.10  imes 10^8$	$3.12  imes 10^9$
13	Pyridine	0.051	0.41	$1.24  imes 10^8$	$2.31  imes 10^9$
14	Dichloromethane	0.17	1.29	$1.32  imes 10^8$	$6.43  imes 10^8$
15	Acetone	0.0095	0.23	$4.13  imes 10^7$	$4.31  imes 10^9$
16	N,N-	0.0066	0.18	$3.67  imes 10^7$	$5.52  imes 10^9$
	Dimethylformamide				
17	Dimethyl sulfoxide	0.0074	0.19	$3.89  imes 10^7$	$5.22  imes 10^9$
18	Acetonitrile	0.0036	0.17	$2.12  imes 10^7$	$5.86  imes 10^9$
19	Isopropanol	0.026	0.21	$1.24  imes 10^8$	$4.64  imes 10^9$
20	n-Butanol	0.017	0.22	$7.73  imes 10^7$	$4.47  imes 10^9$
21	n-Propanol	0.013	0.18	$7.22 \times 10^7$	$5.48  imes 10^9$
22	Ethanol	0.0061	0.14	$4.36  imes 10^7$	$7.10  imes 10^9$
23	Methanol	0.0027	0.13	$2.08 \times 10^7$	$7.67  imes 10^9$



Fig. 7. Quantum yield of I in various solvents. Circles represent aprotic solvents; diamonds represent protic solvents.



Fig. 8. Nonradiative decay constant plotted against fluorescence maxima of I in various solvents. Circles represent aprotic solvents; diamonds represent protic solvents.

positions for their fluorescence maxima, suggesting a hydrogen bonding influence on the nonradiative decay of I. In discussing the major routes for nonradiative decay in aprotic solvents, we separate the data in Fig. 8 into two regions, the region from the minimum to the low frequency side (region 1) and the region from the minimum to the high frequency side (region 2). In region 1,  $k_{\rm nr}$ increases from  $3.3 \times 10^8 \text{ s}^{-1}$  (o-dichlorobenzene,  $v_f = 16,000 \text{ cm}^{-1}$ ) to  $5.9 \times 10^9 \text{ s}^{-1}$  (acetonitrile,  $v_{\rm f}$  = 13,868 cm<sup>-1</sup>). In region 2,  $k_{\rm nr}$  decreases from  $5.8 \times 10^9 \text{ s}^{-1}$  (CCl<sub>4</sub>,  $v_f = 19,487 \text{ cm}^{-1}$ ) to  $3.4 \times 10^8 \text{ s}^{-1}$ (CHCl<sub>3</sub>,  $v_f = 16,597 \text{ cm}^{-1}$ ). Noting that  $k_{nr} = k_{ic} + k_{isc}$ , where  $k_{ic}$  is the rate of internal conversion from  $S_1$  to  $S_0$  and  $k_{isc}$  is the rate of intersystem crossing from the singlet to the triplet manifold of states, we believe that the variation in  $k_{nr}$  shown in Fig. 8 can be attributed to opposing behavior for these two rates with respect to solvent polarity. In shifting from nonpolar (high  $v_f$ ) to polar solvents (low  $v_f$ ),  $k_{ic}$  increases while  $k_{isc}$  decreases. In region 1, where  $k_{nr}$  increases with a decrease in  $v_{\rm f}$ , the increase in  $k_{\rm ic}$  dominates the decrease in  $k_{isc}$ ; whereas in region 2, where  $k_{nr}$  decreases with a decrease in  $v_{\rm f}$ , the decrease in  $k_{\rm isc}$  dominates the increase in  $k_{\rm ic}$ .

The order of magnitude increase in  $k_{nr}$  found in region 1 is attributed to the energy gap law for internal conversion which predicts an exponential dependence of  $k_{ic}$  on the  $S_0$ - $S_1$  energy gap, ( $\Delta E$ ).

$$k_{\rm ic} = \alpha \exp(-\beta \Delta E) \tag{6}$$

According to the energy gap law,  $k_{ic}$  is expected to increase as the  $S_0$ - $S_1$  energy gap decreases due to greater vibrational overlap (Frank–Condon factor) between the  $S_0$  and  $S_1$  states [18].

In region 2, where intersystem crossing is the major nonradiative decay channel, we believe that the solvent modulated location of  $(n, \pi^*)$  states relative to the  $S_1(\pi, \pi^*)$  and  $T_1(\pi, \pi^*)$  states influences the rate of  $S \rightarrow T$  intersystem crossing. The positions of  $(n, \pi^*)$  states and  $(\pi, \pi^*)$  states behave differently under the influence of a change in solvent polarity. Whereas  $(n, \pi^*)$  states undergo a hypsochromic shift with increased solvent polarity;  $(\pi, \pi^*)$  states undergo a bathochromic shift [19]. Data presented in Fig. 5 and Table 2 confirm the bathochromic shift expected for  $S_1(\pi, \pi^*)$ . A mechanism involving thermally activated intersystem crossing from  $S_1(\pi, \pi^*)$  to a higher lying  ${}^3(n, \pi^*)$  state has been offered to explain solvent effects on isc for molecules related to I [20]. We consider vibronic spin–orbit coupling [21] to be an alternative mechanism that is less restrictive than the thermally activated intersystem crossing mechanism in its requirement for the magni-

Table 4

TD-DFT computed energy gaps between the lowest (n,  $\pi^*$ ) and ( $\pi$ ,  $\pi^*$ ) states and experimental  $k_{nr}$ .

	CCl <sub>4</sub>	Toluene	CHCl <sub>3</sub>
$\begin{array}{l} T_{3}(n,\pi^{*}) - T_{1}(\pi,\pi^{*}) \\ S_{2}(n,\pi^{*}) - S_{1}(\pi,\pi^{*}) \\ k_{\mathrm{nr}} \times 10^{-8}/s^{-1} \end{array}$	7138 cm <sup>-1</sup>	7234 cm <sup>-1</sup>	8112 cm <sup>-1</sup>
	4465 cm <sup>-1</sup>	4592 cm <sup>-1</sup>	5384 cm <sup>-1</sup>
	57.7	17.0	3.37

tude of the  $S_1(\pi, \pi^*)$ – $T(n, \pi^*)$  energy gap relative to  $k_BT$ . In this mechanism, spin–orbit coupling between  $\pi$ ,  $\pi^*$  and n,  $\pi^*$  states in different spin manifolds and vibronic coupling within the same spin manifold are operative in promoting intersystem crossing.

A solvent induced increase in the spacing between  $S_1/T_1$  and the appropriate intermediate  $n, \pi^*$  state(s) attenuates the degree of state mixing which in turn reduces the rate of  $S \rightarrow T$  intersystem crossing [22]. Both the thermally activated mechanism and the vibronic spin-orbit coupling mechanism are favored over direct spin–orbit coupling between  $S_1(\pi, \pi^*)$  and  $T_1(\pi, \pi^*)$  because of the well established understanding that the matrix element for spin-orbit coupling between states of different orbital configuration is greater than the matrix element for spin-orbit coupling between states of the same orbital configuration [23]. The smooth decrease in  $k_{nr}$  shown in region 2 is consistent with a gradual, solvent induced increase in the spacing between  $S_1/T_1$  and higher energy  $(n, \pi^*)$  states. Table 4 provides theoretical support for this interpretation with the results of TD-DFT calculations modeled in CCl<sub>4</sub>, toluene, and CHCl<sub>3</sub> solvent environments. It is seen that there is an inverse relation between the magnitude of the computed energy gaps between the lowest  $(n, \pi^*)$  and  $(\pi, \pi^*)$  states and the experimental values for  $k_{nr}$ . At this level of theory, the qualitative trend calculated is expected to be more meaningful than the numeric values calculated for the  $(n, \pi^*)$ - $(\pi, \pi^*)$  energy gaps. It is possible that a combination of thermally activated and vibronic spinorbit coupling mechanisms contribute to solvent dependent  $S \rightarrow T$ intersystem crossing observed for I at room temperature.

The radiative rates ( $k_f$ ) vary less with solvent and, although somewhat scattered, show a general trend toward lower values with lower  $v_f$ , as predicted by Einstein's treatment of electronic transitions [24].

#### 4. Conclusion

The spectroscopic and photophysical properties of **I** have been found to vary considerably with solvent. The natures of the low lying excited states have been assigned with the assistance of experimental and theoretical data. The behavior of  $k_{nr}$  with respect to fluorescence wavelength and solvent polarity can be divided into two regions. In region 1, the increase in the rate of internal conversion dominates the decrease in the rate of intersystem crossing; whereas in region 2, intersystem crossing is the dominant channel of decay from  $S_1$ .

The variation in the rates of internal conversion and intersystem crossing are interpreted to be related to solvent induced changes in energy gaps on the singlet and triplet spin manifolds.

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