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# Structural and photophysical properties of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone dyes



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## ABSTRACT

A series of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone compounds were synthesized. Spectroscopic and photophysical properties of these compounds have been measured in a variety of solvents. Absorption and fluorescence maxima have been correlated with the Empirical Scale of Solvent Polarity (E<sub>T</sub>(30)). Theoretical TD-DFT spectral calculations and Lippert–Mataga analysis support the internal charge transfer (ICT) nature of the S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> excitation for these compounds, with higher degrees of ICT depicted for the alkylamino substituted 2,5-diarylidene cyclopentanones. Photophysical properties consisted of measuring the fluorescence quantum yields ( $\Phi_f$ ) and lifetimes ( $\tau_f$ ) in a variety of solvents. Radiative and nonradiative decay constants have been determined from the  $\Phi_f$  and  $\tau_f$  data. Variation with solvent in the nonradiative rate of decay is interpreted in terms of a competition between internal conversion and intersystem crossing. Lastly, two compounds presented have been shown to undergo excited state protonation in glacial acetic acid.

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### 1. Introduction

The class of organic compounds called diarylidene cycloalkanones are ketocyanine dyes that have received attention in their use as photosensitizers for various electron energy transfer processes [1], fluorescent solvent polarity probes [2], fluoroionophores [3], and nonlinear optical materials [4], particularly in their use as chromophores in undergoing two photon absorption.

Previous work has been done in our lab studying the structural and spectroscopic properties of C<sub>2v</sub> unsubstituted 2,5-diarylidene cyclopentanones, namely (2E,5E)-2,5-dibenzylidene cyclopentanone (1), (2E,5E)-2,5-dicinnamylidene cyclopentanone (2), (2E,5E)-2,5-bis(5-phenyl-penta-2,4-dienylidene) cvcloand pentanone (3) [5,6]. It was found that fluorescence was not observed for 1 in any of the solvents studied (protic and aprotic). Fluorescence was observed for 2 only in protic solvents, and in a number of protic and aprotic solvents for 3. Solvents which were able to induce fluorescence in compounds 2 and 3 were believed to do so by inverting the order of  ${}^{1}(n, \pi^{*})$  and  ${}^{1}(\pi, \pi^{*})$  states. It was also demonstrated that 2 and 3 undergo excited state protonation in glacial acetic acid, with a signature of dual emission in the fluorescence spectra. Additional work in our lab involved studying the photophysical properties of an asymmetrically substituted 2,5cyclopentanone dye, namely (2E,5E)-2-(4diarylidene cyanobenzylidene)-5-(4-dimethylaminobenzylidene) cyclopentanone, in a variety of solvents [7]. This asymmetric push-pull compound exhibits efficient two photon absorption (TPA) when dissolved in chloroform and is known to have potential for applications in TPA [4e]. Lastly, recently published work on the photochemistry of compound I in oxygenated and deoxygenated solutions has been conducted [8]. The testing of I as a direct photosensitizer of singlet state oxygen  $({}^{1}\Delta_{g})$ , a strong oxidant used in photodynamic therapy in destroying targeted tumor and cancerous cells in living organisms, was also carried out in these studies.

This manuscript provides a presentation and discussion of the structural, spectroscopic, and photophysical properties of a series of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone compounds. These class of ketocyanine compounds are of interest due to their electron "push–pull" structures. The two alkylamino substituted 2-arylidene cyclopentanones presented are examples of D–A compounds and the four alkylamino substituted 2,5-diarylidene cyclopentanones are examples of D–A–D compounds (where D is an electron donor group and A is an electron acceptor group). The presence of electron donor groups bonded to the polyene chain should have an effect of the electronic structure



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Fig. 1. Reaction schemes for the preparations of (a) IA and IIA, (b) I and II, and (c) III.

and photophysical properties, making this particular set of compounds different than the compounds presented in Ref. [5]. In addition, several of the compounds presented have longer  $\pi$  conjugated chains compared to compound 1 in Ref. [5] and compound **I** in Ref. [7]. The length of a  $\pi$  conjugated chain also has an effect on electronic structure, spectroscopic and photophysical properties.

A unique feature of these types of electron "push—pull" polyene compounds are their photoinduced internal charge transfer (ICT) properties. The ICT state is an excited state characterized by the transfer of electron density from the electron donor end of the molecule to the electron acceptor end of the molecule upon photoexcitation. The nature of ICT excited states gives rise to lower energies of fluorescence than the locally excited (LE) states. In other words, the fluorescence of an ICT state is red shifted relative to the LE state. A special type of ICT state is termed the twisted internal charge transfer (TICT) state, where the plane of a dimethylamino group is at a twisted angle with respect to the rest of the molecule due to rotation about the C–N bond. TICT states form in highly polar solvent environments and their fluorescence is quenched and red shifted relative to the LE state. A section of this manuscript compares the structural and spectroscopic properties of compounds **II** and **IV**. Compound **II** contains free-moving dimethylamino groups substituted on the aryl moieties and can potentially undergo the formation of a TICT state. On the contrary, compound **IV** is spatially restricted on the aryl moieties due to the presence of closed, saturated ring systems that structurally prevent it from having a TICT state. Comparisons of the spectroscopic and photophysical properties of these two compounds will lead to determining whether or not **II** undergoes the formation of a TICT state.

Furthermore, the work presented in this manuscript is expected to be of importance to those interested in studying the structural, spectroscopic, and photophysical properties of these class of compounds and related compounds. A thorough understanding of the properties of these compounds is pertinent to examining their applications. Step 1



Step 2



Step 3



(1 mol eq)

Fig. 2. Reaction scheme for the preparation of IV.



Fig. 3. Single crystal X-ray structure of I.

#### 2. Experimental and computational methods

# 2.1. Compound syntheses and structural characterizations

Presented in this section are general descriptions for the syntheses of all target compounds. Please refer to the Supplementary Information for detailed descriptions.

Purity of all compounds were confirmed by <sup>1</sup>H NMR spectroscopy (>99% for all target compounds) and thin layer chromatography (TLC), which showed one spot upon development. NMR and IR spectroscopy were the structural characterization methods used. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker<sup>®</sup> AVANCE 400 MHz NMR spectrometer and a Bruker® AVANCE III 500 (500 MHz) NMR spectrometer. ATR-IR spectra were obtained using a Perkin Elmer<sup>®</sup> Spectrum One IR spectrometer.

Fig. 1 shows the reaction schemes for the preparations of compounds IA and IIA (1(a)), I and II (1(b)), and III (1(c)). Compound IA was synthesized by combining an equimolar mixture of cyclopentanone and 4-dimethylaminobenzaldehyde in the presence of N,N-dimethylammonium-N',N'-dimethylcarbamate (DIMCARB) [9,10]. Compound **IIA** was synthesized via an intermolecular basecatalyzed crossed aldol condensation reaction between limiting (E)-4-dimethylaminocinnamaldehyde and excess cyclopentanone. Compounds I and II were synthesized via an intermolecular basecatalyzed crossed aldol condensation reaction between cyclopentanone (1 mole equivalent) and the appropriate aldehyde (2 mole equivalents) (4-dimethylaminobenzaldehyde for I and (E)-4dimethylaminocinnamaldehyde for II). Compound III was



**Fig. 4.** Absorption and fluorescence spectra of **II** in (a) 2,2,2-trifluoroethanol (TFE), (b) 2-propanol, (c) ethyl acetate, (d) acetone, (e) benzene, and (f) carbon disulfide.

synthesized via an intermolecular base-catalyzed crossed aldol condensation reaction between IA and (E)-4-dimethylaminocinnamaldehyde.

Fig. 2 shows the three step reaction scheme for the preparation of compound IV. A solution of julolidine and N.Ndimethylformamide (DMF) was added to a solution of phosphorous oxychloride  $(POCl_3)$ in DMF, vielding 9\_ julolidinylcarbaldehyde [11]. Two carbon homologation of 9julolidinylcarbaldehyde using silver perchlorate (AgClO<sub>4</sub>) catalyzed addition of the zirconocene complex derived from the hydrozirconation of 1-ethoxyethyne with bis(cyclopentadienyl) zirconium hydridochloride followed by acid catalyzed dehydration yielded (E)-3-(9-julolidinyl)-prop-2-en-1-al [12,13]. The final step consisted of running an intermolecular base-catalyzed crossed aldol condensation reaction between cyclopentanone (1 mole equivalent) and (E)-3-(9-julolidinyl)-prop-2-en-1-al (2 mole equivalents), affording IV.

#### 2.2. X-ray diffraction measurements

The X-ray structure of **I** was solved using a Bruker-AXS Kappa APEX CCD Diffractometer, collecting diffraction data at ambient room temperature using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The unit cells and space groups were determined using the SAINT + program [14]. Structures were solved by direct methods and refined by full matrix least-squares using the SHELXTL program [15]. Mercury 2.4 software was used to examine the molecular structure and crystal packing arrangements of the solved X-ray crystal structures [16]. Single crystal X-ray structures were properly refined to give overall refinement values of <5%.

#### 2.3. Spectroscopic and photophysical measurements

Absorption and fluorescence emission spectra were measured at ambient room temperature. Absorption spectra were measured with both a Shimadzu<sup>®</sup> UV2100U spectrometer and a Per-kin–Elmer<sup>®</sup> Lambda 35 UV/VIS spectrometer. Fluorescence emission spectra were obtained with a Perkin–Elmer<sup>®</sup> LS 50B spectrophotometer equipped with a red sensitive R928 phototube detector. All solvents used were spectroscopic or HPLC grade. Fluorescence quantum yields ( $\Phi_f$ ) were determined by comparing the corrected integrated fluorescence spectrum of the sample with that of a standard according to [17]. For  $\Phi_f$  measurements of **IA** and **IIA**, coumarin-481 in acetonitrile ( $\Phi_f = 0.11$ ) was used as the standard [18]; for all 2,5-diarylidene cyclopentanones, fluorescein in 0.1 N NaOH ( $\Phi_f = 0.95$ ) was used [16]. Equation (1) defines  $\Phi_f$ 

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

where A is the absorbance at the excitation wavelength, n is the refractive index of the solvent, and D is the integrated 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 sets of correction factors that were obtained by measuring the spectra of compounds with known emission spectra [17]. Fluorescence lifetimes ( $\tau_f$ ) were obtained with a Photon Technology International<sup>®</sup> TM-3 time resolved spectrofluorometer with pulsed nitrogen/dye laser excitation. All solutions were degassed with N<sub>2</sub> to prevent excited state quenching by molecular oxygen.

## 2.4. Quantum chemical calculations

DFT and TD-DFT quantum chemical calculations were carried out using the Gaussian09 program [19]. Minimum energy structures were confirmed by obtaining all real frequencies for the



Fig. 5. Solutions of II in (a) 2,2,2-trifluoroethanol, (b) ethanol, (c) 2-propanol, (d) acetonitrile, (e) acetone, (f) ethyl acetate, (g) benzene, (h) toluene, and (i) cyclohexane.



Fig. 6. Plot of absorption and fluorescence maxima of (a) IA and I and (b) IIA and II in various solvents against the E<sub>1</sub>(30) scale. Black: IA and IIA; Blue: I and II. Solid symbols represent aprotic solvents; open symbols represent protic solvents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calculated normal modes of vibration. Solvent effect studies were computed using the Self-Consistent Reaction Field (SCRF) Polarizable Continuum Model (PCM) options. The DFT gas phase geometries were used in the solvent calculations without further optimization. Molecular Orbital Package for Spectroscopy-Fujitsu (MOSF) was the molecular orbital program used for carrying out atomic charge calculations both in the ground and excited states for excited state protonation studies [20].

## 3. Results and discussion

## 3.1. Structural and spectroscopic properties

Compound I crystallizes in an orthorhombic system, belonging to the P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group. The single crystal X-ray structure of I, in two views, is shown in Fig. 3. Compound I is essentially planar, with approximately  $3^{\circ}-7^{\circ}$  rotations of the phenyl rings on each end relative to the cyclopentanone ring. Direct comparison between the X-ray geometry and its predicted ground state geometry at the B3LYP/6-31G(d) level of theory shows excellent agreement in both bond lengths and bond angles. Absolute differences between experimental and calculated bond lengths varies between 0.001 Å - 0.025 Å and bond angles between 0.01° - 4.4°. The predicted DFT geometry of I is planar, with ~1° rotation of the phenyl rings relative to the cyclopentanone ring.

In the predicted DFT structures of **IA** and **IIA**, approximately 30° rotational angles were seen within the cyclopentanone ring for each compound, attributed to ring folding. For **IA**, an approximately 11° rotation of the substituted phenyl ring was also observed. In addition to the predicted DFT geometry of **I**, the DFT structures of its higher homologs, **II**, **III**, and **IV** were essentially planar. The folding within the cyclopentanone ring is lost with extended  $\pi$  conjugation.

Absorption and fluorescence spectra of all alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanones were examined in solvents of various polarities (please refer to the Supplementary Information for tabulated data). It has been shown that all compounds undergo bathochromic shifts in absorption and fluorescence with respect to an increase in solvent polarity, some more significant than others. Although minor red shifts are observed in the absorption spectra, a larger degree of red shifting is observed in fluorescence, suggesting that the excited states of these compounds are more polar in nature than the ground state. Absorption and fluorescence spectra of II in six solvents of differing polarity and hydrogen bonding strength (two alcohols, two polar aprotic, and two nonpolar) are shown in Fig. 4. Compound II exhibits a large degree of solvatochromism, as illustrated in Fig. 5, in that its color changes from yellow  $\rightarrow$  orange  $\rightarrow$  red  $\rightarrow$ purple in going from nonpolar to polar, aprotic and protic solvents.



Fig. 7. Lippert–Mataga plots for (a) IA, (b) IIA, (c) I, (d) III, (e) II, and (f) IV. Solid symbols represent aprotic solvents; open symbols represent protic solvents.

The absorption and fluorescence maxima of (a) IA vs. I and (b) IIA vs. II in wavenumbers plotted against the  $E_T(30)$  scale are shown in Fig. 6. It is seen specifically in these plots that the absorption and

Table 1 DFT B3LYP/6-31G(d) calculated  $\mu_g$  and a values, along with Lippert–Mataga results of  $\mu_e$  and  $\Delta\mu$  for all compounds.

Compound	a (Á) (B3LYP/6-31G(d))	$\mu_{g}\left(D\right)\left(B3LYP/631G(d)\right)$	$\Delta \mu$ (D)	$\mu_{e}(D)$
IA	4.88	6.33	10.3	16.6
IIA	5.19	7.39	10.5	17.9
I	5.77	5.22	13.7	18.9
Ш	5.97	5.60	15.5	21.1
П	5.95	5.84	15.2	21.0
IV	6.34	5.76	16.0	21.8

fluorescence maxima are shifted to the red in going from one sided to two sided  $\pi$  conjugation, showing the effect of polyene chain length on spectroscopic location (quantum mechanical particle in a box system).

Excited state dipole moments ( $\mu_e$ ) of all six compounds have been determined by treatment of the Lippert–Mataga method [21,22], using the data for aprotic solvents. The Stokes shifts for each compound have been plotted against the solvent's orientation polarization function ( $\Delta f$ ). The Stokes shift is the difference, in wavenumbers, between the absorbance ( $\tilde{\nu}_A$ ) and fluorescence ( $\tilde{\nu}_F$ ) spectral maxima of a molecule in a solvent. The orientation polarization function ( $\Delta f$ ) is given by

Table 2

Absorbance and fluorescence spectral maxima of I, II, III, and IV in toluene and methanol compared to literature cited compounds.

Compound	Toluene		Methanol		Δλ (methanol- toluene)	
	$\overline{\lambda_{abs}}(nm)$	$\lambda_f(nm)$	$\lambda_{abs}\left(nm ight)$	$\lambda_f(nm)$	$\Delta\lambda_{abs}\left(nm\right)$	$\Delta\lambda_{f}(nm)$
I	452	482	479	635	27	153
II	495	553	523	735	28	182
III	475	530	500	737	25	207
IV	505	588	523	750	18	162
2 [5]*	_	-	408	522	-	-
3 [5]	430	520	451	625	21	105
I [7]	455	558	473	693	18	135

\*No observable fluorescence in aprotic solvents.

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

where  $\varepsilon$  is the dielectric constant and n is the index of refraction of the solvent. Lippert–Mataga plots have been constructed for each compound (compiled set shown in Fig. 7), relating the Stokes shift against the orientation polarization function in various solvents. The Lippert–Mataga equation is defined as

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

where  $\Delta \mu$  is the difference in the electronic dipole moment between S<sub>0</sub> and S<sub>1</sub>, h is Planck's constant, c is the speed of light in a vacuum, and a is the Onsager cavity radius for the spherical interaction of the dipole in a solvent. Ground state dipole moments and



**Fig. 8.** Experimental absorption spectra of **IA** in (a) methanol, (b) chloroform, (c) toluene, and (d) n-hexane and their corresponding TD-DFT oscillator strengths at the B3LYP/6-31G(d) level of theory.

Onsager cavity radii for all compounds were calculated at the DFT B3LYP/6-31G(d) level of theory. The positive slopes observed in the Lippert–Mataga plots are attributed to the internal charge transfer properties portrayed by these compounds and the overall general trend is that both  $\Delta\mu$  and  $\mu_e$  become greater in magnitude from least conjugated (IA) to most conjugated (II and IV) chain lengths. Table 1 presents the computed ground state dipole moments and Onsager cavity radii, along with the Lippert–Mataga results for  $\mu_e$  and  $\Delta\mu$ .

A comparative study between the absorbance and fluorescence maxima locations of **I**, **II**, **III**, and **IV** and cited compounds 2 and 3 (in Ref. [5]) and **I** (in Ref. [7]) in toluene and methanol was investigated. Toluene and methanol are two solvents with significant differences in polarity. It is seen in Table 2 that **I**, **II**, **III**, and **IV** presented in this manuscript exhibit a higher magnitude in the spectral shifts in absorbance and fluorescence in going from toluene to methanol (with more pronounced shifts in fluorescence) when compared to the cited compounds. This data shows that the presence of electron donor functional groups onto the  $\pi$  conjugated polyene chain has an effect on the electronic structural and spectroscopic properties for these class of compounds.

TD-DFT spectral calculations were carried out at the B3LYP/6-31G(d) level of theory from the optimized ground state structures. For IA, in the gas phase, S<sub>1</sub> is predicted to be a weak transition localized at 3.37 eV (368 nm, f = 0.014) with HOMO-1 (n)  $\rightarrow$  LUMO  $(\pi^*)$  as the orbital configuration. Excitation to the S<sub>2</sub> state is predicted to be a strong transition occurring at 3.60 eV (344 nm, f = 0.80) with major CI configuration of HOMO  $\rightarrow$  LUMO, corresponding to a  $(\pi, \pi^*)$  transition. In going from the gas phase to solvent environment, the energy of the  ${}^{1}(\pi,\pi^{*})$  state falls below the  $^{1}(n, \pi^{*})$  state, regardless of solvent polarity. In the gas phase, the  $^{1}(\pi, \pi^{*})$  state, predicted to be S<sub>2</sub>, is localized at 3.60 eV (344 nm). In solvent, S<sub>1</sub> is assigned an orbital configuration of  $(\pi, \pi^*)$  and the energy of this state continuously decreases with respect to an increase in solvent polarity. The energy of the  $S_1(\pi, \pi^*)$  state decreases in the following order: 3.40 eV (365 nm, n-hexane), 3.36 eV (369 nm, toluene), 3.34 eV (372 nm, chloroform), and 3.32 eV (374 nm, methanol). This is characteristic of the typical bathochromic shifting observed with respect to an increase in solvent polarity. The inversion of the  ${}^{1}(\pi, \pi^{*})$  state from S<sub>2</sub> in the gas phase to S<sub>1</sub> in solvent is consistent with the observation of fluorescence in the experimental spectra for all solvents studied.

The <sup>1</sup>(n,  $\pi^*$ ) state inverts from being S<sub>1</sub> in the gas phase to S<sub>2</sub> in solvent. In the gas phase, the <sup>1</sup>(n,  $\pi^*$ ) state is computed to be located at 3.37 eV (368 nm). In solvent, the <sup>1</sup>(n,  $\pi^*$ ) state undergoes a characteristic hypsochromic (blue) shift, increasing in the following order: 3.46 eV (358 nm, n-hexane), 3.47 eV (358 nm, toluene), 3.50 eV (354 nm, chloroform), and 3.54 eV (350 nm,

Table 3

TD-DFT computed energy gaps of the lowest lying  ${}^1(\pi, \pi^*)$  and  ${}^1(n, \pi^*)$  states and f values for the  ${}^1(n, \pi^*)$  states of **IA** and **IIA**.

Solvent	$ \Delta E[^{1}(n, \pi^{*})-^{1}(\pi, \pi^{*})]  (cm^{-1})$	$f[^{1}(n, \pi^{*})]$
IA		
Gas	1896	0.014
n-Hexane	536	0.32
Toluene	833	0.091
Chloroform	1367	0.030
Methanol	1833	0.015
IIA		
Gas	326	0.23
n-Hexane	2004	0.0042
Toluene	2606	0.0026
Chloroform	3177	0.0014
Methanol	3663	0.0008

methanol). As depicted in Fig. 8, good agreement is established between the experimental absorption spectra of **IA** and the TD-DFT calculations in each of the four solvents with excitation to  $S_1(\pi, \pi^*)$  being the strongest electronic transition. It is also shown that from the TD-DFT data, with respect to an increase in solvent polarity, (i) the  $S_2(n, \pi^*)$ - $S_1(\pi, \pi^*)$  energy gap becomes larger, and (ii) the ratio of the oscillator strengths of  $S_2(n, \pi^*)$  to  $S_1(\pi, \pi^*)$  becomes smaller. The increase in the  $S_2$ - $S_1$  energy gap is attributed to the hypsochromic shift of  $(n, \pi^*)$  and the bathochromic shift of  $(\pi, \pi^*)$ .

The unusually large oscillator strength predicted for the lowest  $n \rightarrow \pi^*$  transition of **IA** in n-hexane (f = 0.32) appears to be a manifestation of a well-known limitation with the TD-DFT method, where nearly degenerate excited states undergo strong configuration mixing [23]. This mixing causes a blending of the properties of the nearly degenerate excited states. The energy separation of  $S_1(\pi, \pi^*)$  and  $S_2(n, \pi^*)$  is only 536 cm<sup>-1</sup>, hence the blending of  ${}^1(\pi, \pi^*)$  and  ${}^1(n, \pi^*)$  properties, including the oscillator strength. As seen from Table 3, the larger the  ${}^1(n, \pi^*) - {}^1(\pi, \pi^*)$  energy gap, the smaller the  ${}^1(n, \pi^*)$  oscillator strength. For large gaps, e.g. methanol, the low oscillator strength expected to be computed for an  $n \to \pi^*$  transition is observed (f = 0.015).

Similar trends were found in the TD-DFT calculations for **IIA**. S<sub>1</sub> is predicted to be  $(n, \pi^*)$  in the gas phase and  $(\pi, \pi^*)$  in solvent. In the gas phase, the S<sub>1</sub> state is computed to be a transition at 3.15 eV

(394 nm, f = 0.23) with HOMO-1 (n)  $\rightarrow$  LUMO ( $\pi^*$ ) as the primary CI configuration. Excitation to the S<sub>2</sub> state is predicted to be a strong electronic transition at 3.19 eV (389 nm, f = 0.97) with a major CI configuration of HOMO ( $\pi$ )  $\rightarrow$  LUMO ( $\pi^*$ ). As with **IA**, the unusually large oscillator strength computed for the n  $\rightarrow \pi^*$  transition in the gas phase is a result of configuration mixing of nearly degenerate states ( $\Delta E = 326 \text{ cm}^{-1}$ ) and the inversion of the S<sub>1</sub> state to ( $\pi, \pi^*$ ) in solvent is consistent with the observation of fluorescence seen in the experimental spectra.

The three alkylamino substituted 2,5-diarylidene cyclopentanone compounds, **I**, **II**, and **IV** are all members of the C<sub>2v</sub> point group and for purposes of classification, a C<sub>2v</sub> symmetry is assumed. Table 4 presents the TD-DFT spectral calculations of the lowest lying  ${}^{1}(\pi, \pi^{*})$  and  ${}^{1}(n, \pi^{*})$  states of **I**, **II**, and **IV** in gas and solvent environments (arranged in order of increasing polarity). In the gas phase, TD-DFT computes S<sub>1</sub> as a strong symmetry allowed B<sub>2</sub>  $\leftarrow$  A<sub>1</sub> transition of the  $(\pi, \pi^{*})$  type, arising from the orbital excitation  $a_{2}(\pi) \rightarrow b_{1}(\pi^{*})$ , where  $a_{2}(\pi)$  is the HOMO and  $b_{1}(\pi^{*})$  is the LUMO. The lowest lying  $(n, \pi^{*})$  state was computed to be a symmetry forbidden A<sub>2</sub>  $\leftarrow$  A<sub>1</sub> transition, arising from the orbital excitation  $b_{2}(n) \rightarrow b_{1}(\pi^{*})$ , where  $b_{2}$  is the nonbonding molecular orbital on the oxygen atom. The S<sub>2</sub> state was predicted to be  $(n, \pi^{*})$  for **I** and **II**; S<sub>3</sub> for **IV**. Fig. 9 shows the computed molecular orbitals of **I**, **II**, and **IV**. The HOMO was computed to be a  $\pi$  bonding orbital

#### Table 4

TD-DFT spectral calculations of the lowest lying  ${}^{1}(\pi, \pi^{*})$  and  ${}^{1}(n, \pi^{*})$  states of I, II, and IV in gas and solvents.

Solvent	State	Energy		f
		$\mathrm{cm}^{-1}$	nm	
I				
Gas	$S_1(\pi, \pi^*)(B_2)$	23641	423	1.45
	$S_2(n, \pi^*)(A_2)$	24510	408	0.00
Carbon Tetrachloride	$S_1(\pi, \pi^*)(B_2)$	22124	452	1.66
	$S_2(n, \pi^*)(A_2)$	25253	396	0.00
Carbon Disulfide	$S_1(\pi, \pi^*)(B_2)$	21834	458	1.70
	$S_2(n, \pi^*)(A_2)$	25381	394	0.02
Toluene	$S_1(\pi, \pi^*)(B_2)$	22026	454	1.67
	$S_2(n, \pi^*)(A_2)$	25316	395	0.00
Tetrahydrofuran	$S_1(\pi, \pi^*)(B_2)$	21598	463	1.66
-	$S_3(n, \pi^*)(A_2)$	25907	386	0.00
Dichloromethane	$S_1(\pi, \pi^*)(B_2)$	21505	465	1.67
	$S_3(n, \pi^*)(A_2)$	25906	386	0.00
Dimethylformamide	$S_1(\pi, \pi^*)(B_2)$	21277	470	1.67
-	$S_3(n, \pi^*)(A_2)$	26178	382	0.00
Methanol	$S_1(\pi, \pi^*)(B_2)$	21413	467	1.64
	$S_3(n, \pi^*)(A_2)$	26178	382	0.00
Ш				
Gas	$S_1(\pi, \pi^*)(B_2)$	20492	488	2.02
	$S_2(n, \pi^*)(A_2)$	22523	444	0.00
n-Hexane	$S_1(\pi, \pi^*)(B_2)$	19194	521	2.22
	$S_3(n, \pi^*)(A_2)$	23256	430	0.00
Carbon Disulfide	$S_1(\pi, \pi^*)(B_2)$	18692	535	2.29
	$S_3(n, \pi^*)(A_2)$	23529	425	0.00
Toluene	$S_1(\pi, \pi^*)(B_2)$	18868	530	2.26
	$S_3(n, \pi^*)(A_2)$	23474	426	0.00
Dichloromethane	$S_1(\pi, \pi^*)(B_2)$	18382	544	2.26
	$S_3(n, \pi^*)(A_2)$	23697	422	0.00
Methanol	$S_1(\pi, \pi^*)(B_2)$	18349	545	2.23
	$S_3(n, \pi^*)(A_2)$	23641	423	0.00
IV				
Gas	$S_1(\pi, \pi^*)(B_2)$	19802	505	2.03
	$S_{3}(n, \pi^{*})(A_{2})$	22676	441	0.01
n-Hexane	$S_1(\pi, \pi^*)(B_2)$	18519	540	2.22
	$S_3(n, \pi^*)(A_2)$	23041	434	0.00
Toluene	$S_1(\pi, \pi^*)(B_2)$	18215	549	2.26
	$S_3(n, \pi^*)(A_2)$	23041	434	0.00
Dichloromethane	$S_1(\pi, \pi^*)(B_2)$	17668	566	2.25
	$S_3(n, \pi^*)(A_2)$	22936	436	0.00
Methanol	$S_1(\pi, \pi^*)(B_2)$	17606	568	2.23
	$S_{3}(n, \pi^{*})(A_{2})$	22883	437	0.00



Fig. 9. Computed molecular orbitals of I, II, and IV.

with an even distribution of electron density along the conjugated framework. The LUMO was computed to be a  $\pi^*$  antibonding orbital. The HOMO-2 was computed to be a nonbonding orbital localized on the carbonyl oxygen atom. The same orbital configurations were predicted for **II** and **IV**. Examination of the HOMO and LUMO reveals the internal charge transfer (ICT) nature of the  $S_0 \rightarrow S_1$  excitation, in that  $\pi$  electron density is transferred from the electron donor ends of the molecule in the HOMO to the electron acceptor end of the molecule in the LUMO. In solvent, TD-DFT predicts  $S_1$  as  $(\pi, \pi^*)$  of  $B_2$  symmetry for **I**, **II**, and **IV**. As seen in Table 4, the calculated energy of the  $S_1$  state decreases with respect to increasing solvent polarity, and that the energy of the  ${}^1(n, \pi^*)$  state increases, consistent with the trends observed in the experimental data.

### 3.2. Photophysical properties

Photophysical properties consisted of measuring the fluorescence quantum yields ( $\Phi_f$ ) and fluorescence lifetimes ( $\tau_f$ ) in a variety of solvents. Fluorescence quantum yields were very low for **IA** and **IIA**, with values ranging between 0.0006 (in carbon tetrachloride, carbon disulfide, and diethyl ether) to 0.01 (in N,Ndimethylformamide) for **IA**, and between 0.001 (in n-hexane) to 0.01 (in N,N-dimethylformamide, pyridine, and methanol) for **IIA**. Fluorescence lifetimes for **IA** and **IIA** were not measured due to weak fluorescence. The low  $\Phi_f$  values observed for **IA** and **IIA** are attributed to efficient singlet  $\rightarrow$  triplet intersystem crossing, in accordance to El-Sayed's rule [24].

For compounds I, II, III, and IV, further photophysical measurements involved calculating the radiative  $(k_f)$  and nonradiative  $(k_{nr})$  decay constants from the quantum yield and lifetime data using the following equations

$$k_{f} = \frac{\Phi_{f}}{\tau_{f}} \tag{4}$$

$$k_{nr} = \left(\frac{1}{\Phi_f} - 1\right) k_f \tag{5}$$

The plots in Fig. 10 show the fluorescence quantum yields plotted against the maximum frequency of fluorescence of I, II, and IV in the solvents presented in the tabulated data (see Supplementary Information). The appearance of these plots is reminiscent of two compounds from our previous work [5,7], where similar plots were shown for an unsubstituted 2,5diarylidenecyclopentanone ((2E,5E)-2,5-bis-(5-phenyl-penta-2,4dienylidene) cyclopentanone) [5] and an asymmetrically ((2E,5E)-2-(4substituted 2,5-diarylidene cyclopentanone cyanobenzylidene)-5-(4-dimethylaminobenzylidene) cvclopentanone) [7]. In all three plots, it is seen that  $\Phi_{\rm f}$  reaches a maximum approximately in the middle of the frequency range plotted, then falls off towards higher and lower frequencies.

Related to these results are the plots shown in Fig. 11 of  $k_{nr}$  against the maximum frequency of fluorescence. As shown in the  $k_{nr}$  plot for I (Fig. 11(a)), in carbon tetrachloride,  $k_{nr}$  is high (2.59 × 10<sup>9</sup> s<sup>-1</sup>), reaches a minimum at 17378 cm<sup>-1</sup> in N,N-dimethylformamide (8.80 × 10<sup>8</sup> s<sup>-1</sup>), then rises to 3.36 × 10<sup>9</sup> s<sup>-1</sup> in methanol ( $v_f = 15758 \text{ cm}^{-1}$ ). Fig. 11(a) can be subdivided 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,  $k_{nr}$  increases from 8.80 × 10<sup>8</sup> s<sup>-1</sup> (M,N-dimethylformamide,  $v_f = 17378 \text{ cm}^{-1}$ ) to 3.36 × 10<sup>9</sup> s<sup>-1</sup> (methanol,  $v_f = 15758 \text{ cm}^{-1}$ ). In region 2,  $k_{nr}$  decreases from 2.59 × 10<sup>9</sup> s<sup>-1</sup> (carbon tetrachloride,  $v_f = 20907 \text{ cm}^{-1}$ ) to 8.80 × 10<sup>8</sup> s<sup>-1</sup> (N,N-dimethylformamide,  $v_f = 17378 \text{ cm}^{-1}$ ).

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  $k_{nr}$  seen in Fig. 11(a) can be attributed to opposing behavior of these two rates with respect to solvent polarity. In shifting from nonpolar (higher  $v_f$ ) to polar solvents (lower  $v_f$ ),  $k_{ic}$  increases while  $k_{isc}$  decreases. In region 1, where  $k_{nr}$  increases with respect to a decrease in  $v_{f}$ , the increase in  $k_{ic}$  dominates the decrease in  $k_{isc}$ ; whereas in region 2, where  $k_{nr}$  decreases with respect to a decrease in  $v_f$ , the decrease in  $k_{isc}$  dominates the increase in  $k_{ic}$ . 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 ( $\Delta E$ ).



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

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 [25]. An order of magnitude change in  $k_{nr}$  in this region was also found for **II** (Fig. 11(b)) and **IV** (Fig. 11(c)).

In region 2, where intersystem crossing from the singlet to triplet state manifolds is the major nonradiative decay channel from  $S_1$  to  $S_0$ , we believe that the solvent modulated location of the (n,  $\pi^*$ ) states relative to the S<sub>1</sub>( $\pi$ ,  $\pi^*$ ) and T<sub>1</sub>( $\pi$ ,  $\pi^*$ ) states influence the rate of singlet to triplet 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 [26]. A mechanism involving thermally activated intersystem crossing from  $S_1(\pi, \pi^*)$  to a higher lying <sup>3</sup>(n,  $\pi^*$ ) state has been offered to explain solvent effects on intersystem crossing for I, II, and IV and other related molecules [27]. We consider vibronic spin–orbit coupling [28] to be an alternative mechanism that is less restrictive than the thermally activated intersystem crossing mechanism in its requirement for the magnitude of the S<sub>1</sub>( $\pi$ ,  $\pi^*$ )-T(n,  $\pi^*$ ) energy gap relative to k<sub>B</sub>T. In this mechanism, spin-orbit coupling between  $(\pi, \pi^*)$  and  $(n, \pi^*)$  in different spin manifolds and vibronic coupling within the same spin manifold are operative in promoting intersystem crossing. Recall that I, II, and IV are compounds belonging to the  $C_{2v}$  point group. The  $C_{2v}$  symmetries of these three compounds can be used to make the discussion of vibronic spin-orbit coupling more specific. Group theory demonstrates that states  ${}^{1}B_{2}(\pi, \pi^{*})/{}^{3}A_{2}(n, \pi^{*})$ and  ${}^{3}B_{2}(\pi, \pi^{*})/{}^{1}A_{2}(n, \pi^{*})$  mix through first order spin-orbit coupling and that b<sub>1</sub> corresponds to the irreducible representation of the vibration that induces the vibronic coupling between  $S_1(\pi, \pi)$  $\pi^*$ ) and S<sub>m</sub>(n,  $\pi^*$ ) and T<sub>1</sub>( $\pi$ ,  $\pi^*$ ) and T<sub>m</sub>(n,  $\pi^*$ ) states for these compounds. The scheme below shows the vibronic-spin orbit coupling mechanism applied to these three C<sub>2v</sub> compounds.

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 [29]. 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 electronic states of different orbital configuration is greater than the matrix element for spin-orbit coupling between electronic states of the same orbital configuration [24]. The decrease in the  $k_{nr}$  values shown in region 2 in the plots in Fig. 11 is consistent with a gradual, solvent induced increase in the spacing between  $S_1/T_1$  and higher energy (n,  $\pi^*$ ) states. Table 5 provides theoretical support for this interpretation with the results of TD-DFT spectral calculations modeled in different solvents. From the TD-DFT calculations of I, II, and IV, the decrease in knr is consistent with a gradual solvent induced increase in the spacing between  $S_1/T_1(\pi, \pi^*)$  and the higher energy  $(n, \pi^*)$  states, resulting in an attenuation in the degree of mixing between  $(n, \pi^*)$ and  $(\pi, \pi^*)$  states of either the singlet or triplet manifolds.

**Fig. 10.** Fluorescence quantum yields  $(\Phi_f)$  of (a) I, (b) II, and (c) IV plotted against the fluorescence spectral maxima in various solvents. Circles represent aprotic solvents; diamonds represent protic solvents.



Direct comparison of the TD-DFT computed energy gaps and experimental  $k_{nr}$  values of I to II in toluene, carbon disulfide, and dichloromethane led to another interesting observation. A larger change in the  $k_{nr}$  value of I than II was observed between toluene and dichloromethane, which were directly correlated to the magnitudes of the changes in the energy spacings between  $S_1/T_1(\pi,\pi^*)$  and the appropriate intermediate  $(n,\pi^*)$  states. To exemplify, for I, the  $k_{nr}$  value is reduced from  $19.2\times10^8~s^{-1}$  to  $10.9\times10^8~s^{-1}$  ( $\Delta=8.3\times10^8~s^{-1}$ ). The differences in the lowest lying  $(\pi,\pi^*)$ -(n,  $\pi^*)$  energy gaps were calculated to be 1168 cm^{-1} (triplet) and 1112 cm^{-1} (singlet). Similarly, for II, the  $k_{nr}$  value is reduced from  $6.98\times10^8~s^{-1}$  to  $4.81\times10^8~s^{-1}$  ( $\Delta=2.17\times10^8~s^{-1}$ ) and the corresponding changes in the lowest lying  $(\pi,\pi^*)$ -(n,  $\pi^*$ ) energy gaps were calculated to be 104 cm^{-1} (triplet) and 709~cm^{-1} (singlet).

From a conceptual perspective, the larger change in  $k_{nr}$  observed for I from toluene to dichloromethane is attributed to a larger change in the  $(\pi, \pi^*)$ - $(n, \pi^*)$  energy spacings. The larger difference in energy gaps implies a smaller degree of vibronic coupling between  $(n, \pi^*)$  and  $(\pi, \pi^*)$  states of the same spin manifold, which in turn results in a larger change in  $k_{isc}$  reduction. Conversely, the smaller change in  $k_{nr}$  seen for II is attributed to a smaller difference in the  $(n, \pi^*)$ - $(\pi, \pi^*)$  energy spacings. The smaller difference in energy gaps means a higher degree of vibronic coupling between  $(n, \pi^*)$  and  $(\pi, \pi^*)$  states of the same manifold, which in turn results in a smaller change in  $k_{isc}$  reduction.

Experimental spectroscopic and photophysical results and TD-DFT calculations of **II** and **IV** make it evident that these two compounds behave similarly. Therefore, the tendency for **II** to undergo fluorescence quenching in polar solvents cannot be attributed to twisting of the dimethylamino group to form a polar TICT state since its spatially restricted julolidine analogue, **IV**, behaves in a similar manner.

Compound III exhibited anomalous fluorescence behavior in highly polar solvents, particularly in alcohols, with  $\Phi_{f}$  values ranging between 0.11 (in methanol) to 0.36 (in 1-butanol). To explain the relatively high quantum yield values observed in alcohols, TD-DFT calculations of III in several alcohols were investigated and compared to I and II, in which fluorescence quenching in alcohols was noticeable. Table 6 lists the computed TD-DFT energy gaps for the lowest lying singlet and triplet  $(n, \pi^*)$ - $(\pi, \pi^*)$  states of **I**, II, and III in methanol, ethanol, and 2-propanol with experimentally observed  $\Phi_{\rm f}$  values. TD-DFT predicted the <sup>3</sup>(n,  $\pi^*$ ) state located above the  $S_1(\pi, \pi^*)$  state, suggesting that direct spin–orbit coupling between  $S_1(\pi, \pi^*)$  and  $T_1(\pi, \pi^*)$  is weak (low  $k_{isc}$ ). Vibronic spin-orbit coupling can be offered as a mechanism for explaining the high  $\Phi_{\rm f}$  values observed for III in alcohols. As shown in Table 6, even though the lowest lying triplet (n,  $\pi^*$ )-( $\pi$ ,  $\pi^*$ ) energy gaps of **III** fall in between **I** and **II**, the corresponding singlet  $(n, \pi^*)$ - $(\pi, \pi^*)$ gaps of III are larger than for I and II. The larger energy gap between  $(\pi, \pi^*)$  and  $(n, \pi^*)$  states suggests an attenuation in the degree of vibronic coupling between these two states, resulting in a slower rate of singlet  $\rightarrow$  triplet intersystem crossing. The higher population of molecules in the  $S_1(\pi, \pi^*)$  state remains more populated than the  $T_1(\pi, \pi^*)$  state, thereby inducing fluorescence.

## 3.3. Excited state protonation studies

Both I and III were found to undergo excited state protonation when dissolved in glacial acetic acid (see Fig. 12). In knowing the energies of fluorescence of both the unprotonated (A) and

**Fig. 11.** Nonradiative decay constant  $(k_{nr})$  of (a) **I**, (b) **II**, and (c) **IV** plotted against the fluorescence spectral maxima in various solvents. Circles represent aprotic solvents; diamonds represent protic solvents.

#### Table 5

TD-DFT computed energy gaps of the lowest lying (n,  $\pi^*$ ) and ( $\pi$ ,  $\pi^*$ ) states and experimental k<sub>nr</sub> values for **II** (in comparison to **I** for the same solvents) and **IV**.

	Toluene	Carbon disulfide	Dichloromethane	$\Delta$ (DCM/Toluene)
$ \begin{array}{l} \textbf{II} \\ T_3(n,\pi^*) - T_1(\pi,\pi^*) \\ S_3(n,\pi^*) - S_1(\pi,\pi^*) \\ k_{nr} \times 10^{-8} (s^{-1}) \\ \textbf{I} \\ T_3(n,\pi^*) - T_1(\pi,\pi^*) \\ S_n(n,\pi^*) - S_1(\pi,\pi^*)^{\dagger} \\ k_{nr} \times 10^{-8} (s^{-1}) \end{array} $	$8346 \text{ cm}^{-1} \\ 4606 \text{ cm}^{-1} \\ 6.98 \\ 6547 \text{ cm}^{-1} \\ 3290 \text{ cm}^{-1} \\ 19.2 \\ \end{cases}$	$8464 \text{ cm}^{-1} \\ 4837 \text{ cm}^{-1} \\ 6.87 \\ 6676 \text{ cm}^{-1} \\ 3547 \text{ cm}^{-1} \\ 17.6 \\ \end{cases}$	9360 cm <sup>-1</sup> 5315 cm <sup>-1</sup> 4.81 7715 cm <sup>-1</sup> 4402 cm <sup>-1</sup> 10.9	$1014 \text{ cm}^{-1}$ 709 cm <sup>-1</sup> 2.17 1168 cm <sup>-1</sup> 1112 cm <sup>-1</sup> 8.3
$\begin{split} & \textbf{W} \\ & T_m(n, \pi^*) \text{-} T_1(\pi, \pi^*)^{\ddagger} \\ & S_3(n, \pi^*) \text{-} S_1(\pi, \pi^*) \\ & k_{nr} \times 10^{-8}  (\text{s}^{-1}) \end{split}$		n-Hexane 8449 cm <sup>-1</sup> 4522 cm <sup>-1</sup> 10.0	Toluene 8741 cm <sup>-1</sup> 4826 cm <sup>-1</sup> 7.53	Dichloromethane 9801 cm <sup>-1</sup> 5268 cm <sup>-1</sup> 7.39

 $^{\dagger}In$  toluene and carbon disulfide, m = 2; in dichloromethane, m = 3.

<sup> $\ddagger$ </sup>In n-hexane and toluene, m = 3; in dichloromethane, m = 4.

protonated (HA<sup>+</sup>) forms, the difference in pKa between the excited state and ground state ( $\Delta$ pKa) of each compound were calculated from the Förster cycle [30,31].

$$\Delta pKa = pKa * - pKa = \frac{N_A hc \left(\tilde{\nu}_A^{fI} - \tilde{\nu}_{HA^+}^{fI}\right)}{2.303 RT}$$
(7)

where NA is Avogadro's number, h is Planck's constant, c is the speed of light in a vacuum, R is the universal gas constant, and T is absolute temperature of the solution. Experimental observations show that the unprotonated and protonated forms of I fluoresce at 16750 cm<sup>-1</sup> and 13569  $\text{cm}^{-1}$ , and those for **III** at 15576  $\text{cm}^{-1}$  and 12225  $\text{cm}^{-1}$ . From the emission data, the  $\Delta p$ Ka values of both I and III were found to be 6.7 and 7.1. Positive  $\Delta p$ Ka values are indicative that the compounds are more basic in the singly excited  $(\pi, \pi^*)$  state than in the ground singlet state ( $pKa^* > pKa$ ). Additional quantitative support on the excited state protonation of **I** and **III** in glacial acetic acid involved calculating atomic charges (Q) in both the ground singlet and lowest lying singly excited ( $\pi$ ,  $\pi^*$ ) states, looking specifically at the carbonyl oxygen atom. For I,  $Q_0(S_0) = -0.55$ ,  $Q(^1(\pi, \pi^*)) = -0.66$ ,  $\Delta Q_0 = -0.11$ ; for III,  $Q_0(S_0) = -0.55$ ,  $Q(^1(\pi, \pi^*)) = -0.63$ ,  $\Delta Q_{\Omega} = -0.077$ . The charge of the carbonyl oxygen atom becomes more negative in going from the S<sub>0</sub> to  ${}^{1}(\pi, \pi^{*})$  state, which is supportive that the compounds are stronger bases in the excited state and have a higher affinity of protonation.

## 4. Conclusion

A series of alkylamino substituted 2-arylidene and 2,5-diarylidene cyclopentanone compounds have been synthesized and structurally characterized. The spectroscopic and photophysical properties of all compounds studied have been found to vary with

#### Table 6

TD-DFT computed energy gaps of S<sub>1</sub>/T<sub>1</sub> ( $\pi$ ,  $\pi^*$ ) and the appropriate intermediate (n,  $\pi^*$ ) states of I, II, and III in methanol, ethanol, and 2-propanol with experimentally observed  $\Phi_f$  values.

Compound	$\Delta \mathrm{E}~[\mathrm{cm}^{-1}]$ and $\Phi_\mathrm{f}$			
	Methanol	Ethanol	2-Propanol	
ш	$\begin{array}{l} \Delta E_{S} = 4765 \\ \Delta E_{T} = 8081 \\ (\Phi_{f} = 0.025) \\ \Delta E_{S} = 5292 \\ \Delta E_{T} = 9702 \\ (\Phi_{f} = 0.022) \\ \Delta E_{S} = 5543 \\ \Delta E_{T} = 9672 \\ (\Phi_{f} = 0.11) \end{array}$	$\begin{array}{l} \Delta E_S = 4697 \\ \Delta E_T = 8001 \\ (\Phi_f = 0.11) \\ \Delta E_S = 5326 \\ \Delta E_T = 9624 \\ (\Phi_f = 0.076) \\ \Delta E_S = 5480 \\ \Delta E_T = 9622 \\ (\Phi_f = 0.23) \end{array}$	$\begin{array}{l} \Delta E_{S}=4697\\ \Delta E_{T}=7977\\ (\Phi_{f}=0.18)\\ \Delta E_{S}=5326\\ \Delta E_{T}=9639\\ (\Phi_{f}=0.15)\\ \Delta E_{S}=5480\\ \Delta E_{T}=9603\\ (\Phi_{f}=0.33) \end{array}$	

solvent polarity, some more significant than others. The observation of bathochromic shifts in absorbance and fluorescence, TD-DFT spectral calculations, and Lippert–Mataga analysis are indicative of the internal charge transfer (ICT) natures of the  $S_0 \rightarrow S_1$  excitation portrayed by these compounds. Photophysical properties also showed solvent dependence. The behavior of  $k_{nr}$  with respect to the fluorescence spectral maxima and solvent polarity can be divided into two regions. In region 1, the increase in the rate of internal conversion allows it to dominate over intersystem crossing; whereas in region 2, intersystem crossing is the major nonradiative decay channel 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.

The tendency for compound **II** to undergo fluorescence quenching in polar aprotic and protic solvents cannot be attributed to twisting of the dimethylamino group to form a polar TICT state since is spatially restricted julolidine analogue, **IV**, behaves in a similar manner and is incapable of twisting to form a TICT state.



Fig. 12. Room temperature absorption and fluorescence spectra of (a) III and (b) I in glacial acetic acid.

Direct comparison of the spectroscopic and photophysical properties of **II** and **IV** clearly support this argument. Vibronic spin—orbit coupling and comparative TD-DFT spectral calculations of **III** with **I** and **II** were used to justify the anomalous behavior of fluorescence and high  $\Phi_f$  values observed for **III** in alcohols. A supportive argument of the effect of structural asymmetry on the anomalous fluorescence behavior for **III** in alcohols is still inconclusive.

Lastly, compounds I and III have been found to undergo excited state protonation in glacial acetic acid, consistent with the observed fluorescence spectra and theoretically calculated partial charges of atoms both in the S<sub>0</sub> and lowest lying <sup>1</sup>( $\pi$ ,  $\pi^*$ ) states.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.02.009.

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