Effect of Donor–Acceptor Coupling on TICT Dynamics in the Excited States of Two Dimethylamine Substituted Chalcones

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Supporting Information

ABSTRACT: Significant effect of coupling between the electron donor and acceptor groups in intramolecular charge transfer (ICT) dynamics has been demonstrated by comparing the photophysical properties of two isomeric *N*,*N*-dimethylaminochalcone derivatives (namely, DMAC-A and DMAC-B). In the case of the DMAC-B molecule, the distance between the donor (*N*,*N*-dimethylamiline or DMA) and the acceptor (carbonyl) groups is larger by one ethylene unit as compared to that in the case of DMAC-A. The excited singlet (S₁) states of both the isomers have strong ICT character but their photophysical properties are remarkably different. In polar solvents, fluorescence quantum yields (and the lifetimes of the S₁ state) of DMAC-A are more than 2 orders of magnitude lower (and shorter) than those of DMAC-B. Remarkable differences in the photophysical properties of these two isomers arise due to occurrence of the ultrafast twisting of the DMA group (or the TICT process) during the course of deactivation of the S₁ state of the DMAC-A molecule, but not in the case of DMAC-B. In the later case, because of the presence of a large energy barrier along



the twisting coordinate(s), TICT is not a feasible process, and hence, the S_1 state of DMAC-B has the planar ICT structure. In the DMAC-A molecule, the strength of coupling between the donor and acceptor groups is relatively stronger because of a shorter distance between these groups. Femtosecond transient absorption spectroscopic measurements and DFT/TDDFT calculations have been adopted to establish the above aspects of the relaxation dynamics of the S_1 states of these two isomeric chalcones.

1. INTRODUCTION

Photoinduced charge transfer or electron transfer processes play the fundamental role in conversion of light energy, e.g., photosynthesis in plants, artificial light harvesting systems, and in numerous existing or conceived molecular photonic applications.¹⁻³ Donor and acceptor substituted conjugated organic molecular systems undergo extensive charge transfer upon photoexcitation to the electronically excited state. The photoinduced intramolecular charge transfer (ICT) state may lead to quantitative charge separation by structural reorganization, which makes the ICT process irreversible, and this is highly desirable for solar energy conversion. Thus, the fundamental understanding of the structure and dynamics of the ICT process in the excited states has been of great interest, and hence, numerous donor (D) and acceptor (A) substituted aromatic molecules (D-Ar-A (here, Ar is the aromatic or π conjugated alkene bridge between D and A)) have been studied extensively.⁴⁻¹³ The concept of relaxation of the excited state via twisting of single bond has mainly evolved from the observations of dual fluorescence of 4-dimethylaminobenzonitrile (DMABN) and related molecules. The higher energy emission occurs from the ICT state, whereas the twisted intramolecular charge transfer (TICT) state, in which the dimethylamino (donor) group attains a dihedral angle of about 90° with respect to the molecular plane, is responsible for the lower energy emission.⁴ This twisted geometry allows maximum charge separation between the donor and the acceptor moieties due to the minimum orbital overlap.⁴

On the other hand, strong viscosity dependent fluorescence yield of several diphenyl and triphenylmethane dyes led to the concept of large amplitude structural relaxation to facilitate nonradiative deactivation of the excited state. Ultrafast spectroscopic measurements on these molecules revealed that twisting of the *N*,*N*-dimethylaniline (DMA) group generates nonemissive TICT excited state in pico or subpicosecond time scale depending on the viscosity of the medium.^{8–13} Dimethylamino substituted aromatic ketone derivatives, such as 4-dimethylaminobenzophenone and Michler's ketone, also exhibit similar ultrafast relaxation dynamics involving twisting of the DMA group.^{14–16}

Grabowski et al. have reviewed a large amount work to establish the fact that enhanced charge transfer upon photoexcitation drives the structural relaxation to the TICT state in D-Ar-A molecules.⁴ On the other hand, it has also been established that in many D-Ar-A molecules, the ICT state with strong charge transfer character does not undergo TICT relaxation.^{17–21} For example, 4, 4'-Dimethylaminocyanostilbene has been established to have planar ICT structure in the

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excited state without TICT relaxation.^{20,21} It is intuitive that the ICT dynamics via twisting relaxation will depend on the relative energies of the ICT and TICT states and intervening barrier height along the twisting coordinate. It is highly desirable to understand the structural effect on charge transfer dynamics facilitated by large amplitude twisting motion.

In this paper, we attempt to address this issue by comparing the spectroscopic properties and excited state dynamics of two isomeric 4-dimethylaminochalcones (abbreviated as DMAC-A and DMAC-B, see Scheme 1), where the DMA group and the



carbonyl group act as donor and acceptor, respectively, but the two isomers differ in the relative positions of the donor and the acceptor groups. In the case of the DMAC-B molecule, this distance is larger by one ethylene unit as compared to that in the case of DMAC-A. This small difference in the structures of the molecules leads to different photophysical behaviors because of the difference in the strength of coupling between the donor and acceptor groups. Photophysical properties of DMAC-B were reported earlier in connection with the lipid sensor activity due to prominent solvent polarity dependence of the fluorescence quantum yield.²²⁻²⁴ However, DMAC-A has not been studied so far. Herein, we show that there is remarkable contrast in the photophysical properties and the excited state dynamics of these two isomeric dimethylaminochalcones. Comparison of the steady state and time-resolved spectroscopic properties allows us to unravel the intricate role of the relative positioning of the donor and acceptor groups on intramolecular charge transfer and structural relaxation dynamics. Optimization of the excited state structures using time dependent density functional theory (TDDFT) elucidates the geometrical consequences of the ICT process occurring in the first excited singlet states of these two isomers supporting the experimental observations.

2. EXPERIMENTAL SECTION

2.1. Synthesis. DMAC-A and DMAC-B molecules were synthesized using crossed-aldol condensation reaction following a reported standard procedure.²⁵ DMAC-A was prepared from the reaction between 4-dimethylaminoacetophenone and benzaldehyde using sodium hydroxide as base in aqueous ethanol. For synthesis of DMAC-B, a stronger base, sodium hydride was used and the synthesis was performed in dry tetrahydrofuran (THF). The compounds were purified by column chromatography followed by crystallization from ethanol. The purified samples were characterized by proton NMR and mass spectra analysis, the results of which are given in the Supporting Information (SI) section (Figures S1a–f).

DMAC-A: Yield: 80%, yellow needles, mp 170–172 °C. ¹H NMR(CDCl₃) δ (ppm): 3.06 (s, 6H), 6.73 (d, 2H), 7.39 (m, 3H), 7.58 (d, 1H), 7.64 (m, 2H), 7.78(d, 1H), 8.02 (d, 2H)¹³C NMR (CDCl₃) δ (ppm): 40.3, 111.2, 122.3, 126.4, 128.3, 128.9, 130.1, 130.9, 135.6, 142.7, 153.9, 187.9.

DMAC-B: Yield: 60%, orange crystals, mp 105–107 °C. ¹H NMR(CDCl₃) δ (ppm): 3.04 (s, 6H), 6.70 (d, 2H), 7.34 (d, 1H),7.48 (t, 2H), 7.55 (m, 3H), 7.79 (d, 1H),8.01(d, 2H) ¹³C NMR (CDCl₃) δ (ppm): 40.2, 112.0, 117.1, 122.8, 128.4, 128.5., 130.5, 132.6, 139.2, 145.9, 152.1, 190.8.

Fluorescence excitation spectra of each of these two samples have been compared with its ground state absorption spectrum and excellent agreements between them ensure the absence of any fluorescent impurity in the samples (Figure S2 in the SI section). All solvents were of spectroscopic grade (Spectrochem, India) and were used as received.

2.2. Photophysical Measurements. Steady state absorption spectra were recorded using a Thermo-Electron model Biomate spectrophotometer. Fluorescence spectra, which were corrected for the wavelength dependence of the instrument sensitivity, were recorded using Hitachi model 4010 spectrofluorimeter. Fluorescence measurements were performed with dilute solutions having optical density (OD) < 0.2 at the excitation wavelength to eliminate the error due to reabsorption. Fluorescence quantum yields of DMAC-B in various solvents were calculated using coumarin 30 in acetonitrile as the reference (fluorescence quantum yield, $\phi_{\rm E}$ = 0.67). The fluorescence quantum yields of DMAC-A were calculated relative to that of DMAC-B in acetonitrile. Uncertainty in the quantum yield measurements of DMAC-B is within 10% whereas that for DMAC-A may be up to 20% because of very weak emission.

2.3. Time Resolved Measurements. Fluorescence lifetimes were measured either using time correlated single photon counting (TCSPC) or fluorescence up-conversion techniques. The TCSPC instrument is from Horiba-Jobin-Yvon, IBH (U.K.). The samples were excited using a 408 nm diode laser (1 MHz) and fluorescence was collected at right angles to the excitation source and detected using a microchannel plate (MCP) detector. The IRF of the TCSPC instrument was found to be ~100 ps, which was measured by collecting the scattering light from a TiO₂ suspension in water.

The fluorescence upconversion spectrometer (FOG 100, CDP, Moscow) has been described in detail elsewhere.²⁶ In brief, laser pulses of 400 nm wavelength of 1 nJ energy/pulse and 100 fs duration are generated by frequency doubling the fundamental beam at 800 nm from a self-mode-locked Ti:sapphire oscillator (Tsunami, Spectra Physics) pumped by a 5 W DPSS laser (Millenia, Spectra Physics) using a 1 mm thick type I BBO crystal. These 400 nm femtosecond laser pulses were used to excite the sample in a 1 mm thick rotating quartz cell. The fluorescence photons emitted by the photoexcited sample were upconverted in a nonlinear BBO (β -barium borate) crystal of 0.5 mm thickness by mixing with the gate pulse consist of a portion of the fundamental 800 nm beam. Polarization of the gate pulse was fixed at the magic angle with respect to that of the excitation pulse to eliminate contribution of the reorientational motion of the solute to the population dynamics of the excited state. The upconverted light is dispersed in a double grating monochromator and detected by a photo multiplier tube based photon counter. The instrument response function of the present experimental set up was determined by cross-correlation function obtained using the Raman scattering from ethanol which has a fwhm of 300 fs. The femtosecond fluorescence decays are fitted using a Gaussian function of the same fwhm using as the instrument response function.

Relaxation dynamics of the excited states in various solvents have been measured using subpicosecond time-resolved transient absorption techniques. The pump-probe spectrometer based on a amplified laser system (Thales Optronique SA, Elancourt, France) which provides the pulses of about 40 fs and 1 mJ energy per pulse at a repetition rate of 1 kHz. Pump pulses of 400 nm were generated for excitation of the samples by frequency doubling of one part (100 μ J/pulse) of the 800 nm output of the amplifier in a 0.5 mm thick BBO crystal and another small part (~1 μ I/pulse) of the amplifier output was used to generate the white light continuum (480-1000 nm) probe in a 2 mm thick sapphire plate. The direction of polarization of the pump beam was fixed at the magic angle with respect to that of the probe beam. The energy of the pump beam was maintained at <5 μ J/pulse. The sample solutions were kept flowing through a quartz cell of 2 mm path length. To record the temporal profiles, wavelength regions of 10 nm width were selected using pairs of interference filters. To construct the transient absorption spectra, we recorded the temporal profiles at different wavelengths with 10 nm interval. Following a correction of the zero time arising due to group velocity dispersion at different wavelengths, absorbance values at different delay times were plotted against the wavelength. The overall time resolution of the absorption spectrometer was determined to be about 120 fs. The temporal profiles recorded using different probe wavelengths were fitted with up to three exponentially decaying or growing components by iterative deconvolution method using a sech² type instrument response function with fwhm of 120 fs.

2.4. Computational Method. Ground-state geometry was optimized by using density functional theory (DFT) with B3LYP hybrid functional and by using 6-311G (d, p) basis set.^{27,28} Geometry optimization of the lowest excited singlet state (S_1) was carried out using same functional and basis set in TDDFT formalism. Vibrational frequencies were then calculated on optimized structure to verify the minimum energy geometry. All calculations were carried out using the GAMESS software package.²⁹ Solvent effect was incorporated using the PCM solvation model as implemented in GAMESS.^{30,31}

3. RESULTS AND DISCUSSION

3.1. Steady State Absorption and Fluorescence Studies. Steady state absorption and fluorescence spectra of DMAC-A and DMAC-B molecules have been recorded in solvents of varying polarities and are shown in Figures 1 and 2, respectively. The absorption spectrum of DMAC-A shows a strong absorption band in the 350–480 nm region, which undergoes significant bathochromic shift in polar solvents indicating strong ICT character of the Franck–Condon (FC) excited state. DMAC-B also shows a similar solvent dependent shift of its absorption spectrum revealing the ICT character of the excited state. It is important to point out that in each of these solvents the absorption spectrum of DMAC-B is more red-shifted as compared to that of DMAC-A. This suggests that extended donor–acceptor conjugation in DMAC-B results in larger mesomeric stabilization of the ICT state.

Steady state fluorescence spectra of both the compounds undergo large bathochromic shifts (as large as 125 nm) on changing the solvent from nonpolar cyclohexane to polar DMSO. Systematic increase in fluorescence Stokes shift with solvent polarity suggests strong ICT character of the emissive excited states of both the compounds. Indeed, large increase in dipole moment following photoexcitation of either of these two



Figure 1. Normalized steady state absorption (A) and fluorescence (B) spectra of DMAC-A in cyclohexane (CH), ethyl acetate (EA), acetone (Actn), acetonitrile (Acn), and dimethyl sulfoxide (DMSO). Inset of B shows the Lippert-Mataga plot.



Figure 2. Normalized steady state absorption (A) and fluorescence (B) spectra of DMAC-B in cyclohexane (CH), ethyl acetate (EA), acetone (Actn), acetonitrile (Acn), and dimethyl sulfoxide (DMSO). Inset of B shows the Lippert-Mataga plot.

molecules ($\Delta \mu$ = 11 and 11.8 D for DMAC-A and DMAC-B, respectively) has been calculated from the Lippert-Mataga plots (insets of Figures 1B and 2B).

Although the emissive states of both the isomers have strong ICT character, quantitative measurements of fluorescence yields show astonishing results. DMAC-A is weakly fluorescent in all solvents and the quantum yield decreases with increase in polarity of the aprotic solvents (Table 1). In solvents of large polarity, fluorescence yield is decreased significantly ($\Phi_{\rm f}$ < 10^{-3}). In contrast, the fluorescence yield of DMAC-B increases with an increase in polarity of the aprotic solvents and the emission yield is as large as 0.2 in acetone. Thus, in polar aprotic solvents, emission quantum yield of DMAC-A is more than 2 orders of magnitude less than that of DMAC-B, in spite of similar ICT character of the excited states of both the molecules ($\Delta \mu = \mu_{\rm e} - \mu_{\rm g} \sim 11$ D). Weaker fluorescence of DMAC-A suggests involvement of an additional nonradiative relaxation channel in polar solvents. Another intriguing observation is the difference in the widths of the emission bands of these two compounds (Table 1).

Tab	e 1	. Pho	otopl	hysical	Parameters	of	the	ICT	States	of	DMAC-A	and	DMAC	-B	in	Various	So	ivents
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		DMAC-A					DM	IAC-B		
solvents $(\pi^*)^a$	fl. band fwhm (cm ⁻¹)	$\Phi_{\rm f} \ (10^{-2})$	$(\mathrm{ps})^{b}$	$k_{\rm r} {(10^8 \ {\rm s}^{-1})}$	$k_{ m nr} (10^{11} { m s}^{-1})$	fl. band fwhm (cm ⁻¹)	${\Phi_{\rm f} \over (10^{-2})}$	$(\mathrm{ps})^{b}$	$k_{\rm r} (10^8 { m s}^{-1})$	$k_{\rm nr} (10^9 { m s}^{-1})$
cyclohexane (0.00)	3480	1.2	8.0	9	1.25	3400	0.22	5.2	4.2	192
ethyl acetate (0.45)	5789	0.16	3.1	5	3.2	2580	7.7	600	1.2	1.54
acetone (0.62)	5739	0.097	2.4	5	4.1	2560	19.6	1400	1.4	0.56
acetonitile (0.66)	5780	0.046	1.4	3.5	7.1	2554	10	380	2.6	2.34
DMSO^{c} (1.00)	5644	0.276	4.1	6.5	2.4	2544	13.9	880	1.6	0.97

 ${}^{a}\pi^{*}$ values are taken from ref 32. b Fluorescence lifetimes measured by using fluorescence upconversion technique (for DMAC-A) or TCSPC technique (DMAC-B). c Dimethyl sulfoxide (Typical error in the measured parameters is about ±10%).

Fluorescence spectra of both these molecules in nonpolar solvent, cyclohexane, are characterized by well resolved vibronic bands, suggesting a near planar structure of the excited state. Possibly in the excited state, distribution of conformers formed by rotations about the single bonds becomes much narrower as compared to that in the ground state. In polar solvents, fluorescence spectra of DMAC-A are much broader (fwhm >5000 cm⁻¹) as compared to those of DMAC-B (fwhm ~2550 cm⁻¹). Larger width of the fluorescence spectra of DMAC-A suggests relaxation of the excited state on a shallow potential energy surface along the reaction coordinate, representing twisting about one or more of the single bonds (or conformational relaxation) (vide infra). The excited states of differently twisted conformers populated during conformational relaxation contribute to the total fluorescence. Extremely weak fluorescence yield in the case of DMAC-A also supports the prediction about occurrence of ultrafast excited state conformational relaxation, which is largely absent in the excited state of DMAC-B.

3.2. Time Resolved Fluorescence Measurements. Fluorescence lifetime of DMAC-A has been observed to be much shorter than the time resolution of our TCSPC set up (100 ps). Therefore, the fluorescence lifetimes of DMAC-A in various solvents have been measured by using fluorescence upconversion technique. Temporal fluorescence profiles along with the best-fit functions are shown in Figure 3A. Fluorescence lifetimes of DMAC-B in polar solvents could be determined using the TCSPC technique (Figure 3B). Fluorescence lifetimes of these molecules are given in Table 1. We find that in polar solvents the emissive excited state(s) of DMAC-A is much shorter lived than that of DMAC-B. This is in agreement with the results of fluorescence quantum yield measurements for these two isomers.

Using experimentally measured fluorescence lifetimes and quantum yields, the radiative (k_r) and nonradiative (k_{nr}) rate constants in various solvents have been calculated and the values of these parameters are given in Table 1. Values of k_r for these two molecules are similar ($\sim 10^8 \text{ s}^{-1}$) and also are nearly solvent independent. Whereas the values of k_{nr} for DMAC-A in polar solvents are larger by more than 2 orders of magnitude than those in the case of DMAC-B. Large nonradiative decay rates $(k_{\rm nr} > 10^{11} \text{ s}^{-1})$, low fluorescence yields $(\Phi_{\rm fl} < 10^{-3})$, as well as ultrashort fluorescence lifetimes ($\tau_{\rm fl}$ < 4 ps) of DMAC-A in polar solvents are indicative of the occurrence of ultrafast nonradiative deactivation processes in the excited state(s). To decipher the nature of the excited state deactivation mechanisms, femtosecond transient absorption (TA) spectroscopic measurements have been performed and the results of these measurements are described in the next section.



Figure 3. Temporal fluorescence profiles of DMAC-A measured by fluorescence upconversion (A) and of DMAC-B measured by TCSPC technique (B). In each case, the emission wavelength was set at 550 nm.

3.3. Transient Absorption Studies of DMAC-A. Figure 4A shows the time evolution of the transient absorption (TA) spectra recorded following photoexcitation of DMAC-A in acetonitrile by using 400 nm laser pulses of 50 fs duration. We observe the appearance of an excited state absorption (ESA) band in the 480-950 nm region at 0.15 ps delay time. With increase in delay time up to 0.5 ps, this ESA band in the 550-950 nm region decays leading to the development of a stimulated emission (SE) band with the maximum at 600 nm. During this time domain, however, we observe the rise of ESA in the <550 nm region, thus generating an isosbestic point at ca. 550 nm. On further increase in delay time up to 5 ps, the ESA band in the <550 nm region decays but absorbance in the 550-950 nm region increases leading to the decay of the SE band (Figure 4B). The broad ESA band in the entire spectral region decays within about 25 ps delay time.

Time evolution of the TA spectra suggests population of several excited states during the course of the relaxation process following photoexcitation of DMAC-A. Careful analyses of the temporal absorption profiles recorded at a few selective wavelengths support this prediction and also help us to identify different kinds of excited states or processes associated with the excited state relaxation mechanism. In Figure 4B, we have shown the temporal profiles recorded at 480, 610, and 900 nm along with the best fit functions. Each of these profiles could be



Figure 4. Time evolution of the TA spectra (A) and temporal TA profiles monitored at a few selective probe wavelengths (B) following photoexcitation of DMAC-A in acetonitrile using 400 nm laser pulses of 50 fs duration. Lifetimes (in ps) associated with the components of the mutiexponential fitting functions are given in the insets.

Table 2. Lifetimes of Three Processes Associated with the Excited State Relaxation of DMAC-A in Solvents of Varying Polarities (ε_0 and π^*) and Viscosities (η)

solvent	$\varepsilon_0^a \pi^{*a}$	$\eta(cp)^{b}$	$\langle \tau \rangle_{\rm sol} \ ({\rm ps})^c$	$ au_1$ (ps)	$ au_2$ (ps)	$ au_3$ (ps)
ethyl acetate	6.0, 0.45	0.4	2.5	1.4 ± 0.2	3.1 ± 0.2	22 ± 2
acetone	20.0, 0.62	0.35	0.58	0.7 ± 0.2	2.4 ± 0.2	9 ± 1
acetonitrile	35.5, 0.66	0.44	0.26-0.5	0.3 ± 0.1	1.35 ± 0.1	6 ± 1
DMF^d	36.5, 0.88	0.82	0.91-2.0	0.9 ± 0.2	3.2 ± 0.2	11 ± 1
DMSO	46.5, 1.00	1.99	2.0	1.9 ± 0.2	4.2 ± 0.2	12 ± 1
PC ^e	64.5, 0.83	2.66	3.0	2.5 ± 0.3	5.5 ± 0.2	14 ± 1
^a Reference 32. ^b Refer	ence 33. ^c Reference 3	34. ^d Dimethylforn	namide. ^e Propylene car	bonate.		

fitted using a three exponential function consisting of the rise and decay components and the lifetimes of these components are given in the insets of the Figure 4B. It is important to note that each of them is associated with the time evolution of same three processes with the lifetimes of 0.3 ± 0.1 , 1.32 ± 0.3 , and 6 ps. Association of the ultrafast component with the lifetime of 0.3 ps with the rise of intensity of the SE band in 0.5 ps time domain leads us to assign this component to the vibrational relaxation, which represents the lifetime of the relaxation of the FC state to the local excited (LE) state, which is an ICT or $S_1(ICT)$ state, as the most probable process. However, acetonitrile being a fast dielectric relaxing solvent, contribution of the solvation process for the ICT state in the same time domain cannot be excluded (vide infra).

The second component with the lifetime of 1.32 ps is associated with the decay of the SE band and hence the decay of the $S_1(ICT)$ state. This value agrees well with the fluorescence lifetime determined using the upconversion technique (Table 1). Results of our steady state fluorescence spectroscopy as well as transient absorption and fluorescence spectroscopic techniques lead us to conclude that the $S_1(ICT)$ state, which is weakly emissive, undergoes ultrafast nonradiative relaxation to a nonemissive excited state. Before we confirm this prediction from our solvent dependence study, we tentatively assign the process associated with this lifetime to the twisting of the DMA group (not the only *N*,*N*-dimethylamino moiety, vide infra). Such ultrafast relaxation processes occurring via twisting of the DMA group have already been established by our group in dimethylaminobenzophenone derivatives, auramine, etc.^{15,16} In all those cases, twisting of the DMA group has been established to be a barrierless process. The twisted ICT state, i.e., $S_1(TICT)$ state, decays back to the ground electronic state and has a lifetime of about 6 ps in acetonitrile.

In order to establish the assignments with conformity, we determined the lifetimes of those three processes in solvents of different polarities and viscosities. Temporal dynamics of DMAC-A recorded in several solvents are shown in the SI section (Figures S3-S4) and the lifetimes of three excited state relaxation processes thus estimated along with the solvent parameters are given in Table 2. Referring to the lifetime of the ultrafast process, τ_1 , its value nicely correlates with the average solvation times of the solvents. Therefore, this component should be assigned to the solvation of the $S_1(ICT)$ state rather than the vibrational relaxation process. The later process correlates neither with the polarities nor the viscosities of the solvents and the lifetime in DMSO (about 2 ps) is too long to assign it to the vibrational relaxation process. However, rise of the SE band also suggests that both the vibrational relaxation and solvation processes may be taking place concurrently.

One of the important characteristics of the TICT process is the strong viscosity dependence of the rate of this process due to its association with the large amplitude twisting motion about a single bond. Decrease in the relaxation rate with increase in the viscosity of the solvent may be considered as a direct evidence in favor of its assignment to the twisting process and has been observed in the case of similar molecular

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Figure 5. Time evolution of the TA spectra recorded following photoexcitation of DMAC-B in acetonitrile (A) and temporal decay behaviors at a few selective probe wavelengths (B). Lifetimes determined from mutiexponential fittings of the temporal profiles are given in insets.

systems.^{11–16} The viscosity dependence of the rate of an activated barrier crossing process, like the conformational relaxation via twisting of the DMA group about a single bond in a TICT process, can be fitted fairly well to a power-law function (Kramer–Smoluchowski relationship, eq 1)^{35–40}

$$k_2 = Z\eta^{-\alpha} \exp\left(-\frac{E_a}{RT}\right) (0 < \alpha < 1)$$
⁽¹⁾

$$\ln(k_2) = -\alpha \ln(\eta) + \ln(Z) - \left(\frac{E_a}{RT}\right)$$
(2)

where Z is a pre-exponential factor and the height of the energy barrier, E_{av} for the twisting process, may be considered a constant, if the rates have been measured at a particular temperature and in a set of similar kinds of solvents, in which the energy barrier is not altered significantly. In this condition, eq 2 is likely to represent a linear relation between $\ln(k_2 = \tau_2^{-1})$ and $\ln(\eta)$, with a slope of α . Figure S5 in the SI section presents the Kramer-Smoluchowski plot for all the aprotic solvents, which have been used in the present work. Considering the error in determining the lifetimes of the transient states, we find that a linear relationship between $\ln(k_2)$ and $\ln(\eta)$ is obeyed only in the polar solvents, but in less polar solvents, the rates are much slower. Since population of the $S_1(TICT)$ state is associated with further charge transfer leading to near quantitative charge separation at the twisted geometry, solvent polarity too is likely to influence the energy barrier for the twisting process, and hence the relaxation time, significantly. Therefore, the slower rates of the twisting process in less polar solvents suggests a higher energy barrier in these solvents and twisting is the barrier controlled. But in polar solvents, twisting takes place on a nearly barrierless PES.

The value of α as obtained from the slope of the linear fit in Figure S5 is 0.65. The fractional viscosity dependence of barrierless isomerization reactions have been studied using the mode coupling theory, which finds the value of the slope in the range of 0.5–0.8.³⁸ Therefore, our value (i.e., 0.65), determined for the viscosity dependence of the twisting rate in polar solvents is in close agreement with the theoretical prediction and reveals $\eta^{0.65}$ dependence of viscosity, as predicted and

observed by Förster and Hoffman.³⁹ Several possible explanations for the origin of the fractional viscosity dependence of the rates have been given, such as breakdown of Stokes–Einstein relationship,⁴¹ multidimensionality of the potential energy surface,⁴² time-dependent friction,^{7,43,44} existence of specific solute–solvent interactions, and so on. Therefore, the results of the subps time-resolved transient absorption studies on DMAC-A suggest that the excited state relaxation dynamics is mainly dominated by the large amplitude twisting of the dimethylaniline group.

3.4. Transient Absorption Studies for DMAC-B. Larger fluorescence quantum yields and longer fluorescence lifetimes of DMAC-B in polar solvents as compared to those of DMAC-A (vide supra) possibly suggest absence of the ultrafast nonradiative deactivation channel via twisting of the DMA group in the excited state deactivation of the former molecule. To substantiate this conclusion, we investigated the early time dynamics of the excited states of DMAC-B by using TA spectroscopy in several aprotic solvents. Figure 5A shows the time evolution of the TA spectra following photoexcitation of DMAC-B in acetonitrile by using 400 nm laser pulses of 50 fs duration. TA spectra recorded at 0.15 ps delay time are characterized by a weak SE band in the $480{-}580~\mathrm{nm}$ region and an ESA band in the 600-750 nm region. With increase in delay time, the intensity of the SE band rises up to about 2 ps along with a significant dynamic red shift of the emission maximum. During this period, an ESA band appears in the wavelength region below 500 nm. At 2 ps delay time, the TA spectrum is characterized by a strong SE band with the maximum at 550 nm, which corresponds well to the steady state emission maximum. Thus, like in the case of DMAC-A, the time evolution of the transient spectra in sub-2 ps time domain may be assigned to the vibrational relaxation as well as solvation processes occurring concurrently. On further increase in delay time up to about 30 ps, time evolution of the transient spectra is associated with a small rise of the SE band in the 500-600 nm region. During this time period, rise of the ESA band in the 690-750 nm region has also been observed. Due to much smaller amplitude as that of the SE band, these spectral evolutions are not very evident in the TA spectra shown in

solvent	ε_0^{a} ,	π^{*a}	$\eta(cp)^{b}$	$\langle \tau \rangle_{\rm sol} (\rm ps)^c$	$ au_1(\mathrm{ps})$	$ au_2$ (ps)	$ au_3(\mathrm{ps})$
ethyl acetate	6.0	0.45	0.4	2.5	2.0 ± 0.2	12 ± 1	600 ± 20
acetone	20.0	0.62	0.35	0.58	0.8 ± 0.2	10 ± 1	1400 ± 50
acetonitrile	35.5	0.66	0.44	0.26-0.5	0.6 ± 0.1	12 ± 1	350 ± 10
DMF	36.5	0.88	0.82	0.91-2.0	1.4 ± 0.3	13 ± 1	900 ± 30
DMSO	46.5	1.00	1.99	2.0	1.9 ± 0.3	11 ± 1	880 ± 30
^{<i>a</i>} Reference 32. ^{<i>b</i>} Refe	rence 33. ^c Ref	erence 34					

Table 3. Average Time Constants of the Relaxation Dynamics of DMAC-B in a Few Aprotic Solvents of Varying Polarities and Viscosities

Figure 5A, but can easily be noted from the temporal profiles shown in Figure 5B.

On a longer time scale, the ESA and SE bands appearing in the entire 480–750 nm region decay indicating deactivation of the S₁ state leading to near complete recovery of the ground state. Temporal analyses of the kinetic profiles presented in Figure 5B reveal three exponential dynamics. An ultrafast component with a time constant of 0.4–0.7 ps (wavelength dependent) appears either as decay (in the blue region) or rising component (in the red region) of SE. A similar time constant has been observed to be associated with the temporal profiles recorded in the 690–730 nm region as one of the decay components of the ESA signal. Time evolution of the SE band reveals a dynamic red shift and the time constant of the process essentially agrees well with the average solvation time of acetonitrile ($\langle \tau \rangle_{sol} = 0.5 \text{ ps}^{34}$) and hence these features suggest its assignment to solvation dynamics.

Following solvation, an intermediate relaxation process with the lifetime of 12 ± 2 ps has been seen to be associated with the temporal profiles recorded in the entire spectral region prior to the decay of ESA or SE band with the lifetime of about 350 ps. It can be noted that this long decay component (ca. 350 ps) agrees well with the fluorescence lifetime of DMAC-B in acetonitrile measured by using TCSPC technique, and thus represents the lifetime of the emissive singlet state, which decays populating the ground state. The intermediate component with the lifetime of about 13 ps is possibly associated with some kind of minor intramolecular structural reorganization in the $S_1(ICT)$ state of the molecule to populate structurally relaxed emissive $S_1(ICT')$ state, but maintaining the near planar conformation. Presence of this component has also been evident in the transient fluorescence decay of DMAC-B recorded in acetonitrile solvent using fluorescence upconversion technique (Figure S6 in the SI section).

We have also studied the temporal dynamics of DMAC-B in a few other aprotic solvents and the results are given in Table 3 and Figure S7 in the SI section. Transient decay behavior is similar in all solvents. The first component (τ_1) corresponds well to solvation time of the respective solvent.³⁴ The intermediate component (τ_2) is associated with the population of fully relaxed $S_1(ICT')$ state, which is long-lived (>300 ps). Absence of viscosity dependence of the intermediate (τ_2) component clearly suggests that large amplitude twisting motion is not associated with the relaxation dynamics of the $S_1(ICT)$ state of the DMAC-B molecule, rather some wagging motion including bond length and bond angle reorganization may be associated with this process to populate the relaxed $S_1(ICT')$ state. Long fluorescence lifetime and large emission quantum yield also support the conclusion that large amplitude twisting motion to populate a nonemissive $S_1(TICT)$ state is not involved in the photodynamics of the DMAC-B molecule.

3.5. Exploring the Possibility of Other Relaxation Processes. It is worth mentioning here that we have described the excited state dynamics of two isomeric N₁N-dimethylaminochalcone derivatives only in polar aprotic solvents, in which specific differences in the behaviors of the excited states of these molecules have been observed. In nonpolar solvent, namely cyclohexane, the S1 state of DMAC-B has been reported to undergo efficient triplet formation within 20 ps time scale ($\tau_{\rm ISC}$ = 5 ps).⁴⁵ In the case of DMAC-A too, we observed efficient triplet formation in cyclohexane (Figures S8 and S9 in the SI section). However, the yields of the triplet states of both these molecules are significantly small in polar solvents. This is in agreement with the earlier observations made from both the experimental as well as theoretical studies, that in polar solvents, quantum yield of formation of the triplet state via ISC process reduces significantly because of stabilization of the $S_1(\mathrm{ICT})$ state with respect to the T_1 state.45,46

We have also not ignored the other possible relaxation mechanism, namely the cis-trans isomerization about the ethylenic double bond. We observed no change in the absorption spectra and ¹H NMR spectra of both these molecules even after prolonged photoirradiation in acetonitrile to rule out the possibility of occurrence of cis-trans photoisomerization reaction. Further, our TDDFT calculations reveal that cis-trans isomerization coordinate is associated with a large barrier (vide infra).

3.6. Quantum Chemical Calculations. Results of our steady state and time-resolved absorption and fluorescence studies suggest that the excited state deactivation of DMAC-A involves a large amplitude conformational relaxation channel but not that in the case of DMAC-B, in spite of their structural similarities as well as similarities in the charge transfer properties in the S₁ state. To corroborate those experimental findings, we performed DFT/TDDFT calculations to determine the structures of the molecules in the ground (S_0) state as well as in the S_1 state. Optimization of the geometries of those two isomers in the S_0 and S_1 states have been performed by using DFT/TDDFT theoretical calculations, and the results are shown in Figure S10 (in the SI section) and the bond parameters are given in Table S1 in the SI section. DFT optimized structures show that both the molecules are nearly planar in the S₀ state. Planar structure and extended π conjugation between the donor and the acceptor groups ensure efficient charge transfer upon photoexcitation. HOMO-LUMO compositions clearly indicate that in the S₀ state electron density is localized on the DMA group, whereas in the S₁ state, electron density is localized on the carbonyl group (Figure S11 in the SI section). This delineates the aspect of strong ICT character of the S₁ state as inferred from the experimental results (vide supra). The $S_1 \leftarrow S_0$ transition energies are calculated to be 3.1 and 2.94 eV for DMAC-A and

DMAC-B, respectively, which are in close agreement with those values determined experimentally. Further, the calculated values of the dipole moments of the S₀ and S₁ states of DMAC-A are 6.8 and 20.1 D, respectively, which support strong intramolecular charge transfer ($\Delta \mu = 13.3$ D) following photo-excitation. Similar results have been obtained for DMAC-B, for which the calculated values of the diploe moments of the S₀ and S₁ states are 8.4 and 21.9 D, respectively ($\Delta \mu = 13.5$ D; Table S2 in the SI section).

Starting with the optimized planar structure (i.e., FC geometry) of the S_0 state as the initial guess, geometry optimization for the S_1 state of the DMAC-A by using the TDDFT method leads to a structure of the lowest energy, in which the dihedral angle of the DMA group is twisted by 90° with respect to the rest of the molecular plane (Figure S12 in the SI section). We also constructed the potential energy surface (PES) along the reaction coordinate involving the twisting motion of the DMA group in acetonitrile solvent. We find a barrierless twisting of the DMA group leading to a potential energy minimum at the twist angle of 90° (Figure 6).



Figure 6. Theoretical potential energy surface (PES) diagrams in acetonitrile calculated using DFT/TDDFT methods, representing the changes in potential energies (relative to that of the ground state minimum) along the twisting angles of the DMA group.

This delineates our prediction regarding conformational relaxation of the $S_1(ICT)$ state of DMAC-A via twisting of the DMA group to populate the twisted structure of lower energy. The twisted conformation is characterized by negligibly small oscillator strength (f = 0.001) for spontaneous emission to the S_0 state and thus suggests its nonemissive character. This is in conformity with our experimental results, which describe the ultrafast deactivation of an emissive state, $S_1(ICT)$, to an intermediate nonemissive state, $S_1(TICT)$, prior to deactivation of the S_1 state to the ground state. Thus, both the experimental results and TDDFT calculations clearly establish that large amplitude relaxation motion via twisting of the DMA group is an efficient channel for the nonradiative deactivation of the S_1 state of the DMAC-A molecule.

On the other hand, the TDDFT optimized geometry of the $S_1(ICT)$ state of DMAC-B is similar to that of the S_0 state with the only differences in the bond lengths and bond angles, excluding the possibility of any large amplitude conformational change in the excited state (Table S1 in the SI section). We constructed the PES of twisting of the DMA group in the excited state of DMAC-B in acetonitrile (Figure 6), and we find a energy barrier of about 0.06 eV, which is much larger than the

thermal energy at 298 K (0.025 eV), existing at the twist angle of 40°. Because of this energy barrier, although the potential energy of the fully twisted structure (i.e., with the twist angle of 90°) is very similar (2.87 eV) to that of the $S_1(TICT)$ state of DMAC-A, the twisting process could not experimentally be observed in the S₁ state of DMAC-B. The possible reason for the absence of this channel in DMAC-B is that π -conjugation between the donor and the acceptor is extended by an additional ethylene bond (as compared to DMAC-A), which results in a weaker coupling and hence relatively larger energy barrier along the reaction coordinate involving the twisting motion of the DMA. We have also calculated the potential energy change upon twisting of two other possible torsional channels, namely twisting of dimethylamine group and twisting of the olefinic bond (Figure S12 in the SI section). Twisting along dimethylamine group results in an increase in PE up to about 50°, and the barrier of this twisting is calculated to be 0.24 and 0.22 eV for DMAC-A and DMAC-B, respectively. On the other hand, the double bond twisting appears to have even larger energy barrier (~0.7 eV) for both the molecules. Thus, twisting relaxation around the dimethylamine group or the olefin bond is less probable for both the molecules.

4. SUMMARY AND CONCLUSIONS

Both the isomers of dimethylaminochalcones studied here have strong ICT character in the excited states owing to donoracceptor substitutions. In polar solvents, fluorescence behavior of the two compounds is remarkably different. Weak emission and short fluorescence lifetime of DMAC-A in polar solvents suggest efficient and very fast nonradiative relaxation of the emissive ICT state. Subpicosecond transient absorption studies confirmed ultrafast structural relaxation to a nonemissive TICT state in a few picosecond time scale. Excited state structure optimization further substantiates that the structure with the twisted DMA group has the minimum potential energy. On the other hand, stronger fluorescence ($\Phi_f = 0.1-0.2$) and longer lifetime (350–1400 ps) of the S_1 state of DMAC-B in polar solvents are assigned to the planar ICT state and absence of the dominant nonradiative structural relaxation channel. Large energy gap between the S_1 and S_0 states is responsible for longer lifetime of the S1 state of DMAC-B. The TA experiment reveals that, in addition to solvation, some intramolecular relaxation process with about 10 ps lifetime is involved in the $S_1(ICT)$ state of DMAC-B. This process is not influenced by the solvent viscosities, suggesting an absence of large amplitude structural relaxation. This intermediate relaxation could not unequivocally be characterized in the present study but tentatively assigned to low amplitude changes in bond angles and dihedral angles required to populate the electronically relaxed $S_1(ICT')$ state.

The excited state properties of the two molecules are remarkably different, in spite of the fact that both of them possess strong ICT character. This leads to the conclusion that large charge transfer upon photoexcitation is not the sole criteria for TICT relaxation, rather the structure of the molecule determines the shape of the excited state potential energy surface and thus the excited state reaction dynamics. In the case of DMAC-A, the potential energy surface is quasibarrierless (in polar solvents) along the DMA twisting coordinate, which allows the excited state population to relax to a TICT state on the ultrafast time scale, whereas for DMAC-B, the TICT state is separated from the planar ICT geometry by a significantly large energy barrier and thus relaxation to the

twisted state is kinetically unfavorable. We propose that the relative positioning of the donor and acceptor groups plays an important role on the energetics of the ICT - TICT relaxation process. In comparison to DMAC-A, the DMA group of DMAC-B is in extended conjugation with the carbonyl group by an additional olefin bond which provides significant mesomeric stabilization to the planar ICT state of DMAC-B. This is also evident from the absorption spectra, where DMAC-B absorption is significantly lower in energy as compared to that of DMAC-A in all solvents. Increase of an energy barrier along the torsional coordinate of the excited state with extended π -conjugation has also been reported for polymethine cyanine dyes.⁴⁷ Following the results of the above investigations, the excited state potential energy surfaces have been schematically presented in Figure 7.



Figure 7. Schematic potential energy surface (PES) diagrams illustrating the differences between the photophysical processes occurring in the excited states of DMAC-A (blue) and DMAC-B (red) in polar solvents.

In conclusion, the present study demonstrates that the relative positioning of the donor and acceptor groups is crucial in determining the structural relaxation pathways in the charge transfer excited state. Stronger coupling between the donor and acceptor groups because of their closer proximity facilitates ultrafast twisting of these groups in DMAC-A leading to population of the weakly emissive TICT state. Whereas, in the case of DMAC-B, in which the donor and acceptor groups are weakly coupled, the relaxation process of the excited state does not populate the TICT state, but the planar ICT state is much longer lived and much more strongly fluorescent. We believe that the relative positioning of the donor and acceptor groups strongly influences the relative energies of ICT and TICT states, as well as the barrier along the twisting coordinate in a large class of D-Ar-A derivatives.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b08203.

Proton NMR and mass spectra, fluorescence excitation spectra, temporal dynamics in different solvents, Kramer–Smoluchowski plot for DMAC-A, TA spectra and temporal dynamics in cyclohexane, detailed results of DFT and TDDFT calculation on structural and optical parameters, and potential energy surfaces along the reaction coordinates of twisting about the single bonds of both these molecules (PDF)

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Notes

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