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The role of the $\pi\sigma^*$ state in intramolecular charge transfer of 4-(dimethylamino)benzonitrile

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February 11, 2011

Helen Gray, Publishing Editor
Physical Chemistry Chemical Physics
Royal Society of Chemistry
Thomas Graham House, Science Park
Cambridge CB4 0WF ENGLAND

Dear Ms. Gray:

Attached please find the manuscript, which has been revised following the comments of referee 3, and are listed below:

Our responses to the comments of referee 3 are as follows:

- Significant point: “As it stands Fig. 5 suggest that the TICT state would rise with the decay time of the $\pi\sigma^*$ state, which is not what is indicated in the text”
 - ❖ Our response: The referee somehow missed the fact that TICT state rise with the decay time of the $\pi\sigma^*$ state, which had been indicated in the abstract as well as in the text (pages 3 and 5).
 - Minor points: “In Fig. 3, the fluorescence spectra for DMABN in Acn are shown and are very different”.
 - ❖ Our response: This is due to the fact that DMABN in acetonitrile exhibits a weak LE fluorescence and the strong, red-shifted ICT fluorescence, whereas DMABE exhibits only the LE emission in acetonitrile. This is indicated in the revised manuscript along with their annotations in Fig. 3.
- “Pump probe appears twice. In the first instance, it should be pump and probe, in the second pump-probe”
- ❖ Our response: We have changed the notations accordingly.
- “In the introduction, some comment as to what is meant by $\pi\pi^*$ to $\pi\pi^*$ transitions. Presumably from excited to higher excited state is meant”
- ❖ Our response: Yes, it is correct. We have indicated this in the revised manuscript.

As per your email of January 14, which we are attaching, the figures are prepared in color. I hope you will find the revised manuscript satisfactory.

Sincerely,

Edward C. Lim

ECL/pah

Attachments

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Subject: Physical Chemistry Chemical Physics - manuscript ID CP-COM-11-2010-002706
Date: Friday, January 14, 2011 7:22:00 AM

14-Jan-2011

CP-COM-11-2010-002706 - The Role of $\pi\sigma^*$ State in Intramolecular Charge Transfer of 4-(Dimethylamino)benzonitrile

Dear Dr Lim:

Thank you for your rapid revision of your revised manuscript for Physical Chemistry Chemical Physics. I have considered your reply to the suggestion to extend your work to a full paper, and we would still be happy to publish your work as a Communication if you feel this is the best outlet for your research. Regarding the use of colour in your manuscript, I have looked over the figures and agree that Figure 1 would be significantly enhanced by the use of colour. As this figure will be printed in colour, we can publish all of your other colour figures in colour free of charge.

However, please could I ask you to elaborate more on your responses to the referees, as I am unclear on the changes made, or indeed, whether you feel that the referees have misunderstood some of the work. This will help to speed up the peer-review process.

Once again, thank you for your quick response.

Yours sincerely,

Helen Gray

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The Role of $\pi\sigma^*$ State in Intramolecular Charge Transfer of 4-(Dimethylamino)benzonitrile

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The solvent-polarity dependence and temporal characteristics of the transient absorption of 4-(dimethylamino)-benzonitrile, DMABN, and 4-(dimethylamino)benzethyne, DMABE, demonstrate the presence of the $\pi\sigma^*$ -state absorption at about 700 nm and the $\pi\pi^*$ (LE)-state absorption at about 520 nm and 450 nm. The rise and decay times of the $\pi\sigma^*$ -state transient differ from those of the $\pi\pi^*$ -state transients in both compounds. Moreover, the peak position of the $\pi\sigma^*$ -state absorption is blue-shifted and more intense in acetonitrile as compared to *n*-hexane, whereas the band positions of the $\pi\pi^*$ -state absorptions are essentially the same in the two solvents. For DMABN in acetonitrile, the rise time (~ 4.3 ps) of the twisted intramolecular charge transfer (TICT)-state transient at 330 nm is identical to the decay time of the $\pi\sigma^*$ -state transient. The 4.8 ns decay time of the TICT-state absorption of DMABN is longer than the 2.9 ns decay time of the intramolecular charge-transfer (ICT) fluorescence, indicating that the fluorescent ICT state differs from the TICT state observed in transient absorption. These results are consistent with the presence of a low-lying $\pi\sigma^*$ state in DMABN (and DMABE), and the role the $\pi\sigma^*$ state plays in the formation of the TICT state of DMABN.

Over the past several years, our laboratories have focused on the study of the role the low-lying $\pi\sigma^*$ state plays in the electronic spectra and excited-state dynamics of dimethylamino benzonitriles and benzethynes.¹ We have found that the strong quenching of fluorescence at higher excitation energies in gas phase² and at elevated temperature in non-polar solvents³ can be attributed to the crossing of the fluorescent $\pi\pi^*$ state and a dark $\pi\sigma^*$ state,¹ which arises from the promotion of an electron from the π -orbital of the phenyl ring to the σ^* -orbital localized in the $C\equiv X$ (where X is N or CH) group. In polar solvents, the $\pi\sigma^*$ state of 4-(dimethylamino)benzonitrile, DMABN, has been proposed^{4–6} to be the precursor of the

twisted intramolecular charge transfer (TICT) state,^{4–7} in which the positively charged dimethylamino group lies perpendicular to the negatively charged benzonitrile moiety.

There are several experimental and computational evidence for the presence of a low-lying $\pi\sigma^*$ state in DMABN and very closely related to 4-(dimethylamino)benzethyne, DMABE. First of these is the appearance of a strong transient absorption at about 700 nm, following subpicosecond excitation of the molecules into the L_a ($\pi\pi^*$) state at about 300 nm.^{6,8} The vertical TD/BP86/cc-pVDZ excitation energies, calculated at the optimized CIS geometries of the $\pi\pi^*$ and $\pi\sigma^*$ states, show that only one strongly-allowed (with an oscillator strength of about 0.6) excited state absorption of $\pi\sigma^* \leftarrow \pi\sigma^*$ type occurs at about 640 nm (DMABN),^{4–6} and 750 nm (DMABE).⁹ The $\pi\pi^* \leftarrow \pi\pi^*$ transitions of the lowest-energy $\pi\pi^*$ state (L_b or locally excited; LE state) to the higher-lying $\pi\pi^*$ states are predicted to occur at about 524 nm and 423 nm (in DMABN) with much smaller oscillator strengths.^{4–6} These predictions are in good accord with the experimental observations of a strong excited-state absorption at about 700 nm and weaker absorptions at about 525 and 450 nm.⁶ The different decay times of the 700 and 520 nm transient absorptions in DMABE⁹ prove that the electronic state responsible for the 700 nm absorption is definitely different from that responsible for the 520 nm absorption. Consistent with the assignment of the 700 nm transient to the $\pi\sigma^*$ state with a large dipole moment, the transient absorption (TA) blue-shifts significantly in polar solvent, acetonitrile (680 nm) relative to *n*-hexane (~ 725 nm).^{6,8} The 710 nm transient of DMABE in acetonitrile exhibits a time-dependent blue shift, whereas the 520 nm transient does not, for delay times between 0.2–8 ps.⁹ The peak intensity of the 700 nm transient relative to that of the 520 nm $\pi\pi^*$ transient in DMABE also increases in going from *n*-hexane to acetonitrile,^{6,9} consistent with the increased bifurcation of the initially excited $\pi\pi^*$ (L_a)-state into the highly polar $\pi\sigma^*$ state in polar solvents.^{6,9}

Consistent with the TICT model, the ICT-state absorptions of DMABN in acetonitrile at about 420 nm and 320 nm¹⁰ are essentially identical to the absorption spectrum of benzonitrile radical ion¹¹ in both peak positions and relative intensities.

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The ~ 4.3 ps rise time of the TICT-state absorption in acetonitrile at room temperature is the same as the decay time of the 700 nm absorption, indicating that the highly polar $\pi\sigma^*$ state is the precursor of the TICT state.^{6,7,12} The TICT state absorption at 330 nm decays in ~ 4.8 ns, which is significantly longer than the decay time (2.9 ns) of the ICT fluorescence at 490 nm.⁷ The rise time of the ICT fluorescence, ~ 3.1 ps (which is the same as the fast-component decay time of the LE fluorescence), also differs from that (~ 4.3 ps) of the TICT-state transient absorption (TA) at 420 nm.⁷ The disparity between the rise and decay times of the ICT fluorescence and those of the TICT-state TA suggest that the fluorescence ICT state differs from the TICT state observed in transient absorption.⁷ We have proposed that the fluorescent ICT state is formed from the LE state, whereas the dark TICT state is formed from the $\pi\sigma^*$ state. A very recent *ab initio* CASPT2//CASSCF quantum-chemical calculations assign the TA signal to the 90° twisted TICT state, and the ICT fluorescence to a partially twisted ($\sim 54.4^\circ$) intramolecular charge transfer (pTICT) state.¹²

The results and interpretations, summarized above, have recently been questioned by Zachariasse *et al.*,¹³ who assign the 700 nm transient of DMABN to the absorption spectrum of the LE state. As the main support, they provided the observation of ~ 700 nm $\pi\pi^* \leftarrow \pi\pi^*$ absorptions from 2,6-dimethyl-4X (X = F, Br, CF_3)-*N,N*-dimethylanilines that do not contain a low-lying $\pi\sigma^*$ state. More recently, Glavan *et al.*¹⁴ reported the CASPT2 calculations on the optimized $\pi\pi^*$ (LE) state of DMABN, which indicated the presence of 750 nm LE-state absorption band. This has led the authors to question the validity of assigning the 700 nm transient absorption to the $\pi\sigma^*$ state.

In this communication, we present the new measurement of subpicosecond excited-state absorptions for DMABN in acetonitrile. Combination of the new results with revisit of the picosecond and nanosecond temporal measurements strongly support the occurrence of the $\pi\sigma^*$ -mediated TICT reaction in DMABN and the proposal that the fluorescent ICT state differs from the TICT state observed in transient absorption.

The time-resolved excited-state absorption spectra were measured using a Ti:sapphire-based transient absorption setup described elsewhere.^{6,15} The wavelength-tunable pump pulse was generated by an optical parametric amplifier, which was pumped by an 800 nm of a Ti:sapphire regenerative amplifier. A weak fundamental beam of the 800 nm, traveling through a motorized delay stage, was focused onto a CaF_2 disk to generate a white light continuum (280–780 nm) as the probe pulse. The focusing pump and probe pulses then intersect the sample solution in a flow cell (1.0 mm). The time-resolved transient absorption (TA) spectra were obtained as a function of delay time between the subpicosecond pump-probe pulses (~ 300 fs time resolution), and finally mapped out in a fashion of 2D

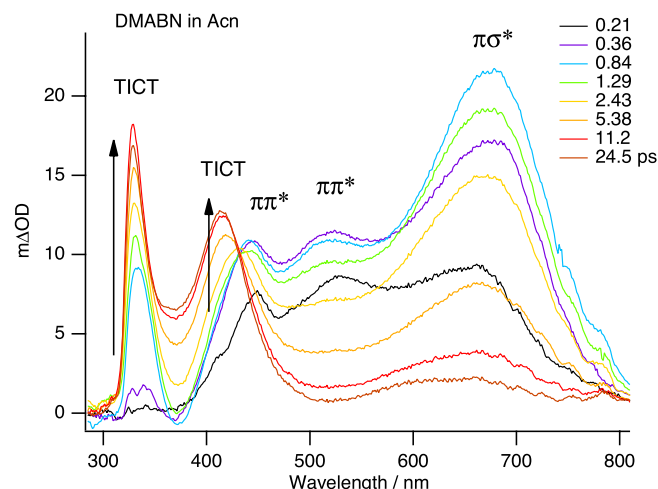


Figure 1 Femtosecond time-resolved excited-state absorption spectra of DMABN in acetonitrile at room temperature, following the excitation at 305 nm. Arrows indicate spectral time-evolutions and assignments of transients are shown as $\pi\pi^*$, $\pi\sigma^*$, and TICT. The wavy features near the red side are due to the interference of 800 nm to the white light continuum. The spectra were chirp-corrected by monitoring a solvent coherent signal, but its spectral response to the wavelength was not corrected.

data (spectra vs. delay times). Note that a linear motion of the sample flow cell was implemented with a crank mechanism to make its surface periodically changed during irradiation of the UV-pump beam. It helped to prevent photo-polymerized sample absorbing onto the inner cell surface, especially in *n*-hexane solution.

The picosecond time-resolved fluorescence spectrum (TRFS) was obtained in a similar setup to the time-resolved excited-state absorption spectra, but employed an optical Kerr-gating (OKG) to detect an emission with an ultrafast optical shutter (open duration: < 1 ps). The detailed TRFS experimental setup is described elsewhere.¹⁶ Temporal decay profiles at a specific fluorescence wavelength were extracted from the mapped TRFS as well as TA spectra, and analyzed by deconvolution procedures with nonlinear least-squares fit with an associated model function.

Fluorescence lifetime measurements for longer decay profiles were carried out by the time-correlated single-photon counting (TCSPC) as described previously.^{6,15} The steady-state UV absorption and fluorescence spectra were measured with a UV/VIS spectrophotometer (Shimadzu; UV-1800) and a spectrofluorometer (Horiba/Jobin Yvon; FluoroMax-4), respectively. DMABN (Aldrich) was used as received. DMABE was synthesized by the reaction of 4-dimethylaminobenzaldehyde with bromomethyl triphenylphosphonium bromide in tetrahydrofuran with excess potassium *t*-butoxide. Purification was performed with chromatography in silica, followed by distillation.

Table 1 The TDDFT/BP86/cc-pVDZ vertical excitation wavelengths and oscillator strengths (in parenthesis) of the excited-state absorptions in DMABN and DMABE.

Transition	DMABN	DMABE
$\pi\sigma^* \leftarrow \pi\sigma^*$	640 nm (0.52) ^a	750 nm (0.61) ^a
$\pi\pi^* \leftarrow \pi\pi^*$	524 nm (0.08) ^a	528 nm (0.15) ^a
$\pi\pi^* \leftarrow \pi\pi^*$	423 nm (0.11) ^a	476 nm (0.076) ^a

^a The average of coordinate and velocity gauges.

The time-dependent DFT (TDDFT) calculations of the excitation energies and oscillator strengths of the excited-state absorptions of the $\pi\pi^*$ and $\pi\sigma^*$ states were performed using TURBOMOLE suite of programs¹⁷ with B-P functional and cc-pVDZ basis set.

Figure 1 presents the time-resolved excited-state absorption spectra of DMABN in acetonitrile at room temperature, recorded with pump–probe time delay of 0.3–25 ps, following excitation of the molecule at 305 nm. The transient absorption (TA) spectra display features at about 680, 525, and 450 nm. It is evident that whereas the 680 nm transient is similar in intensity to that those of 525 and 450 nm at the delay time of 0.2 ps, the 680 nm band becomes much more intense than the shorter-wavelength bands at the pump–probe time delay of 0.8 ps. The rise and the decay times of 680 nm transient clearly differ from those of the shorter-wavelength transients. In *n*-hexane, the 680 nm band shifts to 750 nm, whereas the 525 and 450 nm bands remain essentially the same. Comparison of the observed band positions with the TD/BP86/cc-pVDZ vertical excitation energies in Table 1 indicates that the 680 nm TA can be assigned to the strongly allowed ($f \simeq 0.55$) $\pi\sigma^* \leftarrow \pi\sigma^*$ transition predicted at about 640 nm, and the 450 and 525 nm TA transients can be assigned to the $\pi\pi^* \leftarrow \pi\pi^*$ (LE) transitions which are expected at about 423 and 524 nm, respectively. These assignments are consistent with the differing solvent-polarity dependence of the spectral positions, and differing rise and decay times of the 680 nm transient as compared to those of the 450/525 nm bands (Fig. 1). In acetonitrile, the excited-state absorption spectra of DMABN reveal the presence of the TICT bands at about a 330 and 420 nm, which correspond to the absorption spectra of the ground state of benzonitrile radical anion.¹¹ As previously reported,^{6,7} the time scale of the formation of the TICT state is identical to the decay time of the $\pi\sigma^*$ -state, consistent with the occurrence of the $\pi\sigma^*$ -mediated ICT reaction in DMABN. It is interesting that the intensity of the $\pi\sigma^*$ -state transient at about 700 nm, relative to that of the $\pi\pi^*$ -state absorption, is significantly stronger in acetonitrile than in *n*-hexane. Moreover, the $\pi\sigma^*$ -state absorption is blue-shifted in acetonitrile, as compared to that in *n*-hexane.

Time-resolved fluorescence spectra (TRFS) of DMABN in acetonitrile at earlier times were recorded by using the OKG as shown in Fig. 2a. The time resolution of the system was es-

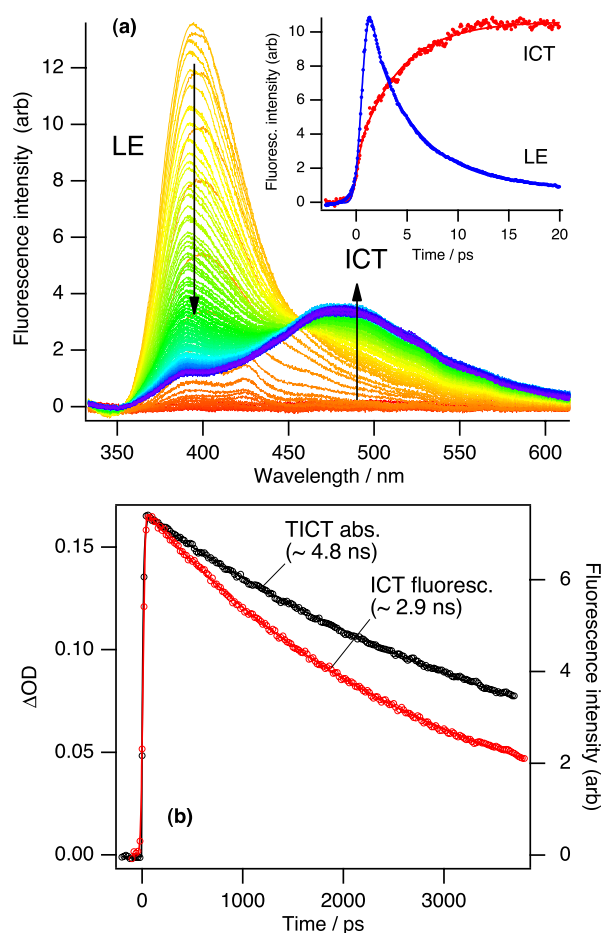


Figure 2 (a) Picosecond time-resolved fluorescence spectra of DMABN in acetonitrile at room temperature obtained with the optical Kerr-gating (OKG). Arrows indicate the time-evolution of the spectra in the short time range (-2 to 25 ps with an interval of 0.1 ps). Inset: Temporal profiles of LE and ICT fluorescence which were obtained with a band-integration of each time-resolved spectrum. (b) Comparison of the slow decay time (~ 4.8 ns) of the TICT-state absorption at 330 nm with the fluorescence lifetime (~ 2.9 ns) of the ICT emission at 490 nm (from the time-resolved fluorescence). The lifetime obtained for the ICT emission is consistent with that obtained with the TCSPC measurement.

timated to be ~ 600 fs (FWHM) from a solvent Raman signal when benzene was used as an OKG medium. The inset figure shows the temporal profiles for the LE and ICT fluorescences that were extracted from the TRFS with band-integrations. The rise time of the ICT band is identical to the decay time of LE band, indicating a precursor–successor relationship between the LE and the ICT states. The decay/rise constants (~ 3.7 ps) obtained by a global fit in the TRFS reasonably support the result (3.1 ps)⁷ from the higher time-resolved up-conversion measurements.

Figure 2b, on the other hand, compares the slow decay rate

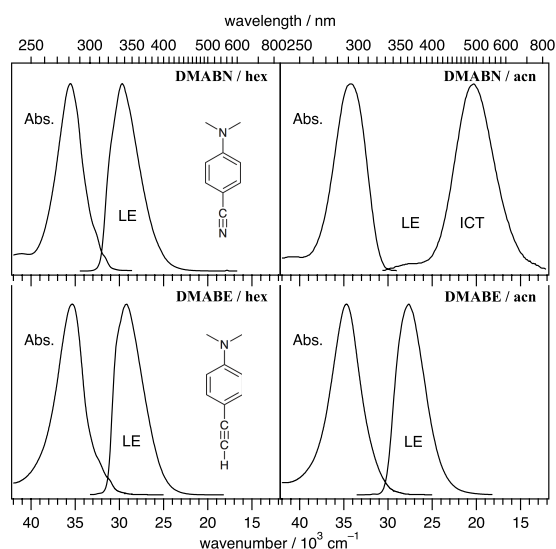


Figure 3 The steady-state absorption and fluorescence spectra of DMABN and DMABE in acetonitrile and *n*-hexane at room temperature.

of the ICT fluorescence with that of the TICT-state absorption at 330 nm for DMABN in acetonitrile. It is apparent that the decay time (~ 4.8 ns) of the TICT-state absorption is significantly longer than that of the decay time (~ 2.9 ns) of the ICT fluorescence. Similar discrepancies also exist between the rise time (~ 3.1 ps)⁷ of the ICT emission and that (~ 4.3 ps) of the TICT-state absorption. The differing temporal characteristics of the ICT fluorescence and those of the TICT-state absorption demonstrate that the two ICT states are different, as previously proposed.⁷ Temporal characteristics of DMABN in both acetonitrile and *n*-hexane using various time-resolved studies are summarized in Table 2.

4-(Dimethylamino)benzethyne (DMABE) is isoelectronic with DMABN, and the electronic structures and electronic spectra of the two compounds bear very close resemblance, as illustrated by the very similar steady-state absorption and fluorescence spectra (Fig. 3) of the two compounds in *n*-hexane. It is evident that fluorescence of DMABE in acetonitrile is also entirely from the lowerest-energy $\pi\pi^*$ state (LE state), consistent with the absence of the ICT reaction of the molecule even in the polar solvents⁹. Figure 4a presents the excited-state absorption spectra of DMABE in *n*-hexane and acetonitrile. As in the corresponding spectra for DMABN, the $\pi\sigma^*$ -state absorption at about 700 nm is more intense than the $\pi\pi^*$ -state absorption at about 520 nm in acetonitrile, whereas it is less intense than the $\pi\pi^*$ -state transient in *n*-hexane. Moreover, the peak position of the $\pi\sigma^*$ -state absorption is blue shifted in acetonitrile (~ 675 nm) as compared to *n*-hexane (~ 720 nm), whereas the band positions of the $\pi\pi^*$ -state absorption are essentially the same in the two solvents. The assignment of the 700 nm absorption to the $\pi\sigma^*$ state, and the 520 nm

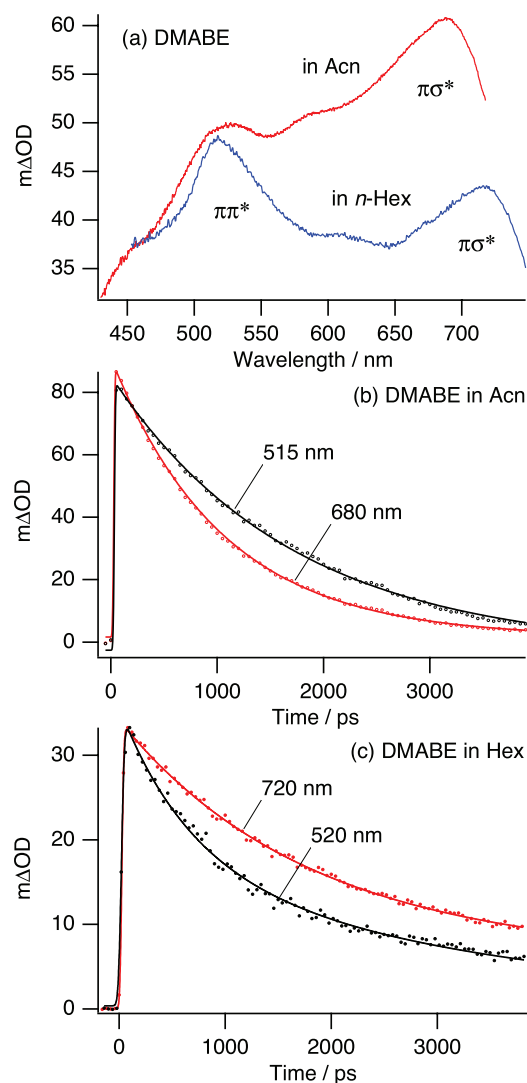


Figure 4 (a) The excited-state absorption spectra of DMABE in acetonitrile (Acn) and *n*-hexane (Hex) at room temperature, recorded with pump-probe delay of 0.6 ps, following 305 nm excitation. (b) The temporal profiles of 680 and 515 nm transient absorptions of DMABE in acetonitrile. (c) The temporal profiles of 720 and 520 nm transient absorptions of DMABE in Hex. The detailed decay constants obtained by a least-squares fit were listed in Table 2.

absorption to the $\pi\pi^*$ state, are supported by the TD/BP86/cc-pVDZ vertical excitation energies, which predict the presence of a highly allowed $\pi\sigma^* \leftarrow \pi\sigma^*$ transition at about 750 nm ($f \simeq 0.6$), an allowed $\pi\pi^* \leftarrow \pi\pi^*$ transition at about 528 nm ($f \simeq 0.15$), and a weak $\pi\pi^* \leftarrow \pi\pi^*$ transition at about 476 nm ($f = 0.076$), Table 1. Figures 4b and 4c compare the decay times of the 700 and 520 nm TA transients in acetonitrile and *n*-hexane. It is evidence that the decay times of the $\pi\sigma^*$ -state and the $\pi\pi^*$ -state transients are different in the two solvents. In acetonitrile, the decay time is shorter for the $\pi\sigma^*$

Table 2 Summary of the experimental results for photoexcited DMABN and DMABE in acetonitrile (Acn) and *n*-hexane (Hex) from various time-resolved spectroscopic measurements.

System	Transition ^a	λ^b (nm)	τ_1 (ps)	τ_2 (ns)
DMABN/Acn	ICT \leftarrow ICT	330	4.3 (rise) ^c	$\sim 4.8^c$
	$\pi\sigma^*\leftarrow\pi\sigma^*$	680	4.3 ^c	
	ICT \rightarrow S ₀	485	3.1 (rise) ^d	$\sim 2.9^e$
	LE \rightarrow S ₀	350	3.1 ^d	2.92(1) ^f $\sim 2.7^e$ 2.55(1) ^f
DMABN/Hex	$\pi\pi^*\leftarrow\pi\pi^*$	450		$\sim 2.1(4)^c$
	$\pi\sigma^*\leftarrow\pi\sigma^*$	700		$\sim 3.2(3)^c$
	LE \rightarrow S ₀	320		2.39(4) ^f
DMABE/Acn	$\pi\sigma^*\leftarrow\pi\sigma^*$	675		1.09(1) ^c
	$\pi\pi^*\leftarrow\pi\pi^*$	575		1.76(2) ^c
	$\pi\pi^*\leftarrow\pi\pi^*$	510		1.74(2) ^c
	LE \rightarrow S ₀	365		1.33(4) ^c
DMABE/Hex	$\pi\sigma^*\leftarrow\pi\sigma^*$	720		2.58(4) ^c
	$\pi\pi^*\leftarrow\pi\pi^*$	520		1.55(5) ^c
	LE \rightarrow S ₀	345		2.85(2) ^c

^aExcited-state absorption (left arrow) and excited-state emission (right arrow). ^bAbsorption/emission band center wavelength. ^cFemtosecond Time-resolved transient absorption (refs. 6,7). ^dFemtosecond fluorescence upconversion (ref. 7). ^ePicosecond time-resolved fluorescence with OKG. ^fTime-correlated single-photon counting. The suffix number in the parentheses indicates a standard deviation (1 σ).

transient than for the $\pi\pi^*$ transient, whereas the opposite is the case in *n*-hexane. The differing decay times of the 700 and 520 nm transients prove that the electronic state responsible for the 700 nm absorption is different from that responsible for the 520 nm absorption, consistent with the assignment of the 700 nm transient to the $\pi\sigma^*$ state, and the 520 nm transient to the $\pi\pi^*$ state. We have proposed that the absence of the TICT state in DMABE supports the $\pi\sigma^*$ -mediated TICT model, as the TICT state of the molecule lie above the $\pi\sigma^*$ state, whereas the opposite is the case in DMABN.⁹ Figure 5 illustrates a schematic energy diagram of DMABN (in acetonitrile) for the proposed $\pi\sigma^*$ -mediated ICT reaction mechanism.

In summary, the differing temporal characteristics and differing solvent-polarity dependence of the 700 and 520 nm transient absorptions in DMABN and DMABE, provide a definitive support to the conclusion that these two transients are electronic absorption spectra of different excited states. Comparison of the positions and relative intensities of these transients with the TD/BP86/cc-pVDZ vertical excitation energies of the $\pi\sigma^*$ state and $\pi\pi^*$ state demonstrate that the 700 nm band is the absorption spectrum of the $\pi\sigma^*$ state and the 520 nm band is the absorption spectrum of the $\pi\pi^*$ (LE) state. In acetonitrile, the TICT-state absorption spectra of DMABN rises at the same time scale (4.3 ps) as the decay time of

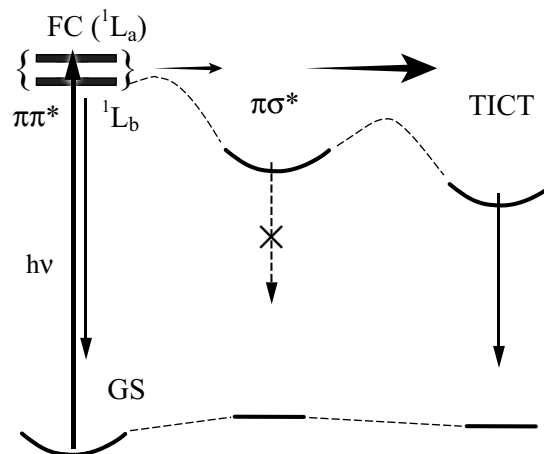


Figure 5 Schematic energy level diagram for the $\pi\sigma^*$ -mediated intramolecular charge transfer of DMABN in polar solvents. Comparison of the excited-state absorption spectra and their temporal characteristics show that the TICT state of DMABN is accessible via the $\pi\sigma^*$ state, whereas the TICT state of DMABE is not energetically reachable from the $\pi\sigma^*$ state even in a polar environment. The $\pi\sigma^*$ state is a dark state (non-emissive) and the final-relaxing excited singlet state of DMABE.

the $\pi\sigma^*$ -state absorption. The rise and the decay time of the TICT-state absorption are different from those of the ICT fluorescence for DMABN in acetonitrile, indicating that the ICT fluorescence and the TICT-state transient absorption originate from different excited states. These results corroborate the presence of a low-lying $\pi\sigma^*$ state in DMABN and DMABE, and the role it plays in the formation of the TICT state for DMABN in polar solvents.

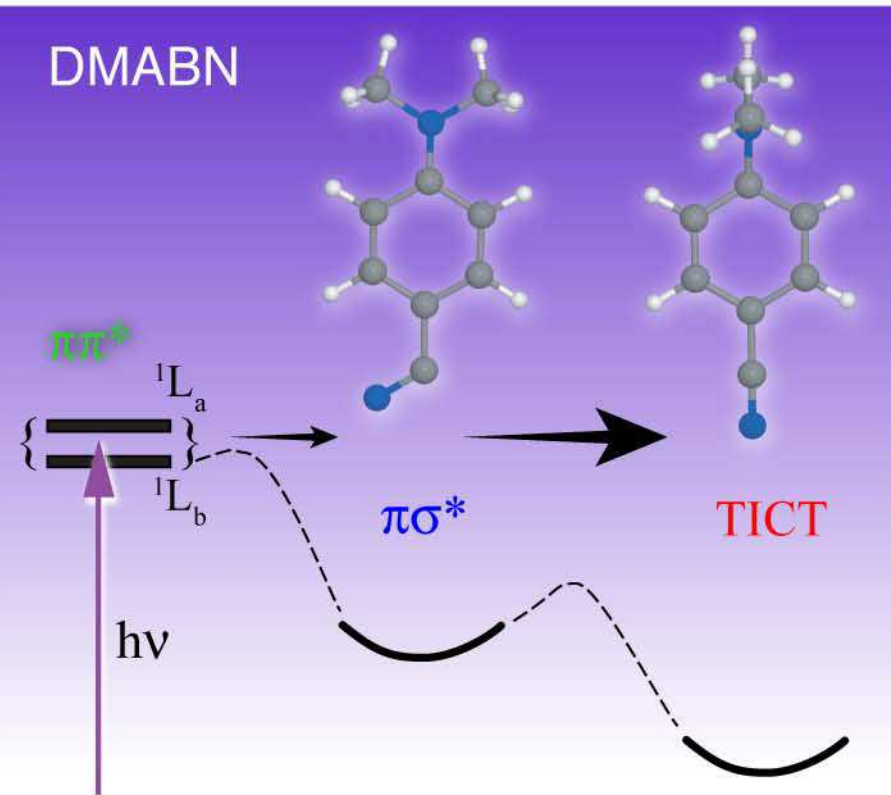
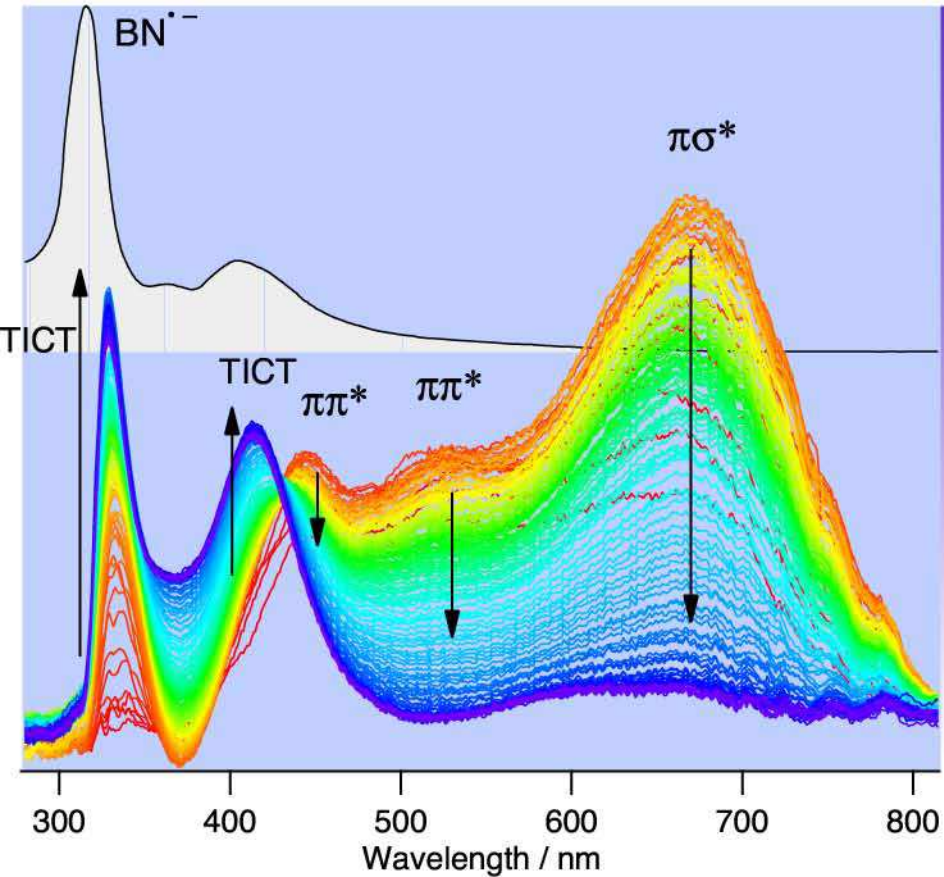
Acknowledgment

We are very grateful to Professor Carlos E. Crespo-Hernández of the Case Western Reserve University for allowing us to use his ultrafast transient absorption setup for a comparative study, and to Dr. Christian Reichardt and Mr. R. Aaron Vogt for the technical guidance and assistance.

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The time-resolved spectroscopic studies demonstrate that the intramolecular charge-transfer reaction in 4-(dimethylamino)benzonitrile occurs through a $\pi\sigma^*$ state.