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Journal of Photochemistry and Photobiology A: Chemistry 121 (1999) 7–15

Journal of Photochemistry and Photobiology A:Chemistry

Numerical self-consistent reaction field study of the excited-state properties of *p*-(dimethylamino)-benzonitrile derivatives

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Received 3 August 1998; received in revised form 2 September 1998; accepted 23 October 1998

Abstract

Since the first observation of the dual fluorescence of *p*-(dimethylamino)-benzonitrile (*p*-DMABN) by Lippert et al. [E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge, I.Seilbold-Blankenstein, Angew. Chem. 21, (1961) 695], many theories were proposed to explain this interesting behaviour. So far, the model proposed by Rotkiewicz in 1973 [K. Rotkiewicz, K.L. Grellman, Z.R. Grabowski, Chem. Phys. Lett. 19, (1973) 315] has gained the widest acceptance, despite doubts being expressed about its validity. Zachariasse et al. [K.A. Zachariasse, Th. von der Haar, A. Hebecker, U. Leinhos, W. Kühnle, Pure. Appl. Chem. 65, (1993) 1745 ; K.A. Zachariasse, Th. von der Haar, U. Leinhos and W. Kühnle, J. Inf. Rec. Mats. 21, (1994) 501] base their critique, beside other experimental observations, on the lack of dual fluorescence in two groups of *p*-DMABN derivatives. One comprises the methyl substituted isomers *p*-(amino)-benzonitrile (*p*-ABN) and *p*-(methylamino)-benzonitrile (*p*-MABN), the other the cyano substituted isomers *m*-(dimethylamino)-benzonitrile (*m*-DMABN) and 3,5-dicyanodimethylaniline (DCDMA). Although these derivatives are structurally not too different from *p*-DMABN, it is not obvious whether the similarity is large enough to provide evidence for the invalidity of the TICT model in the parent compound. In this contribution, therefore, we will present the results of a semi-empirical study using a numerical self-consistent reaction field model to describe the solvent influence on the excited state properties of the above mentioned derivatives. As will be demonstrated, the non-existent anomalous fluorescence can be rationalized by the changed electronic properties of the different compounds. The different photophysical behaviour of the *p*-DMABN derivatives alone cannot be used to doubt the validity of the TICT model in case of *p*-DMABN. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photoinduced electron transfer; TICT; *p*-DMABN; Solvation effects; Self-consistent reaction field; SCRF; *p*-DMABN derivatives; Dual fluorescence

1. Introduction

Lippert et al. [1,6] observed in 1961 that the fluorescence spectra of *p*-(dimethylamino)-benzonitrile(*p*-DMABN, see Scheme 1) show a remarkable dependence on solvent polarity. Only one emission band is found in nonpolar solvents. With increasing solvent polarity, the intensity of this so-called normal fluorescence band is reduced. At the same time, a second, more red shifted fluorescence band appears whose intensity increases with increasing solvent polarity. In addition, this second band, which is named anomalous fluorescence, shows a very large bathochromic solvent shift.

In the following years, a variety of models [1–18] were proposed to explain this dual fluorescence. Nowadays, the twisted intramolecular charge transfer state (TICT) model [7–10] is the most widely accepted one. According to it, the dimethylamino group is twisted by 90° in the anomalous fluorescing state. At the same time, an electron is transferred from the amino group to the π-system of the cyano benzene fragment, thereby forming the TICT state. Due to the large polarity of this intramolecular charge transfer state, it is energetically more stabilised in polar solvents than the nontwisted, normal fluorescing state.

In a first approximation, the energy of a TICT state (E_{TICT}) can be expressed by the following equation [19]

$$E_{\mathrm{TICT}} = \mathrm{IP_D} - \mathrm{EA_A} + C + E_{\mathrm{solv}} \quad (1)$$

Here, $\mathrm{IP_D}$ is the ionization potential of the donor, $\mathrm{EA_A}$ the electron affinity of the acceptor, and C the coulombic interaction between donor cation and acceptor anion. The change of the solvation energy in the charge separated state

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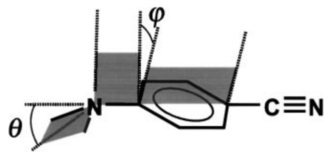
PII: S1010-6030(98)00440-7



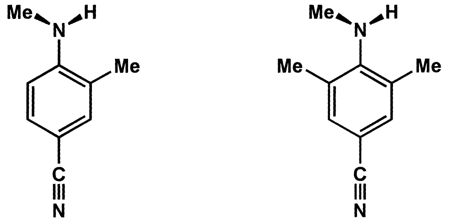
Scheme 1. Definition of torsional angle φ and pyramidalisation angle θ for *p*-(dimethylamino)-benzonitrile (*p*-DMABN) and derivatives.

is E_{solv}. It is therefore possible to change the energy of the TICT state by varying the ionization potential of the donor or the electron affinity of the acceptor. This idea was the starting point of a series of studies in which the cyano group of *p*-DMABN was substituted by e.g. an aldehyde, a keto, or a carboxyl group [8]. The second approach was carried out by substitution of the methyl(s) of the amino group with one or two hydrogens [15,20]. The ionization potential of the amino group and therefore the energy of the TICT state should decrease in the order *p*-DMABN < *p*-MABN < *p*-ABN [2]. As a consequence, TICT state formation should be less likely in *p*-MABN and *p*-ABN (structures see Scheme 2) and indeed, anomalous fluorescence is not observed for *p*-MABN and *p*-ABN. In contrast to this, the *ortho* methylated methylaminobenzonitriles (2-MMABN and 2,5-DMMABN) show dual fluorescence, whereas the corresponding *ortho* methylated aminobenzonitriles do not [15,20].

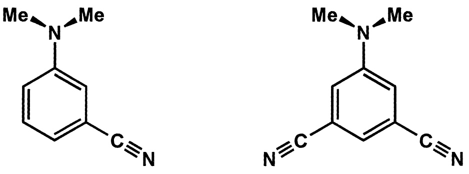
Even though these experimental facts are clear, their interpretation is still subject to controversial discussions. Rotkiewicz and Rettig [20] based their explanation on the TICT model. They suggested that, although TICT state formation is energetically feasible for *p*-MABN, the activation energy for this process is too large and therefore the torsion kinetically hindered. On *ortho* methyl substition, the steric interaction between the amino group and the aromatic system increases in the planar conformation. This reduces the activation energy and consequently the TICT state formation is enabled.

An alternative explanation was given by Zachariasse et al. [15]. They looked for similarities in the experimental data of a variety of *p*-DMABN derivatives and found that anomalous fluorescence is only observed if the two lowest absorption bands ($S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$) overlap. The absorption spectra of the methyl substituted isomers, *p*-ABN, *p*-MABN, and *p*-DMABN are in accordance with this postulate. In the model of Zachariasse et al. (solvent induced Jahn–Teller distortion), the energy difference between the nonpolar ^1L_b and the polar ^1L_a states represents the important factor. If in the relaxed conformation, the energies of these states would become equal in zero order, a vibrationally induced coupling between the two states causes a splitting of the degenerate energy levels and thereby a considerable energetical stabilisation of one state. Emission from the state of lower energy so created should be strongly red shifted and give rise to the anomalous fluorescence.

(a) *p*-ABN (b) *p*-MABN



(c) 2-MMABN (d) 2,5-DMMABN



(e) *m*-DMABN (f) DCDMA

Scheme 2. Abbreviations and structures of the compounds referenced in the text.

Another class of *p*-DMABN derivatives to which this model seems to apply are the cyano substituted isomers, *m*-(dimethylamino)-benzonitrile (*m*-DMABN) and 3,5-dicyanodimethylaniline (DCDMA). In both cases, the absorption bands are separated and no dual fluorescence was found. Considering Eq. (1) one would expect a different behaviour at least for DCDMA. The ionization potential $\mathrm{IP_D}$ of the donor should stay constant, the coulomb interaction C and the solvent stabilisation E_{solv} should not change too much. This should also be true for the electron affinity $\mathrm{EA_A}$ of the cyano benzene fragment in *p*- and *m*-DMABN. Therefore, one would expect similar energetic properties of the two compounds and thus dual fluorescence for *m*-DMABN. The latter expectation should be even more true for DCDMA. Here, the larger electron affinity of the two cyano substituents should lead to a greater stabilisation of the TICT state. Zachariasse et al. concluded that the fact that anomalous fluorescence is not observed for *m*-DMABN and DCDMA should be used as evidence against the validity of the TICT model. More so, TICT state formation cannot be the reason for dual fluorescence in *p*-DMABN. On the contrary, these compounds support the above-mentioned model of a solvent induced pseudo Jahn–Teller distortion.

Rettig [10] contradicted this argumentation and pointed out that the coulombic interaction, which stabilizes the TICT

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[2] Compare the ionization potentials of the following amines $\mathrm{MeNMe_2}$ (7.11 eV) < MeNMeH (7.85 eV) < $\mathrm{MeNH_2}$ (8.76 eV) [33]

state, is smaller in *m*-DMABN than in *p*-DMABN. He argued that for the electron accepting orbital the coefficient of the carbon to which the dimethylamino group is connected is smaller and, therefore, so is the coulombic interaction. This qualitative and rather crude explanation might be correct, but a thorough, more quantitative discussion is necessary to clarify this dispute. Moreover, DCDMA also needs to be discussed. In this case, the acceptor strength of the aromatic system is larger than in *p*-DMABN. Also, due to the different symmetry of the compound with respect to *m*-DMABN, the argument of Rettig might not be appropriate for DCDMA.

In this contribution, we will present the results obtained with the numerical self-consistent reaction field (SCRF) method [21] described previously [22–24] concerning the solvent dependence of the excited state properties of the four compounds, *p*-ABN, *p*-MABN, *m*-DMABN and DCDMA and compare them with those published previously.

Even though there is a multitude of theoretical studies of *p*-DMABN, for example the DFT/SCI calculations by Parusel et al. [25] and the CASPT2 calculations by Domcke and Sobolewski [26], theoretical studies of the *p*-DMABN derivatives are scarce. Rettig and Bonačić-Koutecký [27] determined the stability of the TICT state of *p*-DMABN and *p*-ABN using CNDO/S-CI calculations. Serrano-Andres et al. [28] compared *p*-DMABN and *p*-ABN using (CAS)SCF ab initio calculations with CASPT2 pertubation theory. Both studies are in favour of the TICT model, but do not take the solvent effect into account. In a more recently published work [29], this was done on the basis of AM1-CI calculations using the simple Onsager model [30]. We already discussed in a previous study [24] that such an approach largely overestimates the solvent stabilisation of the TICT state. To our knowledge, theoretical studies of the other compounds have not yet been carried out.

2. Computational method

For all calculations, we used the standard AM1 method [31] as implemented in the semiempirical molecular orbital package VAMP [32]. Under the assumption of a planar dimethylamino group ($\theta = 0°$, see Scheme 1), a couple of fully optimised ground state geometries of the compounds were created for various torsional angles φ between 0° and 90° (in 5° steps). As we have already shown in the previous study of *p*-DMABN, the assumption of a planar dimethylamino group is necessary for a proper description of the excited states.

For each conformer, excited state energies and dipole moments were determined with a CISD calculation taking into account all single and double excitations between five highest occupied and five lowest unoccupied orbitals. For *p*-ABN, we used four occupied and four unoccupied orbitals. The size of the CI calculations was chosen so that the same orbitals were used along the torsional coordinate.

To calculate the solvent influence on excited state properties and absorption energies, the previously described numerical SCRF method [22–24] was used. These SCRF calculations were carried out for the solvents: hexane, diethylether, methylene chloride, and acetonitrile. This way, a large range of the dielectric constant ϵ from 1.9 to 36 was covered.

3. Results and discussion

3.1. The influence of methyl substitution (p-ABN and p-MABN)

First, we look at the excited state properties in vacuo. Fig. 1 displays the variation of the excited state energies as a function of the torsional angle φ. To simplify the following

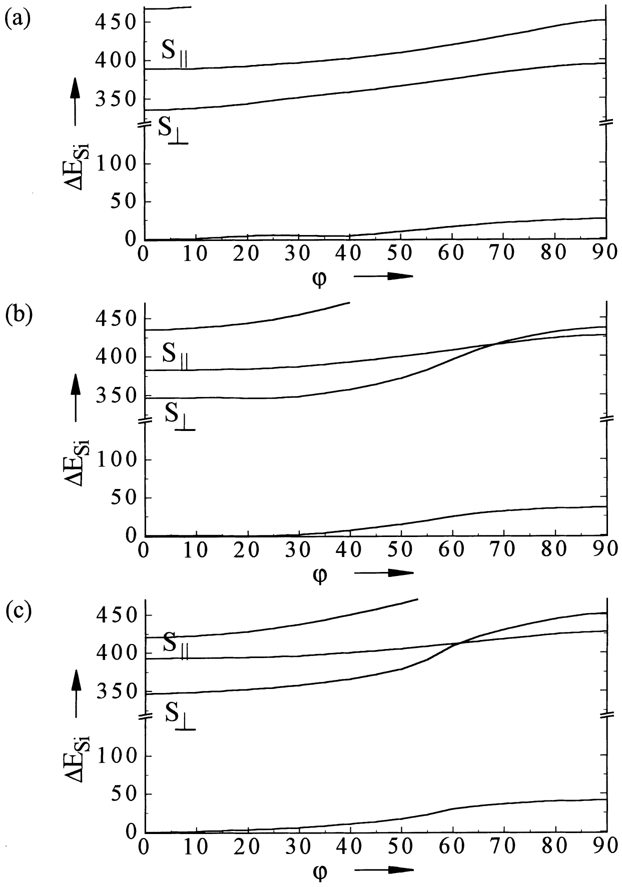


Fig. 1. Calulated excited state energies of (a) *p*-ABN, (b) *p*-MABN, and (c) *p*-DMABN in vacuo dependent on the torsional angle φ. The energy differences ΔE_{S_i} (given in kJ/mol) are calculated with respect to the minima of the corresponding ground state. The figure include the energies of the S_0, $S_{\|}$, $S_{\perp}$ and S_3 states. The third excited singlet state is a locally excited state that does not play a role in the photophysical behaviour of the compounds. (AM1CISD calculation using 8 (*p*-ABN) or 10 orbitals (*p*-MABN and *p*-DMABN); the amino group was kept planar).

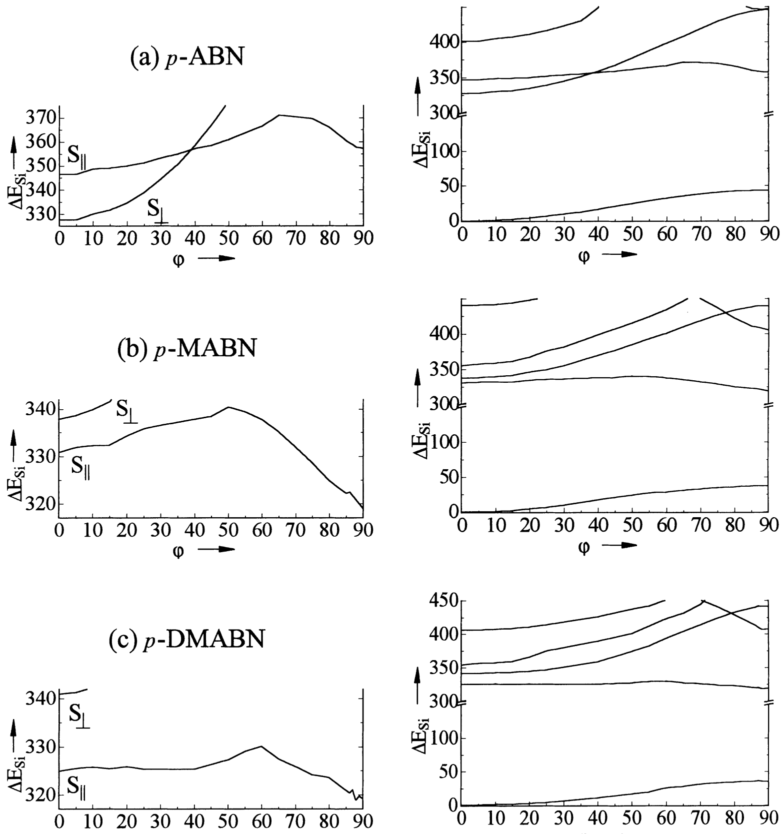


Fig. 2. Calculated excited state energies of p-ABN, p-MABN, and p-DMABN in CH_3CN as a function of the torsional angle φ. The energy differences ΔE_{S_i} to the minima of the corresponding ground state are given in kJ/mol. The photophysically interesting region is drawn enlarged on the left side. The deviation of the curves from a smooth line gives an impression of the numerical inaccuracies of the used method. (AM1-SCRF-CISD calculation using 8 (p-ABN) or 10 orbitals (p-MABN and p-DMABN); the amino group was kept planar).

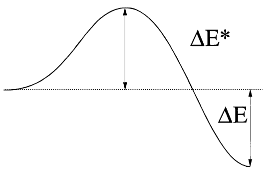
discussion, we will enumerate the excited states in the order as found at $\varphi = 0°$.

For each compound, the polarization of the $S_\perp \leftarrow S_0$ transition is perpendicular to the long molecular axis (determined by the C–N bond) and that of the $S_\parallel \leftarrow S_0$ transition parallel to it. Thus, the $S_\perp$ state has the character of the ^1L_b state, the $S_\parallel$ state that of the ^1L_a state. At $\varphi = 90°$, the $S_\perp$ state turns into a locally excited state and the $S_\parallel$ state becomes a TICT state. Comparing the different curves in Fig. 1, one finds that the non-methylated p-ABN behaves drastically different from the methylated compounds. While in p-MABN and p-DMABN the $S_\perp$ and $S_\parallel$ energy curves cross, such a crossing is not found for p-ABN. It is also interesting to note the change of the torsional barrier in the $S_\parallel$(^1L_a-TICT) potential energy curve. It decreases from 62 kJ/mol in p-ABN to 44 kJ/mol in p-MABN and 34 kJ/mol in p-DMABN. This reduction can be easily explained by the stabilisation of the positive charge on the nitrogen

Table 1
Dependence of ΔE^* and ΔE on solvent polarity for the compounds p-ABN, p-MABN and p-DMABN

Solvent	p-ABN		p-MABN		p-DMABN	
	ΔE^* (kJ/mol)	ΔE (kJ/mol)	ΔE^* (kJ/mol)	ΔE (kJ/mol)	ΔE^* (kJ/mol)	ΔE (kJ/mol)
Vacuum	–	58/115	–	81	–	75
Hexane	73	72	30	29	–	21
Diethylether	61	52	15.8	6.2	5.9	1.1
CH_2Cl_2	49	37	10.9	−7.4	6.4	−0.5
CH_3CN	43	30	9.6	−12	5.1	−6.1

ΔE^* is the activation energy for the rotation of the amino group from the planar to the twisted conformation in the excited state.
ΔE is the reaction energy for this process.
Result of AM1-SCRF-CISD calculations using 8 (p-ABN) or 10 orbitals (p-MABN and p-DMABN). The amino group is kept planar.



Scheme 3. Reaction scheme for the TICT state formation. ΔE^* is the activation energy for the rotation of the amino group from the planar to the twisted conformation in the excited state. ΔE is the reaction energy for this process.

in the TICT state by the methyl group. In contrast, the torsional barrier of the $S_\perp$ state increases from 58 kJ/mol (*p*-ABN) to 91 kJ/mol (*p*-MABN) and 105 kJ/mol (*p*-DMABN).

Upon solvation, the energetic relations are considerably changed for all three compounds. As an example, Fig. 2 shows the calculated potential energy curves in the very polar acetonitrile. Table 1 summarizes the results that reflect the energetic properties in the excited state (see Scheme 3) for various solvents.

The non-methylated compound *p*-ABN is unable to form a TICT state independent of the polarity of the solvent. Even in the polar solvent acetonitrile, the energy difference between the planar and the twisted conformer is ≈30 kJ/mol. This is in accordance with the experimental result that anomalous fluorescence is not observed for *p*-ABN. In contrast, Soujanya et al. calculated a stabilisation of the TICT state relative to the lowest singlet state in the planar conformation of almost 90 kJ/mol. This means that TICT state formation is thermodynamically feasible. The fact that anomalous fluorescence is not observed is explained by them with the calculated torsional barrier of ≈40 kJ/mol. But as we already showed in a recent publication [24], their calculation largely overestimates the stabilisation of the TICT state and must be treated with caution.

For *p*-MABN, TICT state formation becomes thermodynamically possible in polar and very polar solvents. But even in CH_3CN, the activation energy of ≈10 kJ/mol is almost twice as large as the reaction barrier of TICT state formation in *p*-DMABN (≈5 kJ/mol). Although TICT state formation is thermodynamically possible in polar solvents, the reaction barrier is too large to allow the reaction to take place on a reasonable time scale (lifetime of the planar $S_\parallel$ state). Therefore, anomalous fluorescence should, in accordance with experimental fact, not be observed in any solvent. An extensive comparison of the experimental and theoretical results for *p*-DMABN can be found in a previous publication and will therefore not be repeated here [24].

It should be mentioned, in addition, that the *ortho* methylated compounds 2-MMABN and 2,5-DMMABN exhibit anomalous fluorescence. We have not carried out calculations for these two compounds, but only for *ortho* methylated *p*-DMABN derivatives [23]. The steric interaction between the substituted amino group and the additional methyl group destabilises the planar conformation. This reduces the activation energy for rotation of the amino group into the perpendicular conformation considerably. Thus, rotation can occur efficiently.

To discuss the model of Zachariasse et al. [15], it is necessary to look at the calculated absorption energies of the planar conformation. These are summarised and compared to experimental data in Table 2. The calculated energies are approximately 7000 cm^{-1} too low, but the experimentally observed solvent shifts are reproduced very good. A discussion of this can be found in [24].

The transition energy of the perpendicularly polarized, weak, long wavelength absorption is almost independent of the solvent. The second, intense and structureless absorption

Table 2
Comparison of experimental and calculated excitation energies of the compounds *p*-ABN, *p*-MABN and *p*-DMABN in different solvents

		Calculated		Experimental	
		$S_\perp$ (^1L_b) (cm^{-1})	$S_\parallel$ $S\|\|(^1L_a)(cm^{-1})$	$S_\perp$ (^1L_b) (cm^{-1})	$S_\parallel$ ^1L_a) (cm^{-1})
p-ABN	Hexane	27 540	30 710	33 330 (sh)	38 460
	Diethylether	27 540	30 020	33 330 (sh)	37 170
	CH_2Cl_2	27 480	29 470	–	–
	MeOH	27 700	29 160	–	–
p-MABN	Hexane	28 490	29 750	32 260 (sh)	36 800[a]
	Diethylether	28 500	28 980	32 260 (sh)	36 100
	CH_2Cl_2	28 450	28 330	–	–
	MeOH	28 750	28 120	–	35 500[a]
p-DMABN	Hexane	28 840	29 330	32 260 (sh)	35 710
	Diethylether	28 780	28 580	n.b.	35 210
	CH_2Cl_2	28 730	27 910	–	–
	MeOH	29 050	27 690	–	34 000[a]

The AM1-SCRF-CI calcultions used 8 (*p*-ABN) or 10 orbitals (*p*-MABN and *p*-DMABN).
The experimental data were taken from Zachariasse et al. [15] and Rotkiewicz and Retting [20].
[a] Data taken from [20].

band shows a strong bathochromic shift on changing from nonpolar to polar solvents. Zachariasse et al. determined shifts of 500–1300 cm^{-1} between hexane and diethylether. The shifts calculated for the three compounds are 690–770 cm^{-1}. Between hexane and methanol, a solvatochromic shift of $\approx$1700 cm^{-1} is observed experimentally whereas the calculation predicts $\approx$1600 cm^{-1}.

For *p*-DMABN in heptane, the $S_\perp$ absorption is observable as a weak shoulder of the intense $S_\parallel$ bands. In diethylether and more polar solvents, the $S_\parallel$ band is so much red shifted that the two bands overlap, the $S_\perp$ absorption can not be observed. For *p*-ABN the $S_\perp$ band is clearly separated from the $S_\parallel$ band in diethylether. In the case of *p*-MABN, the $S_\perp$ band is weak in diethylether.

The SCRF-CI calculation predicts a separation of the $S_\perp$ and $S_\parallel$ absorption bands of 500 cm^{-1} for *p*-DMABN in hexane. In diethylether, the excitation energy to the $S_\parallel$ state is already 200 cm^{-1} lower than to the $S_\perp$ state. For the monomethylated *p*-MABN the energy of the $S_\parallel \leftarrow S_0$ transition is still 400 cm^{-1} larger than for the $S_\perp \leftarrow S_0$ transition. In more polar solvents, both bands will overlap. In case of the non-methylated compound (*p*-ABN), the absorption bands should be clearly separated in all solvents. The $S_\perp$ state is always below the $S_\parallel$ state.

The presented results are in accordance with the experimental observation that the overlap of the two absorption bands and the observation of anomal fluorescence usually coincide. But in contrast to the argumentation of Zachariasse et al. [15], the theoretical results suggest an explanation that is in agreement with the TICT model. To observe anomalous fluorescence, two requirements must be fullfilled. First, the energy of the TICT state must be lower than the energy of the polar $S_\parallel$ state in the planar conformation. This requirement is not fullfilled by *p*-ABN. Second, the energy of the planar, perpendiularly polarized state $S_\perp$ must also be higher than the TICT state energy. The latter requirement is fullfilled if $S_\perp$ lies above $S_\parallel$ in the planar state, because $S_\perp$ is destabilised with rotation of the amino group. If $S_\perp$ lies below $S_\parallel$ in the planar state, the energy difference must be small for the $S_\perp$ state to be nearly isoenergetic with the TICT state, since the energetic stabilisation of the TICT state relative to $S_\parallel$ is fairly small (<15 kJ/mol) even in polar solvents.

The second condition stated above shows up in the overlap of the two lowest absorption bands. If they are clearly separated, TICT state formation must be endothermic. But if they overlap, the polar $S_\parallel$ state has an energy equal or lower than the $S_\perp$ state. TICT state formation is then only determined by the energetic properties (activation energy) of the $S_\parallel$ state along the torsional coordinate.

3.2. The influence of cyano substitution (m-DMABN and DCDMA)

Table 3
Selected calculated ground state properties of the compounds DMA, *p*-DMABN, *m*-DMABN, and DCDMA

Compound	ΔE_{HF} (0° → 90°) (kJ/mol)	Pyramidalisation θ	
		$\varphi = 0°$	$\varphi = 90°$
DMA	5.5	30.7	44.9
m-DMABN	5.7	29.6	45.0
DCDMA	6.8	27.9	44.8
p-DMABN	10.5	25.3	44.7

In Table 3, the torsional barrier in the electronic ground state of the compounds dimethylaniline (DMA), *m*-DMABN DCDMA and *p*-DMABN are compared. As can be seen, the height of the barrier of both *meta* substituted compounds is comparable to that of the unsubstituted DMA. The higher barrier in *p*-DMABN reflects the electron withdrawing effect of the cyano group in *para* position. Looking in more detail, one finds that the *meta* substituted *m*-DMABN and even more so DCDMA show an increase of the rotation barrier. As another effect of the increased interaction of the aromatic system with the amino group, the amino group becomes more planar. The pyramidalisation angle θ is reduced from 30.7° in DMA to 29.6° in *m*-DMABN to 27.9° in DCDMA, and 25.3° in *p*-DMABN. It is also reflected in the decreased energies for planarization of the amino group (DMA: 5.5 kJ/mol *m*-DMABN: 1.9 kJ/mol, DCDMA: 1.4 kJ/mol, *p*-DMABN: 1.1 kJ/mol). For the twisted conformation ($\varphi = 90°$), the pyramidalisation angle is practically independent of the substituents, a fact which shows that the interaction between the dimethyl amino group and the aromatic system is switched off in this conformation.

The above considerations show that the position of the cyano substituents influences the electronic structure only in the planar, but not in the twisted conformation. Furthermore, we see that the torsion from the planar to the twisted conformation is even made easier for the *meta* substituted compounds in the ground state.

Next, we will discuss the excited state properties (see Table 4). We can classify the excited states in the *meta* substituted compounds similar those in *p*-DMABN. For the planar conformation, two locally excited states are found, one polarized parallel ($S_\parallel$) and the other polarized perpendicular ($S_\perp$) relative to the $\mathrm{C{-}N_{amino}}$ bond. This is not

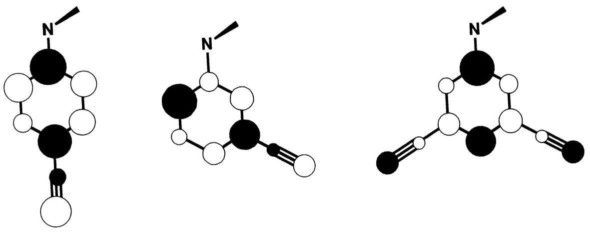
Table 4
Calculated excited state properties for the two lowest excited singlet states of *p*-DMABN, *m*-DMABN, and DCDMA in vacuo

State		*p*-DMABN	*m*-DMABN	DCDMA
$S_\perp \leftarrow S_0$	ΔE (kJ/mol)	340	345	325
	$\Delta\mu$ ($\times 10^{-30}$cm)	4.5	9	9.5
$S_\parallel \leftarrow S_0$	ΔE (kJ/mol)	380	400	390
	$\Delta\mu$ ($\times 10^{-30}$cm)	15	11	14
$\mathrm{TICT} \leftarrow S_0$	ΔE (kJ/mol)	420	425	405
	$\Delta\mu$ ($\times 10^{-30}$cm)	35	34	37

precisely exact for *m*-DMABN, but looking at the CI wavefunctions of these two states, one can identify similar one-electron transitions as found for *p*-DNABN and DCDMA. For the sake of clarity and simplicity, we use the same nomenclature for the excited states of *m*-DMABN as for *p*-DMABN. The energy differences of these states relative to the ground state are comparable. But their dipole moments differ considerably and this is important for the magnitude of the solvent effect. As we have obtained in the case of *p*-DMABN, the CI calculation of the compounds in vacuo give low lying TICT states for the twisted conformation ($\varphi = 90°$).

It is interesting to compare the excited state properties of the three compounds. First, we look at *p*-DMABN and *m*-DMABN. The $S_{\|}$ state of *p*-DMABN is more stabilised than the $S_{\|}$ state of *m*-DMABN due to the stronger influence of the cyano group on this state. The $S_{\perp}$ states of the two compounds are energetically almost equivalent. In consequence, the energy difference between $S_{\|}$ and the $S_{\perp}$ states is in *p*-DMABN (40 kJ/mol) smaller than in *m*-DMABN (55 kJ/mol). In addition, the change in dipole moment between ground and excited states also differs significantly. In *p*-DMABN, the $S_{\perp}$ state is only slightly more polar (5×10^{-30} cm) than the ground state, whereas the $S_{\|}$ state is much more polar (15×10^{-30} cm). Therefore, we can expect that the solvent stabilisation of the $S_{\|}$ state will be larger than that of the $S_{\perp}$ state. In contrast, the change of the dipole moment is almost equal for both states in the case of *m*-DMABN (9×10^{-30} cm and 11×10^{-30} cm). Here, we see clearly that the cyano group in *meta* position interacts with both states. The solvent stabilisation should be similar for the two and, therefore, the separation of the two states be preserved.

In DCDMA, the interaction of the two cyano groups leads to a stronger stabilisation of the $S_{\perp}$ state compared to *m*-DMABN and *p*-DMABN. The change in dipole moment is with 9×10^{-30} cm comparable to that of *m*-DMABN. Again, this reflects the influence of the cyano groups. The energetic difference to the $S_{\|}$ state is largest for DCDMA (70 kJ/mol). The combined effect of the two cyano groups leads to a change of the dipole moment in the $S_{\|}$ state that is comparable to *p*-DMABN.



Scheme 4. The electron accepting π^* orbitals of the TICT state for the three componds *p*-DMABN, *m*-DMABN, and DCDMA. The size of the orbital coefficients is indicated by the size of the circles.

The leading term in the CI-representation of the TICT state wavefunction is the single excited configuration in which an electron is promoted from the nitrogen lone-pair to an aromatic π^* orbital. For each of the three compounds this π^* orbital is displayed in Scheme 4. The orbital coefficient at the aromatic carbon atom next to the dimethylamino group is significantly smaller for *m*-DMABN than for *p*-DMABN or DCDMA. With this result in mind, we can look at the argumentation of Rettig [10] who postulated that the stabilising electrostatic interaction between donor and acceptor, which is related to the size of this coefficient, is smaller in *m*-DMABN than in *p*-DMABN. Therefore, the TICT state of *m*-DMABN should be less stable than that of *p*-DMABN. With this line of argument, the TICT state of DCDMA should be stabilised by electrostatic interaction approximately as much as the TICT state of *p*-DMABN. This conclusion is in contradiction with the experimental observation that anomalous fluorescence is not observed in DCDMA. The argumentation of Rettig, based solely on orbital coefficients, is obviously not sufficient to explain the experimental facts.

In Fig. 3, the excited state energies of the two lowest excited singlet states, $S_{\perp}$ and $S_{\|}$, in the planar conformation ($\varphi = 0°$) and of the lowest TICT state in the twisted conformation ($\varphi = 90°$) are shown in dependence of solvent

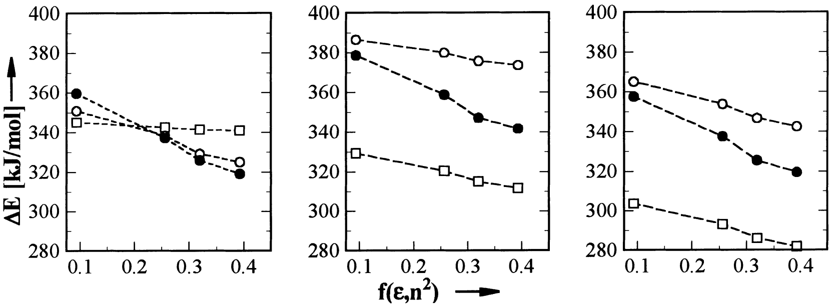


Fig. 3. Solvent influence on the excited state energies of *p*-DMABN (left), *m*-DMABN (center), and DCDMA (right). Planar conformation ($\phi = 0°$, $\theta = 0°$): ○ $S_{\|}$, □ $S_{\perp}$. Twisted confromation ($\phi = 90°$, $\theta = 0°$): ● TICT. Excited state energies are plotted aganist the solvent polarity function $f(\epsilon, n^2)$ (see footnote in Section 3.2).

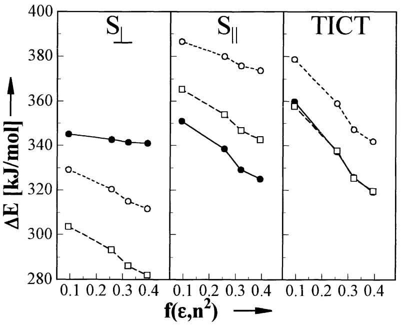


Fig. 4. Comparison of the solvent influence on the excited state energies of *p*-DMABN (●), *m*-DMABN (○), and DCDMA (□), for the three states $S_\perp$ (left), $S_{||}$ (center), and TICT (right).

Table 5
Influence of solvent polarity on the energy difference between the two lowest singlet states for the three compounds *p*-DMABN, *m*-DMABN and DCDMA

Solvent	Energy difference ΔE ($S_{\|\|} - S_\perp$) (kJ/mol)		
	p-DMABN	*m*-DMABN	DCDMA
Vacuum	46.3	54.9	63.3
Hexane	25.1	57.4	61.3
Et_2O	−4.2	59.2	60.9
CH_2Cl_2	−12.2	60.8	60.5
CH_3CN	−15.9	62.0	60.6

The energy difference ΔE ($S_{||} - S_\perp$), given in kJ/mol, was calculated for the planar conformation using an AM1-SCRF-CI calculation with five occupied and five unoccupied orbitals.

polarity [3]. A different form of presentation of the numerical results is given in Fig. 4, where the relative solvent stabilisation of the different states can more easily be compared than in Fig. 3. Table 5 gives the energy difference between $S_\perp$ and $S_{||}$ as a function of solvent polarity. Several conclusions need to be pointed out.

1. TICT state formation is allowed for energetic reasons only for the *para*-substituted compound (*p*-DMABN), but not for *m*-DMABN or DCDMA. This is in agreement with the experimental observations.
2. The energy of the perpendicular polarized state $S_\perp$ remains almost independent of f for *p*-DMABN whereas it has a solvent stabilisation for *m*-DMABN and DCDMA that is comparable to that of $S_{||}$. As already pointed out, this difference is due to the stronger interaction with the cyano groups in the $S_\perp$ state.
3. In the model of Zachariasse et al. [15] the energy difference between the $S_{||}$ and the $S_\perp$ states is a crucial factor. As can be seen in Table 5 and Fig. 3, this difference is large and almost constant for all solvents for the two *meta* substituted compounds. Therefore, a solvent induced interaction, as is necessary according to Zachariasse et al. for anomalous fluorescence to occur, is not possible.
4. In *p*-DMABN, on the other hand, the energy difference is small and for polar solvents the $S_{||}$ is even energetically below the $S_\perp$ state. This is due to the much stronger dipole moment of the $S_{||}$ state compared to the $S_\perp$ state.
5. The solvent stabilisation of the TICT state is comparable for all three compounds, as can be seen in the Lippert–Mataga plot (Fig. 4).

At first glance, the results seem to be in good agreement with the model of Zachariasse et al. But from a different point of view, the *meta* substituted compounds are not suitable model systems to discuss the reason for anomalous fluorescence in *p*-DMABN. In neither of the two compounds, the $S_{||}$ or the TICT state comes energetically even in the proximity of the $S_\perp$ state. The solvent stabilisation of the $S_\perp$ state is too large due to the strong interaction in this state with the cyano groups. Altogether, this means that modifying the substitution position of the cyano group induces changes in the electronic structure and the properties of the excited states which are too large for this compound to act as equivalent model compounds.

4. Conclusions

As we have seen from the results presented in Section 3.1, the photophysical behaviour of the compounds *p*-ABN and *p*-MABN can be understood and explained in the framework of the TICT model. TICT state formation is thermodynamically not possible for the non-methylated *p*-ABN. This is due to the fact that the stabilisation of the positively charged nitrogen via hyperconjugative interaction with methyl groups is missing. In the presence of one methyl group *p*-MABN, part of the stabilisation is regained and the TICT state energy accordingly lowered. But the activation barrier in the excited state is larger for *p*-MABN than for (*p*-DMABN) so that the rotation of the amino group becomes kinetically less favourable for the prior.

The simultaneous appearance of anomalous fluorescence and overlap between the two lowest absorption bands was also reproduced by the calculations. The overlap between both absorption bands is only necessary so far as the TICT state is correlated to the parallel polarized state $S_{||}$ and TICT state formation is thus simplified, if the $S_{||}$ state is lower in energy than the perpendicular polarized state $S_\perp$. The assumption of a strong interaction between $S_\perp$ and the $S_{||}$ states as proposed by Zachariasse et al. is therefore not justified for the studied compounds.

As the reported results show, low lying TICT states with large dipole moments can also be found in the *meta* cyano substituted dimethylanilines, *m*-DMABN and DCDMA. Due to solvation, the energy of these states is considerably

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[3] In the Lippert-Mataga plots the f-values were calculated from the equation [34]

$$f(\epsilon, n^2) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}$$

lowered, but neither for *m*-DMABN nor for DCDMA is this stabilisation large enough to make the TICT state the lowest excited singlet state. Even in very polar solvents like CH_3CN, a locally excited state $S_\perp$ with planar conformation is favoured.

The main reason for the different photophysical behaviour is found in the interaction of the two locally excited singlet states ($S_\parallel$ and $S_\perp$) with the cyano substituents. For *p*-DMABN, this interaction is only important for the parallel polarized state. In the *meta* substituted compounds, *m*-DMABN and DCDMA, both locally excited states interact with the cyano group(s). This different interaction pattern is also reflected in the dipole moment of the excited states. In consequence the $S_\perp$ is significantly lowered on solvation for *m*-DMABN and DCDMA but not for *p*-DMABN. This explains why the locally excited state $S_\perp$ stays energetically below the TICT state in *m*-DMABN and DCDMA. TICT state formation is therefore not possible in these compounds.

This difference between *p*-DMABN and the two *meta*-substituted compounds clearly shows that the changes caused by the different position of the cyano group change the properties of the excited states very much. Therefore, neither *m*-DMABN nor DCDMA are suitable model compounds to discuss the validity of the TICT model in *p*-DMABN. The fact that anomalous fluorescence is not observed for the two other compounds, is not due to changes of the properties of the TICT state. Rather, the properties of the locally excited states differ considerably compared to *p*-DMABN.

This example clearly demonstrates how cautious one needs to be, if model compounds are studied. Even apparently small changes in the chemical structure can cause considerable changes in the excited state properties, that rule out the validity of the model compound. Here, theoretical calculations can help to justify the suitability of proposed model systems.

In summary, we find that the calculations are in favour of the validity of the TICT model in case of *p*-DMABN and explain why dual fluorescence does not occur in the other derivatives studied in this contribution. We therefore believe that the experimental data provided by the derivatives are not a sound basis for the rejection of the TICT model and the introduction of the pseudo Jahn–Teller model for *p*-DMABN.

Acknowledgements

The authors wish to thank Dr. T. Clark for the stimulating discussions. Financial support by Deutsche Forschungsgemeinschaft and Fonds der Chemie is gratefully acknowledged. P.G. thanks the Studienstiftung des Deutschen Volkes for a fellowship.

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