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THE NATURE OF THE EXCITED STATES OF p-NITRO-N,N-DIMETHYLANILINE

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Contrary to numerous derivatives of p-substituted N,N-dimethyl-aniline, p-nitro-N,N-dimethylaniline, does not form the TICT state. This behaviour is predicted by INDO/S calculations. The calculations also reveal an important role of the Coulomb interaction term in the evolution of intramolecular charge-transfer excited-state energy upon twisting of the dimethylamino group.

1. Introduction

During the last ten years it was discovered that numerous para-substituted aromatic molecules of the type D–Ar–A (where D/A represent an electron donor/acceptor group and Ar an aromatic ring system) undergo relaxation in the excited singlet state to a highly polar state, preferentially in fluid polar solvents, and the emission occurs from two different excited states. Numerous attempts were published in order to explain the experimental results [1–6]. However, the twisted intramolecular charge transfer (TICT) state formation hypothesis [7] seems to be better founded than the other proposals to explain this behaviour (see fig. 1).

The aim of our studies is to investigate whether p-nitro-N,N-dimethylaniline (I) in a polar solvent shows a relaxation to the TICT state. For the sake of comparison with I, three model compounds were synthesized: II, with the dialkyl amino group fixed, III and IV, with the dialkylamino or nitro group twisted around the respective N–C bond (see fig. 2).

The TICT state formation of I seems to be

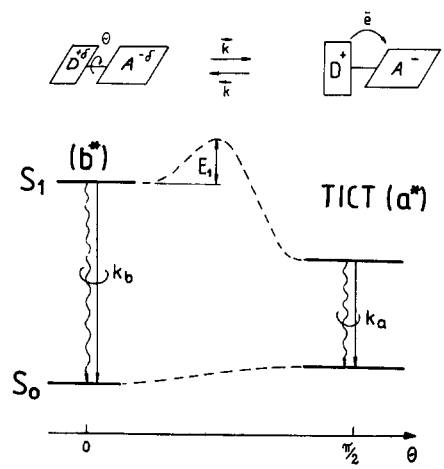


Fig. 1. TICT model. Schematic cross-section of the ground state and lowest excited singlet state potential hypersurfaces along the reaction coordinate represented here by the twist angle θ.

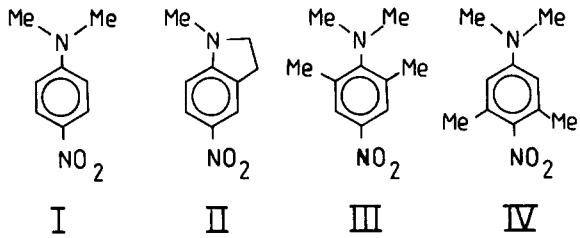


Fig. 2. Formulae of the studied compounds.

possible from the thermodynamical point of view. The linear correlation of the TICT fluorescence maxima with the difference of the oxidation potential of the donor and the reduction potential of the acceptor group was found for a series of molecules emitting TICT fluorescence [8].

The energy of the TICT fluorescence may be estimated as [8]

$$hc\tilde{\nu} = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) + E_{coul} - E_{dest}, \qquad (1)$$

where $E^{ox}_{1/2}(D)$, $E^{red}_{1/2}(A)$ are the polarographic half-wave potentials of one electron oxidation of the donor (D), or reduction of the acceptor (A), respectively, and E_{coul} is the coulombic energy of bringing the opposite charges to the fixed distance. The entropy term is expected to be roughly constant within the considered series of p-derivatives of N,N-dimethylaniline and was neglected [8].

The emission from the highly polar TICT state leads to the Franck–Condon (FC) nonpolar ground state of the twisted conformer. This FC state is more energetic than the solvent-equilibrated ground state by the destabilisation energy, E_{dest}.

For different para-substituted dimethylanilines $E^{ox}_{1/2}(D)$, E_{coul} and $E_{dest} \approx$ const, therefore the observed TICT fluorescence maxima were correlated with the reduction potentials of acceptors only (fig. 3, table 1).

This correlation allows us to evaluate the energy of the fluorescence maximum emitted from the hypothetical TICT state created by internal rotation of the $N(CH_3)_2$ group; the estimated value: $E_{TICT} = 10\,600$–$12\,000$ cm^{-1}.

For nitro compounds, in many cases, the efficient photoreactions take place and consequently, the new absorption and emission bands are ob-

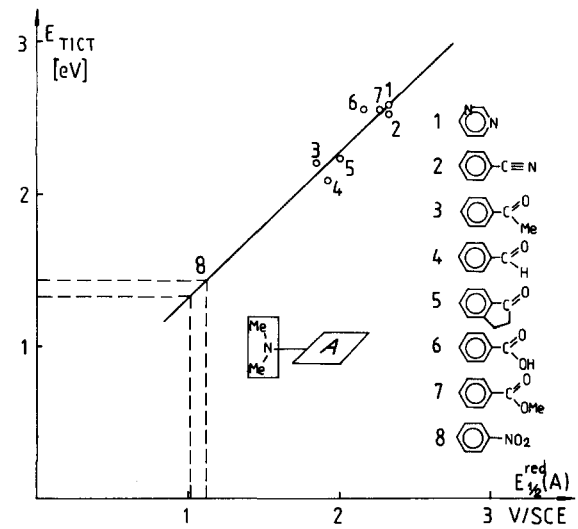


Fig. 3. Energy of the TICT fluorescence maximum for the compounds 1–7 in acetonitrile solutions against the polarographic half-wave potentials of one-electron reduction of the acceptors (A) in acetonitrile or dimethylformamide solutions, correlation coefficient $r' = 0.91$–0.94. Vertical dashed lines indicate the region of the measured values of $E^{red}_{1/2}(A)$ for I (table 1). According to the correlation (points 1–7) the expected emission maximum of the hypothetical TICT state of I is indicated by horizontal dashed lines.

Table 1
Polarographic half-wave potentials of one-electron reduction of acceptors (A), in V vs SCE, in acetonitrile or dimethyl formamide solution, and energies of the fluorescence a transition ($hc\tilde{\nu}_a$) in acetonitrile solutions

No.	Acceptor	$-E^{red}_{1/2}(A)$ (V)	Ref.	$hc\tilde{\nu}_a$ (eV)	Ref.
1	pyrimidine	2.34	9	2.60	10 [a]
2	benzonitrile	2.35	12	2.57	1
3	acetophenone	1.87	9	2.24	13, 14
4	benzaldehyde	1.93	9	2.08	14
5	1-indanone	2.01	15	2.27	14
6	benzoic acid	2.17, 2.24	9	2.58	16
7	methyl benzoate	2.29, 2.32	9	2.58	16
8	nitrobenzene	1.01, 1.13	9		

[a] Recently it has been discovered the TICT fluorescence of the 4-dimethylamino-pyrimidine (DMAP) to be observed only in polar protic solvents [11]. For the ortho-methylated derivative of DMAP (5-Me-DMAP) the observed maximum of the TICT fluorescence in ethanol is at the same spectral position as for DMAP, that is why we can use the $hc\tilde{\nu}_a$ value measured in acetonitrile for the 5-Me-DMAP molecule.

served [17]. In the case of I–IV, in our experimental conditions we did not observe any new detectable absorption or emission bands.

2. Experimental and calculations

p-Nitro-N,N-dimethylaniline (I) has been prepared according to Fitch [18a], and carefully separated from the m-isomer.

1-Methyl-5-nitroindoline (II) (1.62 g) was prepared via 5-nitroindoline (5-NI) [18b] by the following methylation procedure: 1.64 g 5-NI + 0.8 g Na_2CO_3 anhydrous + 2.13 g CH_3I and 3 ml of absolute methanol were refluxed for 12 h. The residue after evaporation of the solvent was sublimed at $p = 5$ Torr and $t = 220\,^\circ$C. The product was additionally purified by recrystallizations from chloroform (mp 126 °C), and checked by MS.

N,N-2,6-tetramethyl-4-nitroaniline (III) was synthesized as described earlier [19].

p-nitro-3,5-N,N′-tetramethylaniline (IV) was prepared via 3,5,N,N′-tetramethylaniline [TMA] by the following nitration procedure: 1.5 g of TMA was dissolved in 20 ml of concentrated sulphuric acid and 1.3 g of $NaNO_2$ was added at $t = 0\,^\circ$C. After 2 h stirring at room temperature the solution was cooled and neutralized by NH_3. The residue after filtration was crystallized from benzene.

I, II, III and IV were purified by sublimation, n-propanol (Merck, for fluorescence) was used without further purification. Luminescence measurements were done with the Jasny-type spectrofluorimeter [20].

The standard INDO/S method [21] was used for calculations of transition energies (E), oscillator strengths (f), dipole moments (μ) and electron charge distribution. All singly excited configurations lying below 10 eV were taken into account in the CI procedure. The following values were used in the input geometries: r_{CC}(phenyl ring) = 1.4 Å, ∢CCC = 120°, r_{CN}(phenyl carbon–amino nitrogen) = 1.37 Å, r_{NC}(amino nitrogen–methyl carbon) = 1.5 Å, r_{CN}(phenyl carbon–nitro nitrogen) = 1.4 Å, r_{NO} = 1.25 Å, r_{CC}(phenyl carbon–acetyl carbon) = 1.47 Å, r_{CO} = 1.2 Å, r_{CC}(acetyl group) = 1.47 Å, r_{NO}(nitroso group) = 1.2 Å, ∢CNO = 108° [22], r_{CH}(phenyl ring) = 1.08 Å, r_{CH}(methyl group) = 1.09 Å.

Two different input geometries were used:

(A) the "idealized" one with the above mentioned values of distances and angles,

(B) the one based on crystal structure data [23].

The calculations were performed for various angles of twisting of the dimethylamino group with respect to the phenyl ring: 0°, 30°, 60°, and 90°; sp^2 hybridisation of the amino nitrogen was assumed.

3. Results and discussion

3.1. Low-temperature spectra

Low-temperature luminescence spectra (fig. 4) of I and III in n-propanol are characterized by strong phosphorescence and weak fluorescence in contrast to II, which emits strong fluorescence and weak phosphorescence. These results suggest that k_{ISC} for p-N,N-dimethylnitroaniline and its derivatives strongly depends on the relative positions of the singlet and triplet states. Indeed, the first absorption-band of II is red shifted by 1000 cm^{-1} with respect to I and III. Kasha and Rawls [24a] discovered that the quantum yields of phosphorescence of aromatic amines depend on the twist angle of the NMe_2 group. This mechanism can also play a role here; there is, however, no experimental evidence indicating the deviation from planarity in the case of p-nitro-N,N-dimethylaniline. For IV no detectable luminescence is observed.

The difference between fluorescence and phosphorescence excitation spectra of I (fig. 4) was first observed by McGlynn [24b] and ascribed to a very efficient intersystem crossing from S_2 competing with internal conversion (IC) to S_1. Recently, the nature of the excitation-dependent luminescence of I was examined by Wild and his students [25]. Their results indicate that the anomalous luminescence behaviour of I can be explained not only in terms of k_{ISC} dependence on λ_{exc} but may also be due to the subtle difference in the molecular environment and/or presence of different ground state conformers. The

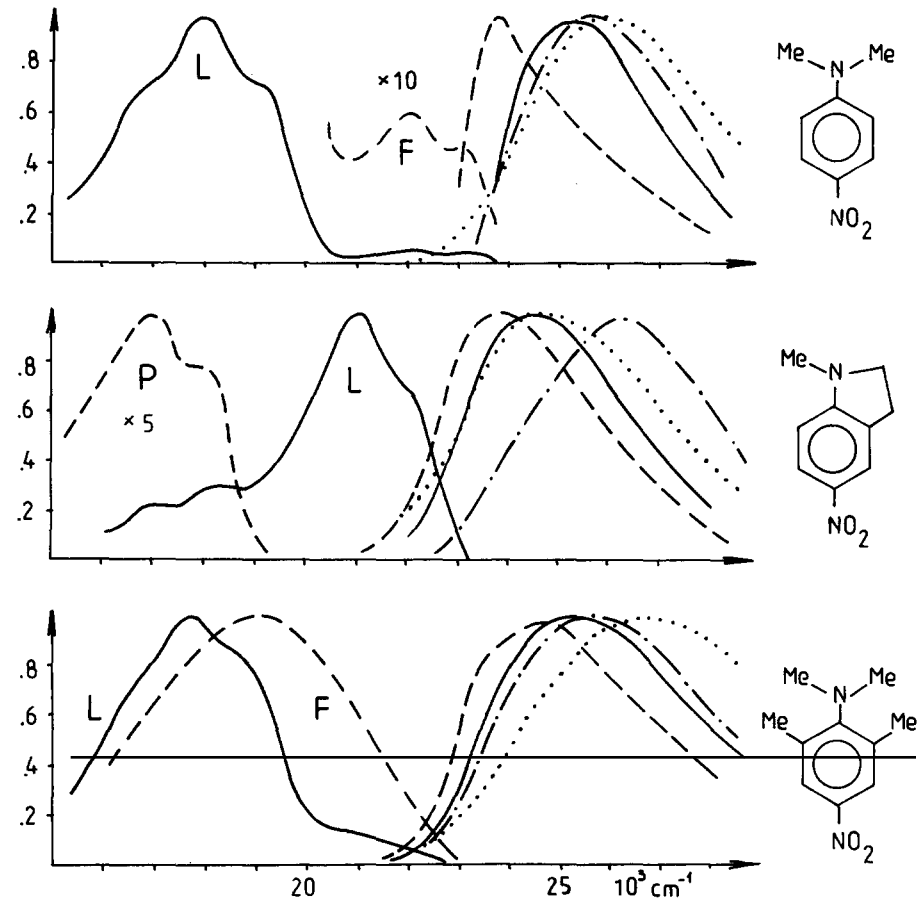


Fig. 4. Normalized low-temperature spectra of I–III in n-propanol at 100 K. L = total luminescence, F = fluorescence, P = phosphorescence. In the higher energy range: solid line, absorption; dashed line, fluorescence excitation; dash-dot line, phosphorescence excitation. The dotted curves indicate the absorption spectra at room temperature. The fluorescence spectrum of III was recorded at 120 K.

difference between fluorescence and phosphorescence excitation spectra was observed also for aniline and dimethylaniline [26,27].

3.2. Room and intermediate temperature

Room temperature luminescence of I–III in n-propanol is undetectable in the range of 13 500 cm^{-1}–25 000 cm^{-1}. When lowering the temperature the fluorescence bands of I–III appear. The relatively small Stokes shift, weakly dependent on temperature, indicates that the fluorescence originates from the primarily excited species (b*). The dependence of the relative fluorescence quantum yield of I–III on temperature is shown in fig. 5.

It was established for many para-substituted dimethylanilines in fluid n-propanol, that the process of TICT state formation at 293 K is much faster than the other depopulation channels [28–30] and the barriers of the excited state reactions (E_1) are 1000–1200 cm^{-1} (table 2).

The comparison of the E_1 values (table 2) with the known activation energies of viscous flow (1320 cm^{-1} for n-propanol [28]) suggests that the TICT formation kinetics of p-cyano and carbonyl derivatives of N-,N-dimethylaniline in n-propanol is viscosity-controlled. The height of the barrier

evaluated from the temperature dependence of $\ln(\eta/\eta_0)$ for I in n-propanol (600 cm^{-1}) is evidently less than in the molecules emitting dual fluorescence (table 2).

The lack of TICT fluorescence in I may be caused by:

(1) fast nonradiative process $S_1 \rightarrow S_0$, other than TICT state formation,

(2) intense nonradiative process TICT $\rightarrow S_0$,

(3) nonexistence of the TICT state at lower energy than the primary (planar) excited state S_1.

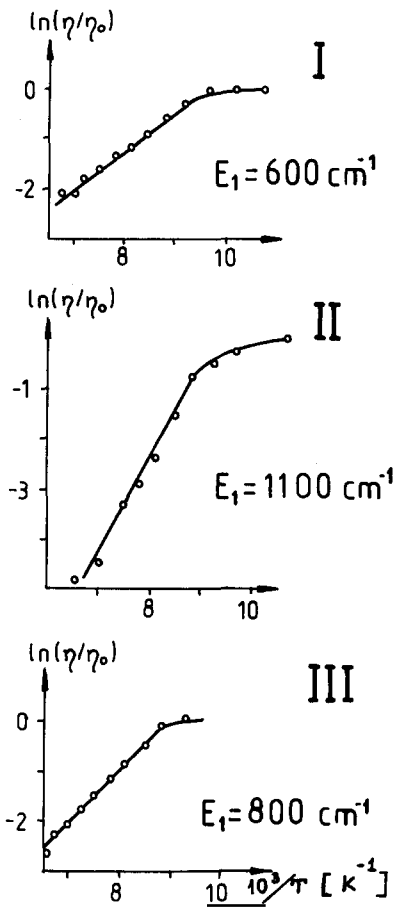
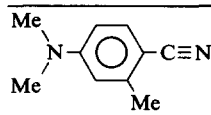
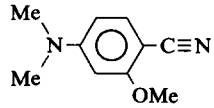
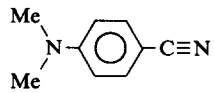
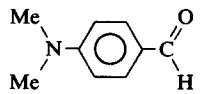
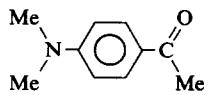


Fig. 5. Dependences of the relative fluorescence quantum yields of I, II and III on temperature in n-propanol. η_0, fluorescence quantum yield at lowest temperature; E_1, activation energies: $E_1(I) = 600\ cm^{-1}$, $E_1(II) = 1100\ cm^{-1}$, $E_1(III) = 800\ cm^{-1} \mp 100\ cm^{-1}$.

Table 2
The barriers (E_1) and rate constants of TICT state formation ($\vec{k}$) at room temperature for some derivatives of dimethylaniline in n-propanol

Compound	E_1 (cm^{-1})	$\vec{k}$ (293K) (s^{-1})
	1000∓40 [28]	
	1210∓40 [28]	
		5×10^{10} [29]
	1190∓70 [30]	$\sim10^{11}$ [30]
	1100∓100 [30]	$\sim10^{11}$ [30]

(1) Kallir observed at 10 K and 77 K a double exponential decay of the fluorescence of I in ethanol, characterized by the lifetimes 4.2 ∓ 0.2 ns and 1.1 ∓ 0.2 ns, ascribed to two slightly different fluorescence bands [25]. Assuming k_{ISC} to be temperature-independent, the rate constant of the triplet formation of I at room temperature should be about $10^{+9}\ s^{-1}$. A similar value of k_{ISC} was found for carbonyl derivatives of dimethylaniline [14] whereas the TICT state formation for cyano and carbonyl derivatives of dimethylaniline is evidently faster (table 2).

(2) Photorotamerisation of excited I to a TICT state should reveal stronger temperature dependence of $\ln(\eta/\eta_0)$ than in the case of II where the reaction is excluded (fig. 5). The opposite effect is observed experimentally.

These facts (1, 2) suggest that I, in contrast to numerous other p-derivatives of dimethylaniline, does not relax to the TICT state (3).

4. Quantum chemical calculations

In order to investigate the behaviour of the excited electronic states of I upon twisting of the dimethylamino group $N(CH_3)_2$ or the nitro group NO_2 we have performed an INDO/S calculation for different values of the twist angle of these groups. A comparison of the observed and calculated absorption spectra of I–IV is given in fig. 6. *Planar molecule*: The calculated S_1 and S_2 transitions correspond to n, π^* excitations (fig. 6, table 3) with electron redistribution mainly localized within the NO_2 group (fig. 7). The calculated

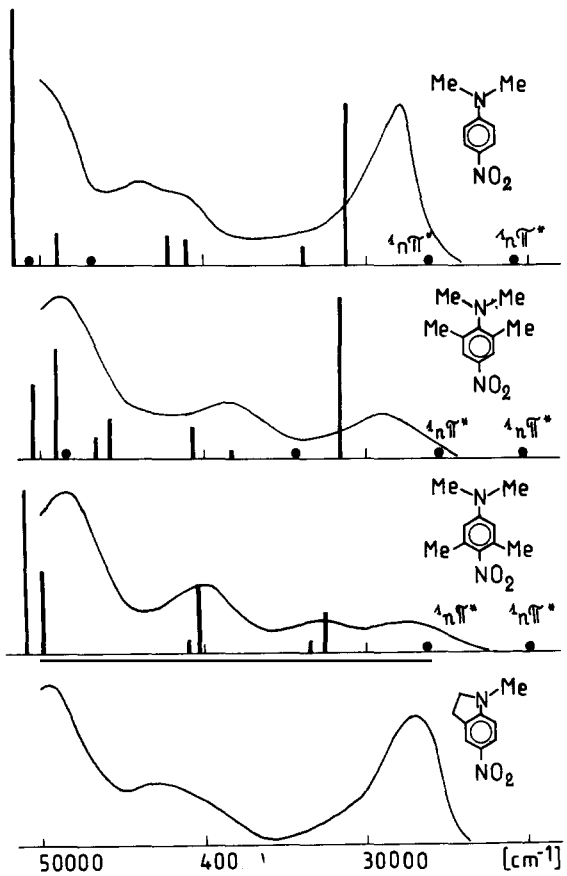


Fig. 6. Room-temperature absorption spectra of I–IV in methylcyclohexane and calculated transitions (geometry A), twist angles 0° or 60°. Circles indicate that oscillator strengths are smaller than 0.01. The maxima of the absorption spectra of I, III and IV are recorded to the higher energy region in comparison with the data published before [31].

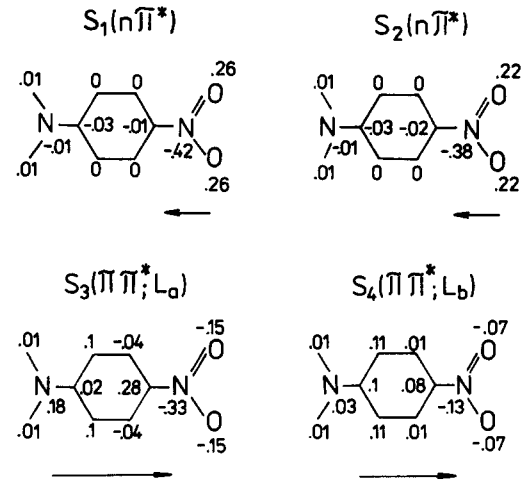


Fig. 7. The changes in electron distribution Δq_i upon excitation calculated for S_1–S_4 states of planar I, $\Delta q_i(S_k) = q_i(S_k) - q_i(S_0)$; i and k indicate, respectively, the number of the atom and the state. The flow of the negative charge is indicated with an arrow. Charges on the omitted hydrogen atoms are not shown.

energy of the lowest n → π* transition is evidently lower than the experimental one measured for nitrobenzene [33], while it is a general result obtained within the INDO/S algorithm [34,35] (see, however, that Bigelow et al. [36] succeeded in calculating the lowest nπ* triplet and singlet states in close agreement with experiment using the CNDO/S–CT method with selected parameter options).

Two π → π* transitions ($S_0 - S_3$, S_4) have been computed in the low-energy region which correspond to the ^1L_a and ^1L_b states (figs. 6, 7). The long-axis polarized transition $S_0 \rightarrow {}^1L_a$ reveals a significant charge transfer contribution from the amino nitrogen to the nitrobenzene moiety. On the contrary, the other, short-axis polarized transition to $^1L_b(S_4)$, is almost exclusively localized on the benzene ring. The dependence of the energy on the geometry is observed mainly for the second nπ* ← S_0 and $^1L_a \leftarrow S_0$ transitions (table 3).

Twisted conformers: The results of the INDO/S calculations for the conformers with the planes of $N(CH_3)_2$ or NO_2 substituents perpendicular to the ring are shown in fig. 8. The ground state rotation energy barriers of the $N(CH_3)_2$ and NO_2 substituents (the same as for p-dimethylamino-

Table 3
The results of INDO/S calculations for different geometries A and B (see text) and experimental data for planar I molecule; ϵ = extinction coefficient

	INDO/S (B)			INDO/S (A)			Experimental data		
	E (cm^{-1})	μ [D]	f	E (cm^{-1})	μ [D]	f	E (cm^{-1})	μ [D]	$\epsilon(\tilde{\nu})$ / ϵ (28100 cm^{-1})
S_0		9.6			8.4			6.9, 5.1, 5 [32]	
S_1	19400	6.9	0	20500	6.5	0	29400 [a]		[a]
S_2	22500	7.3	8×10^{-6}	26100	6.9	5×10^{-5}			
S_3	27100	20.9	0.66	31200	21.3	0.48	28100	15, 13, 12 [32]	1
S_4	33200	13.7	0.002	33900	11.1	0.06	32200 (s) [b]		0.25
S_5	39100	17.2	0.05	41100	19.8	0.08	41200 (s)		0.39
S_6	42000	13.8	0.11	42700	14.7	0.09	42800 (s)		0.48
S_7	44700	6.4	0.39	46900	10.9	0.002	44300		0.5
S_8	47400	8.6	0.003	49000	6.7	0.1			
S_9	51600	13.9	3×10^{-4}	50800	9.7	4×10^{-4}			
S_{10}	53600	16.5	0	51600	11.4	0.78	> 50000		>1

[a] ϵ = 140 for ^{1}n, π^* of nitrobenzene [33].
[b] s = shoulder.

benzaldehyde [37]) were taken into account in order to attain correct energy levels of the two twisted conformers in comparison with the planar one. For the planar molecule and for a conformer with the twisted $N(CH_3)_2$ group the calculated energies, dipole moments and oscillator strengths

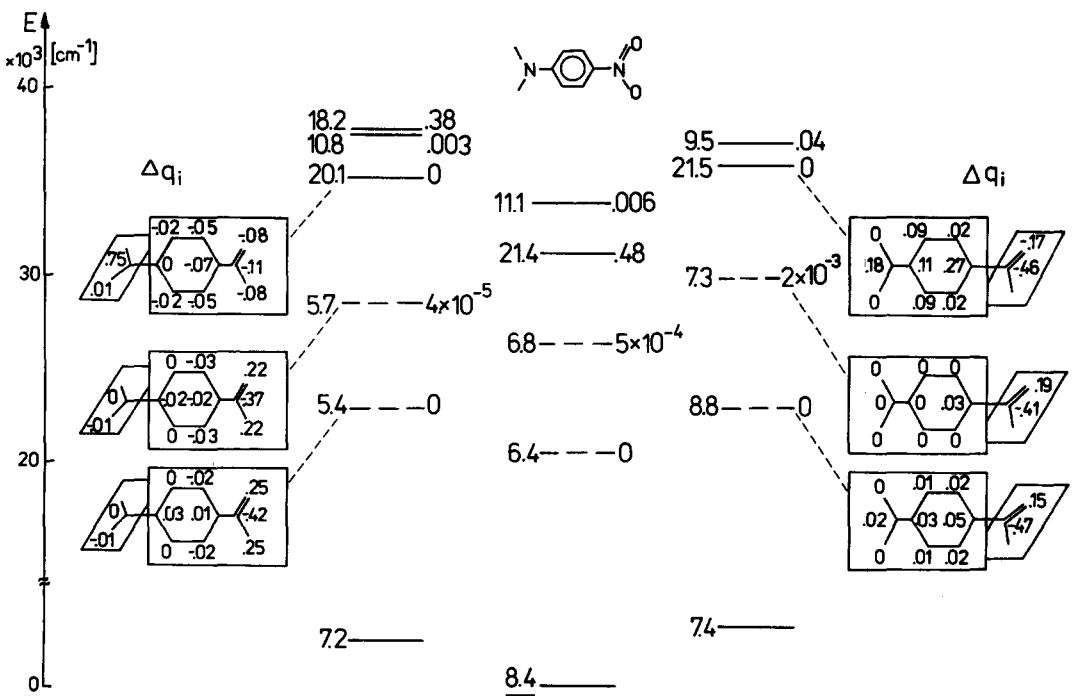


Fig. 8. Scheme of the energy levels of planar molecule I and two twisted conformers calculated by the INDO/S method (geometry A). Numbers of the left side indicate the dipole moments (in Debye units) while the oscillator strengths are shown on the right. Δq_i are the changes in electron distribution upon excitation, as defined in fig. 7.

for $n \rightarrow \pi^*$ transitions are similar (fig. 8). Very small oscillator strength and a large dipole moment ($\mu = 20.1$ [D], 0.8 electron transfer between donor and acceptor subunits) of the S_3 state of the conformer with the twisted $N(CH_3)_2$ group (fig. 8) corresponds to the TICT model. The TICT state generated by the rotation of the $N(CH_3)_2$ group is energetically higher, about 4000 cm^{-1}, than the ^1L_a state of a planar molecule. As the TICT emission has been observed mostly in polar solvents, the possibility of energetic stabilisation due to solvation must be taken into account [30]. The calculations gave the same values (within $\pm 10\%$, depending on geometry) of dipole moments in planar and twisted conformers. Thus, the role of solvent stabilisation does not seem to be important for inversion of these states.

For the conformer with the NO_2 group perpendicular to the ring the lowest calculated $n \rightarrow \pi^*$ transition has some admixture of the charge transfer configuration (fig. 8). Consequently, the dipole moment of the state is higher ($\mu = 8.8$ [D]) than the dipole moment of the lowest $^1n, \pi^*$ state of the planar molecule ($\mu = 6.4$ [D]). The energies, dipole moments and oscillator strengths of the second $^1n, \pi^*$ states are similar for the planar and twisted conformer. The lowest $^1\pi, \pi^*$ state ($\mu = 21.5$ [D)] is energetically higher than the lowest $^1\pi, \pi^*$ state of the planar molecule ($\mu = 21.4$ [D]). Again, from a comparison of the dipole moment values, one can exclude a possibility of the solvent stabilization of the twisted form with respect to the planar one. In consequence, the TICT formation is highly improbable.

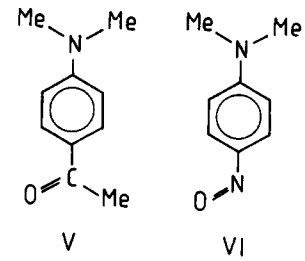


Fig. 9. Formulae of compounds V and VI.

In summary, INDO/S calculations indicate that I after excitation in fluid polar solvents cannot relax to the TICT stage generated by the rotation of neither the $N(CH_3)_2$ nor NO_2 group. This result is consistent with the suggestion of Cowley and Peoples [38] that for strong acceptors, nitrobenzene or s-triazine, the TICT emission cannot be observed.

To check the reliability of the INDO/S method in predicting the energy of TICT stages we performed the calculations for the compound which is known to undergo excited state intramolecular electron transfer – p-N,N-dimethylaminoacetophenone (V), [13,14,30,39] (fig. 9).

In this case, the computed energy of the ^1L_a state slightly decreases upon twisting of the electron donor group (table 4, fig. 10). Simultaneously, the value of the dipole moment increases from $\mu = 11.5$ [D] at 0° to $\mu = 14$ [D] at 90°

Table 4
The results of INDO/S calculations (geometry A) and experimental data (from ref. [13]) for planar and twisted molecule V in n-heptane

INDO/S				Experimental data [13]			
State	E (cm^{-1})	μ [D]	f	State	E (cm^{-1})	μ [D]	ϵ
S_0		5.3		S_0		5.6 [a]	
S_1 (n, π^*)	25700	2.2	4×10^{-5}	$^1n, \pi^*$	28500		150
S_2 (L_b)	34300	6.6	0.019	L_a	31000	13 [a]	29000
S_3 (L_a)	38100	11.5	0.56	L_b	32000		
TICT	35400	14	1×10^{-6}	TICT	28000 – 33000 [b]		

[a] For p-dimethylaminobenzaldehyde [32].
[b] 18000 cm^{-1} fluorescence maximum in acetonitrile [13]; the extrapolation of the solvatochromic correlation to nonpolar solvent leads to the values 28000–33000 cm^{-1} depending on the model.

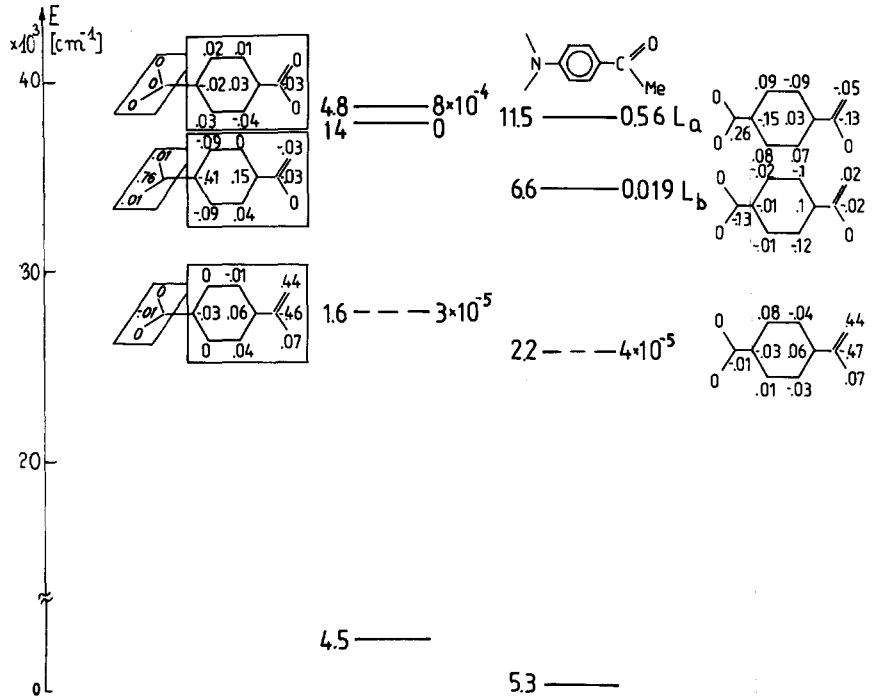


Fig. 10. Scheme of the energy levels of planar molecule V and twisted conformer ($N(CH_3)_2$) calculated by the INDO/S method (geometry A). Numbers on the left side indicate dipole moments (in D units) while oscillator strengths are shown on the right. Δq_i are as defined in fig. 7.

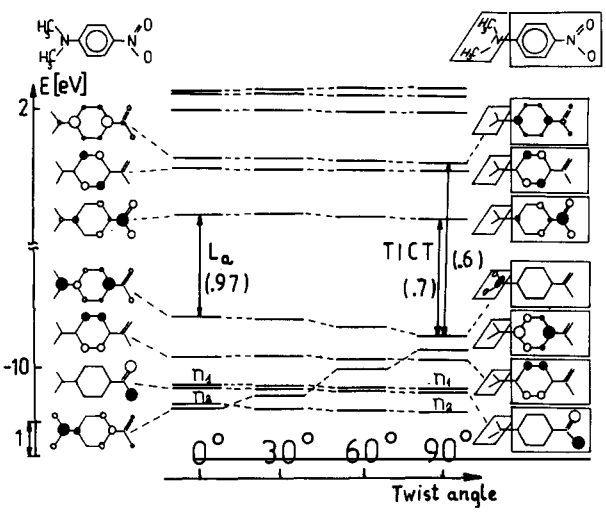


Fig. 11. Scheme of the molecular orbitals of planar molecule I and the conformer with the twisted $N(CH_3)_2$ group calculated by INDO/S method (geometry A).

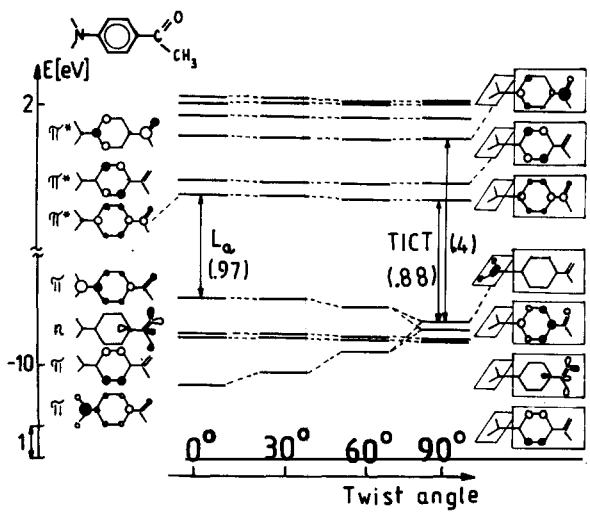


Fig. 12. Scheme of the molecular orbitals of planar molecule V and the conformer with the twisted $N(CH_3)_2$ group calculated by INDO/S method (geometry A).

Table 5
The results of INDO/S calculations for I and V for various angles of twisting of the dimethylamino group with respect to the phenyl ring, c_i the contribution of the "i" configuration to the wavefunction of the ^1L_a state. J and K are Coulomb and exchange integrals. The $2K$ value for the planar molecule is equal to the singlet–triplet separation, for the TICT state K should be zero [7]

Twist angle	I				V			
	c_i	$\lvert J-2K\rvert$ (cm^{-1})	$\lvert 2K\rvert$ (cm^{-1})	$\lvert J\rvert$ (cm^{-1})	c_i	$\lvert J-2K\rvert$ (cm^{-1})	$\lvert 2K\rvert$ (cm^{-1})	$\lvert J\rvert$ (cm^{-1})
0°	0.971	25400	4000	21400	0.969	26900	7000	19900
30°	0.965	25200			0.958	27100		
60°	0.921	24800			0.890	28000		
90°	0.744	23100	0	23100	0.884	30800	0	30800

which additionally should stabilize the TICT state in polar solvents.

Thus, the calculations predict two opposite reactions of the ^1L_a state energy on the twisting of the dimethylamino group in the two molecules (figs. 8, 10). The reason for this may be found upon inspection of the factors contributing to the transition energy. For a single configuration corresponding to the electron jump from an orbital "i" to an orbital "k" this value is given by:

$$\Delta E = \epsilon_k - \epsilon_i - J_{ik} + 2K_{ik} \qquad (2)$$

ϵ_j denotes the energy of the orbital "j", J and K are the Coulomb and exchange integrals, respectively.

In both molecules, the ^1L_a state is very well described by a single configuration corresponding to the promotion of an electron from the highest occupied to the lowest unoccupied orbital (figs. 11, 12). Upon twisting of the dimethylamino group, the orbital energy difference evolves similarly in both molecules. It is the opposite behaviour of the $(-J+2K)$ terms which differentiates between I

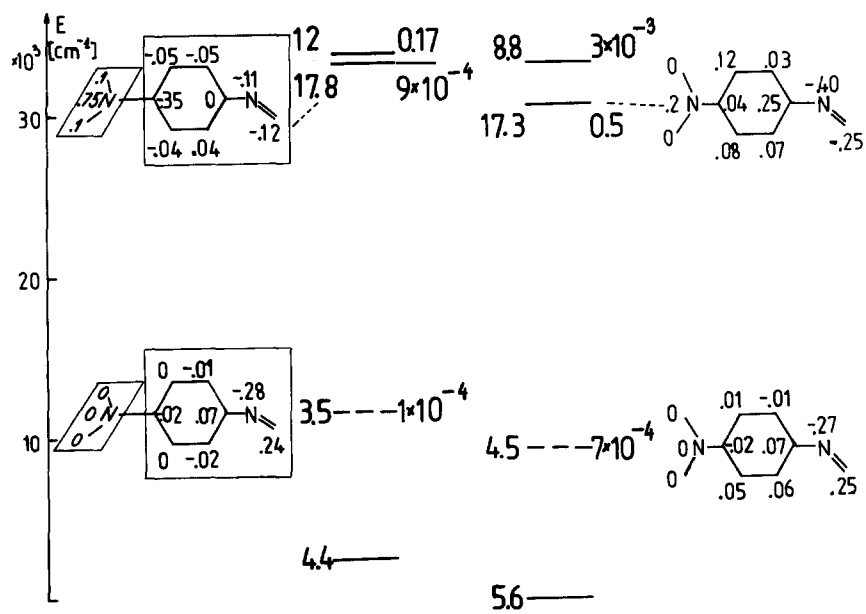


Fig. 13. Scheme of energy levels of planar molecule VI and conformer with twisted $N(CH_3)_2$ group calculated by the INDO/S method (geometry A). Numbers on the left side indicate the dipole moments (in D units) while oscillator strengths are shown on the right. Δq_i are as defined in fig. 7.

Table 6
The results of INDO/S calculations (geometry A) and experimental data for the planar molecule VI

INDO/S			Experimental data [41]			
E (cm^{-1})	μ [D]	f	E (cm^{-1})	μ [D]		ϵ
	5.6			6.9, 6.5 [32]		
9300	4.5	1×10^{-4}	13790			48
30600	17.3	0.5	25200	13	[32]	31000
33200	8.8	0.003	32790			3600
40500	15.8	0.16	37740			6000

and V (table 5) leading to the stabilization of the transition energy in the latter and to destabilization in the former.

The different fluorescence bands observed for amino derivatives of coumarine have been also explained in terms of the different Coulomb interaction in excited states depending on the different position of the substitution of the NH_2 group [40].

The results of calculations show that one should be careful while trying to estimate the TICT energy from thermodynamical considerations presented in the beginning of this work, the Coulomb stabilisation energy may widely differ in specific cases (in the first approximation [8] it has been taken as $-e^2/\epsilon r$ where r was the idealized mean distance of charge separation, ϵ the macroscopic dielectric constant of the solvent).

We have also made the calculations for a molecule containing a nitroso group (VI) as the electron acceptor. Nitrosobenzene is a stronger acceptor ($E^{red}_{1/2} = -0.81$ V [9]) than nitrobenzene. Similarly to I a destabilization of the TICT state for the twisted conformer with respect to the L_a state of the planar molecule was calculated (fig. 13), which leads to a prediction that this compound probably would not reveal a TICT fluorescence.

5. Conclusions

The experimental results and quantum chemical calculations demonstrate that I after excitation in fluid polar solvent does not relax to the TICT state generated by the rotation of the $N(CH_3)_2$ or NO_2 group.

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