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

\[
\begin{align*}
\text{TICT} (\alpha^*) \\
\text{S}_0 \\
\text{S}_1 (\text{S}^*) \\
\text{D–Ar–A} \\
\end{align*}
\]

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 \( \theta \).
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]

\[ h\bar{v} = E_{1/2}^\text{ox}(D) - E_{1/2}^\text{red}(A) + E_{\text{coul}} - E_{\text{dest}}, \]

where \( E_{1/2}^\text{ox}(D) \) and \( E_{1/2}^\text{red}(A) \) are the polarographic half-wave potentials of one electron oxidation of the donor (D), or reduction of the acceptor (A), respectively, and \( E_{\text{coul}} \) 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, \( E_{\text{dest}} \).

For different para-substituted dimethylanilines \( E_{1/2}^\text{ox}(D) \), \( E_{\text{coul}} \) and \( E_{\text{dest}} = \text{const} \), 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 \( \text{N}(\text{CH}_3)_2 \) group; the estimated value: \( E_{\text{TICT}} = 10600 - 12000 \text{ cm}^{-1} \).

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

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Acceptor</th>
<th>( - \bar{E}_{1/2}^\text{ox}(A) ) (V)</th>
<th>Ref.</th>
<th>( h\bar{v}_{\text{FL}} ) (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pyrimidine</td>
<td>2.34</td>
<td>9</td>
<td>2.60</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>benzonitrile</td>
<td>2.35</td>
<td>12</td>
<td>2.57</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>acetonophenone</td>
<td>1.87</td>
<td>9</td>
<td>2.24</td>
<td>13, 14</td>
</tr>
<tr>
<td>4</td>
<td>benzaldehyde</td>
<td>1.93</td>
<td>9</td>
<td>2.08</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>1-indanone</td>
<td>2.01</td>
<td>15</td>
<td>2.27</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>benzoic acid</td>
<td>2.17, 2.24</td>
<td>9</td>
<td>2.58</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>methyl benzoate</td>
<td>2.29, 2.32</td>
<td>9</td>
<td>2.58</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>nitrobenzene</td>
<td>1.01, 1.13</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ h\bar{v}_{\text{FL}} \equiv \text{measured value in acetone for the 5-Me-DMAP molecule.} \]

\( \text{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-MeDMAP) 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 } h\bar{v}_{\text{FL}} \text{ value measured in acetone 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$_2$CO$_3$ anhydrous + 2.13 g CH$_3$I 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 $t = 220°C$. 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 $t = 0°C$. 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 ($\mu$) 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, $\angle$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, $r_{NO}$(phenyl carbon–nitro group) = 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, $\angle$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,N-dimethyl-Nitroaniline 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 $\lambda_{exc}$ but may also be due to the subtle difference in the molecular environment and/or presence of different ground state conformers. The
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 13500 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 \( S_1 \).

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_1 ) (cm(^{-1}))</th>
<th>( k ) (293K) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>1000 ± 40</td>
<td>[28]</td>
</tr>
<tr>
<td>Me</td>
<td>1210 ± 40</td>
<td>[28]</td>
</tr>
<tr>
<td>Me</td>
<td>5 × 10(^{10})</td>
<td>[29]</td>
</tr>
<tr>
<td>Me</td>
<td>1190 ± 70</td>
<td>~10(^{11})</td>
</tr>
<tr>
<td>Me</td>
<td>1100 ± 100</td>
<td>~10(^{11})</td>
</tr>
</tbody>
</table>

(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 \( k_{\text{ISC}} \) 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 \( k_{\text{ISC}} \) 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(CH₃)₂ or the nitro group NO₂ 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 S₁ and S₂ transitions correspond to n, π⁺ excitations (fig. 6, table 3) with electron redistribution mainly localized within the NO₂ group (fig. 7). The calculated 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 (S₁ → S₃, S₄) have been computed in the low-energy region which correspond to the 1Lₐ and 1L₇ states (figs. 6, 7). The long-axis polarized transition S₁ → 1Lₐ reveals a significant charge transfer contribution from the amino nitrogen to the nitrobenzene moiety. On the contrary, the other, short-axis polarized transition to 1L₇(S₄), is almost exclusively localized on the benzene ring. The dependence of the energy on the geometry is observed mainly for the second nπ⁺ → S₀ and 1Lₐ → S₀ transitions (table 3).

**Twisted conformers:** The results of the INDO/S calculations for the conformers with the planes of N(CH₃)₂ and NO₂ substituents perpendicular to the ring are shown in fig. 8. The ground state rotation energy barriers of the N(CH₃)₂ and NO₂ 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; 
\( \varepsilon \) = extinction coefficient

<table>
<thead>
<tr>
<th></th>
<th>( E ) (cm(^{-1}))</th>
<th>( \mu ) [D]</th>
<th>( f )</th>
<th>( E ) (cm(^{-1}))</th>
<th>( \mu ) [D]</th>
<th>( f )</th>
<th>( \varepsilon ) (E)</th>
<th>( \varepsilon ) (28100 cm(^{-1}))</th>
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<td>( S_0 )</td>
<td>19400</td>
<td>9.6</td>
<td>0</td>
<td>20500</td>
<td>8.4</td>
<td>0</td>
<td>29400</td>
<td>6.9, 5.1, 5 [32]</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>22500</td>
<td>6.9</td>
<td>0</td>
<td>26100</td>
<td>6.5</td>
<td>0</td>
<td>26100</td>
<td>5 \times 10^{-5}</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>27100</td>
<td>7.3</td>
<td>8 \times 10^{-6}</td>
<td>31200</td>
<td>21.3</td>
<td>0.48</td>
<td>28100</td>
<td>15, 13, 12 [32]</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>33200</td>
<td>13.7</td>
<td>0.002</td>
<td>33900</td>
<td>11.1</td>
<td>0.06</td>
<td>32200 (s)</td>
<td>0.25</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>39100</td>
<td>17.2</td>
<td>0.05</td>
<td>41200</td>
<td>19.8</td>
<td>0.08</td>
<td>42800 (s)</td>
<td>0.39</td>
</tr>
<tr>
<td>( S_5 )</td>
<td>42000</td>
<td>13.8</td>
<td>0.11</td>
<td>42700</td>
<td>14.7</td>
<td>0.09</td>
<td>42800 (s)</td>
<td>0.48</td>
</tr>
<tr>
<td>( S_6 )</td>
<td>44700</td>
<td>6.4</td>
<td>0.39</td>
<td>46900</td>
<td>10.9</td>
<td>0.002</td>
<td>44300</td>
<td>0.5</td>
</tr>
<tr>
<td>( S_7 )</td>
<td>47400</td>
<td>8.6</td>
<td>0.003</td>
<td>49000</td>
<td>6.7</td>
<td>0.1</td>
<td>44300</td>
<td>0.5</td>
</tr>
<tr>
<td>( S_8 )</td>
<td>51600</td>
<td>13.9</td>
<td>3 \times 10^{-4}</td>
<td>50800</td>
<td>9.7</td>
<td>4 \times 10^{-4}</td>
<td>50000</td>
<td>&gt;1</td>
</tr>
<tr>
<td>( S_9 )</td>
<td>53600</td>
<td>16.5</td>
<td>0</td>
<td>51600</td>
<td>11.4</td>
<td>0.78</td>
<td>&gt;50000</td>
<td>&gt;1</td>
</tr>
</tbody>
</table>

\( a) \ \varepsilon = 140 \text{ for } 1H, 1H of nitrobenzene [33].

\( b) \ \varepsilon = \text{shoulder.} \)

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

![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. \( \Delta q_i \) are the changes in electron distribution upon excitation, as defined in fig. 7.](image-url)
for \( n \to \pi^* \) 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 \( S_0 \) state of the conformer with the twisted \( \text{N(CH}_3\text{)}_2 \) group (fig. 8) corresponds to the TICT model. The TICT state generated by the rotation of the \( \text{N(CH}_3\text{)}_2 \) group is energetically higher, about 4000 cm\(^{-1} \), than the \( 1^1L_a \) 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 \( n \to \pi^* \) 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 \( 1^1n, \pi^* \) state of the planar molecule (\( \mu = 6.4 \) [D]). The energies, dipole moments and oscillator strengths of the second \( 1^1n, \pi^* \) 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.

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 \( \text{N(CH}_3\text{)}_2 \) 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 \( 1^1L_a \) 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 \( 0^\circ \) to \( \mu = 14 \) [D] at \( 90^\circ \)

### Table 4

<table>
<thead>
<tr>
<th>INDO/S</th>
<th>State</th>
<th>( E ) (cm(^{-1} ))</th>
<th>( \mu ) [D]</th>
<th>( f )</th>
<th>Experimental data [13]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 )</td>
<td>( S_0 )</td>
<td>25700</td>
<td>5.3</td>
<td>( 4 \times 10^{-5} )</td>
<td>( S_0 )</td>
</tr>
<tr>
<td>( S_1 ) (( n, \pi^* ))</td>
<td>34300</td>
<td>6.6</td>
<td>0.019</td>
<td>( 1^1n, \pi^* )</td>
<td>31000</td>
</tr>
<tr>
<td>( S_1 ) (( L_a ))</td>
<td>38100</td>
<td>11.5</td>
<td>0.56</td>
<td>( L_a )</td>
<td>32000</td>
</tr>
<tr>
<td>( S_1 ) (( L_a ))</td>
<td>35400</td>
<td>14</td>
<td>( 1 \times 10^{-6} )</td>
<td>TICT</td>
<td>28000–33000 (^b)</td>
</tr>
</tbody>
</table>

\(^a\) 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(CH₃)₂) calculated by the INDO/S method (geometry A). Numbers on the left indicate dipole moments (in D units) while oscillator strengths are shown on the right. Δq, are as defined in fig. 7.

Fig. 11. Scheme of the molecular orbitals of planar molecule I and the conformer with the twisted N(CH₃)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(CH₃)₂ group calculated by INDO/S method (geometry A).
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, \( c \), the contribution of the "i" configuration to the wavefunction of the \( \text{1L}_a \) state. \( J \) and \( K \) are Coulomb and exchange integrals. The 2\( K \) value for the planar molecule is equal to the singlet–triplet separation, for the TICT state \( K \) should be zero [7].

| Twist angle | \( c \) | \( |J - 2K| \) \( \text{cm}^{-1} \) | \( 2K \) \( \text{cm}^{-1} \) | \( |J| \) \( \text{cm}^{-1} \) | \( c \) | \( |J - 2K| \) \( \text{cm}^{-1} \) | \( 2K \) \( \text{cm}^{-1} \) | \( |J| \) \( \text{cm}^{-1} \) |
|-------------|------|-----------------|--------------|-------------|------|-----------------|--------------|-------------|
| 0°          | 0.971| 25 400          | 4000         | 21 400      | 0.969| 26 900          | 7000        | 19 900      |
| 30°         | 0.965| 25 200          |              |             | 0.958| 27 100          |             |             |
| 60°         | 0.921| 24 800          |              |             | 0.890| 28 000          |             |             |
| 90°         | 0.744| 23 100          | 0            | 23 100      | 0.884| 30 800          | 0           | 30 800      |

which additionally should stabilize the TICT state in polar solvents.

Thus, the calculations predict two opposite reactions of the \( \text{1L}_a \) 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:

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

\( \epsilon_j \) denotes the energy of the orbital "j", \( J \) and \( K \) are the Coulomb and exchange integrals, respectively.

In both molecules, the \( \text{1L}_a \) 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

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**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. \( \Delta q_d \) are as defined in fig. 7.
Table 6
The results of INDO/S calculations (geometry A) and experimental data for the planar molecule VI

<table>
<thead>
<tr>
<th>INDO/S</th>
<th>Experimental data [41]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (cm$^{-1}$)</td>
<td>$\mu$ (D)</td>
</tr>
<tr>
<td>9300</td>
<td>5.6</td>
</tr>
<tr>
<td>30600</td>
<td>17.3</td>
</tr>
<tr>
<td>33200</td>
<td>8.8</td>
</tr>
<tr>
<td>40500</td>
<td>15.8</td>
</tr>
</tbody>
</table>

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 $-e^2/er$ where $r$ was the idealized mean distance of charge separation, $\epsilon$ 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 ($E_{1/2}^{red} = -0.81$ 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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