

SOLVENT AND CONFORMATIONAL EFFECTS ON THE LUMINESCENCE OF INTRAMOLECULAR  
CHARGE-TRANSFER STATES

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The dual fluorescence of p-dimethylaminobenzonitrile (DMABN) has aroused much controversy [1] concerning the emitting states, and has been ascribed to a solvent-induced inversion of electronic states, to a solvent exciplex formation, to protonation of excited species, to excimers, and to isomerisation of the excited molecule via internal rotation of the  $\text{NMe}_2$  group.

The latter rotational isomerisation model advocated by Grabowski and coworkers [2] has been further explored to reveal the existence of excited electronic states involving the full transfer of electronic charge from donor D to acceptor A moieties, and characterised by a mutually perpendicular conformation of D and A groups in the molecule D-A. Such states are designated TICT (twisted intramolecular charge transfer).

Theoretical and experimental evidence in support of these ideas is presented.

1. PPP-SCF-MO-CI calculations

A number of benzene derivatives, D-Ar-A have been examined. Rotation about the Ar-A bond does not appear to have the same importance as rotation about the D-Ar bond as far as the energies are concerned. Results for DMABN, as representative of several compounds, are collected in the Figure.

The calculated energy of the  $2^1A_1$  state ( $^1L_a$ ) for the planar form is too high by ca.  $4000\text{ cm}^{-1}$  compared with the experimental absorption band energy, but the transition ( $S_2 \leftarrow S_0$ ) is of the correct intensity and polarisation (long axis, Z).

On twisting about the  $\text{Me}_2\text{N}-\text{C}$  bond, the  $^1L_a$  (CT state) rises initially but then falls sharply in energy, the ICT character becomes more pronounced, while the transition intensity falls toward zero but retains its long-axis polarisation.

Thus the maximum energy difference in the emissions from the planar ('b') and twisted ('a') forms is calculated to be  $9700\text{ cm}^{-1}$  (experimental, DMAEN in  $\text{CH}_2\text{CN}$ ,  $7200\text{ cm}^{-1}$ ).

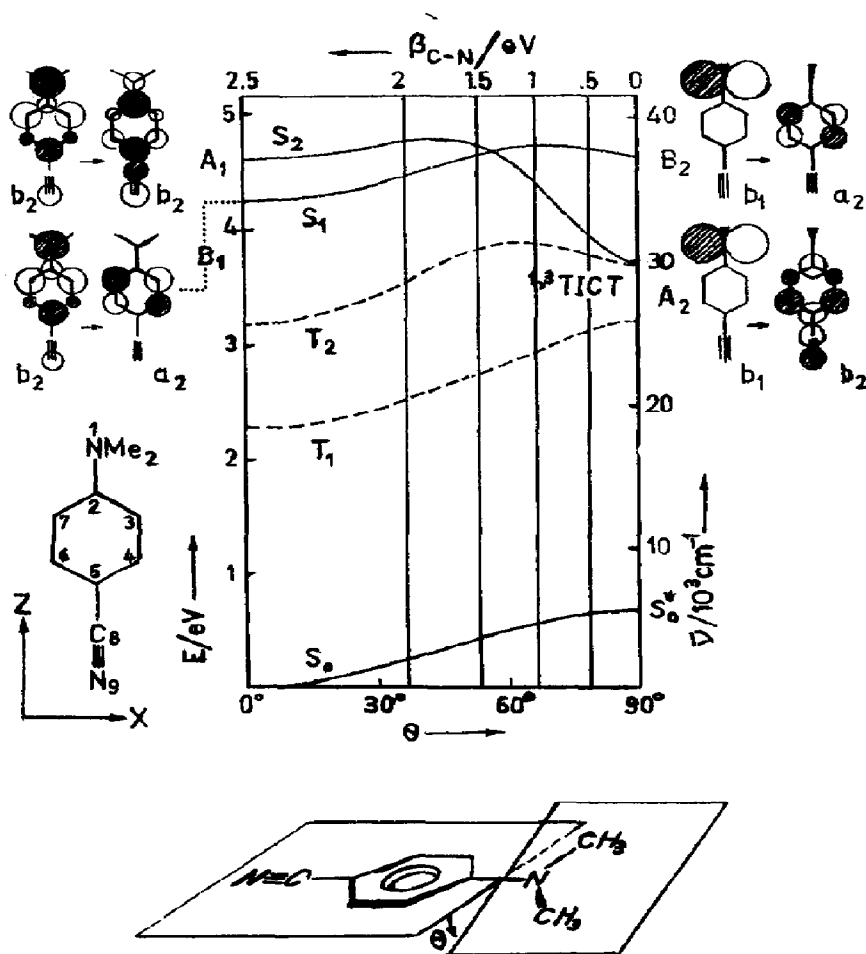


Figure: Electronic energy levels of p-N,N-dimethylaminobenzonitrile. Effects of rotation about the  $\text{Me}_2\text{N}-\text{C}$  bond.

The out-of-plane rotation model appears to be feasible to account for the dual fluorescence observed in the para isomers of  $\text{Me}_2\text{NC}_6\text{H}_4\text{A}$ , where A is carbonyl, aldehyde, carboxylic acid or ester [3]. The MO characteristics of the meta isomers preclude such behaviour.

## 2. Luminescence of p-N,N-dimethylaminobenzoic acid (DMABA) and its methyl ester (DMABM).

Both DMABA and DMABM show a dual fluorescence in  $\text{CH}_3\text{CN}$  at room temperature, but only single emissions in cyclohexane [4]. Meta-DMABA shows only one fluorescence peak at 435 nm with  $\text{CH}_3\text{CN}$  as solvent.

Compound	Solvent	$\lambda_a$ (nm)	$\phi_a$	$\lambda_b$ (nm)	$\phi_b$
DMABA	C <sub>6</sub> H <sub>12</sub>	-	-	323	0.21
	CH <sub>3</sub> CN	480	0.0013	346	0.022
DMABM	C <sub>6</sub> H <sub>12</sub>	-	-	332	0.24
	CH <sub>3</sub> CN	480	0.0029	343	0.005

Excitation wavelength 290 nm

The electronic state energy diagrams for DMABA and DMABM are similar to that of DMABN (see Figure). Increase in solvent polarity lowers the small activation barrier to internal rotation of the Me<sub>2</sub>N group in the CT excited state via the greater solvation energy of the developing more dipolar TICT form.

In n-propanol glass at 77 K, DMABA and DMABN shows phosphorescence characteristics of locally-excited  $\pi, \pi^*$  aromatic triplets e.g. dimethylaniline, with bands at 428 and 420 nm, lifetimes 1.5 and 1.85 respectively. The phosphorescence energy is higher than that of the low energy (a) fluorescence emission observed in CH<sub>3</sub>CH solution. Matrix relaxation effects are responsible in part but such an occurrence is quite feasible on the basis of the TICT model (see Figure).

The existence of TICT states poses a challenge

- (a) theoretically, to justify and generalise the findings on the minimum orbital overlap in the TICT states
- (b) photochemically, to find whether the TICT states behave as the radical cations and anions, especially since the state population is expected to be high.

### References

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