INFLUENCE OF SOLVENT POLARITY ON THE DUAL FLUORESCENCE OF p-N,N-DIMETHYLAMINOBENZONITRILE: AN AM1 THEORETICAL STUDY

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Twisting of the NMe_2 group in p-N,N-dimethylaminobenzonitrile (DMABN) was investigated using AM1 semiempirical method with configuration interaction. Effect of polar media was considered by placing + and — charge centers ("sparkles") at appropriate places opposite the molecule. Optimized ground state geometry of DMABN is slightly twisted with the lowest vertical excited state of ^1B character. As the polarity of media inreeases and/or the —NMe_2 group twists, the symmetric ^1A excited state having considerable charge separation becomes energetically favorable. Anomalous long-wavelength emission of DMABN comes from this state.

More than twenty years ago, a simple benzene derivative, p-N,N-dimethylamino-benzonitrile (DMABN) was discovered to emit two fluorescence bands in polar solvents. Many authors attempted to explain this phenomenon. Rotkiewicz, Grellmann and Grabowski were the first to suggest[1] that the anomalous long-wavelength emission comes from a conformation with the dimethylamino group twisted perpendicularly to the molecular plane. The emitting state was named a twisted intramolecular charge-transfer (TICT) state and DMABN became a first member of a TICT series of molecules. The number of compounds able to form TICT states is rapidly increasing, currently more than one hundred of such molecules is known[2]. They are mostly dialkylamino derivatives of aromatic hydrocarbons but also systems composed of two aromatic moieties linked with a single bond, and other molecules.

From the point of view of a simple MO theory the TICT system consists of two parts, a donor (D) and a acceptor (A), which are conjugated in the ground state. After excitation an electron jumps from D to A. The two moieties twist themselves and become nearly orthogonal, i.e. orbitally decoupled. Resulted polar excited state is strongly stabilized by the solvent and its emission may compete with those from the Franck–Condon state.

Molecular processes including charge separation play the key role in many biological and technical phenomena, e.g. vision, transformation of sunlight into chemical energy, organic conductors and semiconductors, production and storage of electricity,

and therefore, the knowledge of electronic structure of TICT molecules is of great importance.

Quantum chemical methods were successfully used in this connection, e.g. in the study of the NMe_2 twist in DMABN (refs[3-6]) and related compounds[7,8], and charge separation in aminoborane after excitation[9].

In the present work excited states of DMABN were studied using AM1 approximation with inclusion of solvent effect.

RESULTS AND DISCUSSION

Half-electron version[10] of the AM1 method[11] with configuration interaction was used for the calculations. In CI 17 monoexcited configurations relative to the reference biradical configuration were used (i.e. also some biexcited configurations from the closed shell ground state). This method was shown[12-14] to give good results in the study of energies and geometries of organic molecules in excited states.

Effect of polar media was considered by placing + and − charge centers (called "sparkles" by Dewar), incorporated in MOPAC series of programs, at appropriate places opposite the molecule. "Sparkles" can be regarded as unpolarizable ions with no orbitals, a zero heat of formation and ionization. "Sparkles" were placed on the molecular axis, namely + "sparkle" opposite the cyano group and − "sparkle" opposite the dimethylamino group. An increase of solvent polarity was simulated by approaching of "sparkles" to the molecule. The model is very simple, it cannot reflect specific interactions between solvated molecule and the solvent which are believed to play an important role here[15], in spite of that we believe it can yield useful information about effect of solvation on the excited states of DMABN.

The DMABN molecule is composed of benzene ring and two substituents, a dimethylamino group which is a π donor, and a cyano group with strongly withdrawing character. AM1 optimization of ground state geometry does not give planar (C_{2v}) structure, as might be expected but a geometry with a NMe_2 group about of 30° distorted from the benzene ring. Recent experimental results based on the analysis of the gas phase photoelectron spectra also refer about distorted structure of DMABN in the ground state[6].

In spite of the slight twist of NMe_2 group an effective conjugation of nitrogen lone pair with π electrons of the aromatic ring is still possible. The conjugation is hindered only when the NMe_2 group is perpendicularly twisted. It can be clearly seen from Fig. 1, where HOMO, LUMO, and LUMO + 1 orbitals of planar and twisted DMABN are schematically shown. The lowest excited singlet state in perpendicularly twisted conformation is of HOMO → LUMO nature, where an electron from the lone pair on nitrogen jumps to the substituted aromatic ring and resulted polar excited state may be effectively stabilized by the solvent.

On Figs 2a – 2d calculated torsion potentials for NMe_2 twist in DMABN for three lowest singlet states are given. Optimized ground state geometry was considered for the calculations, only the NMe_2 twist angle was changed. Different distances of "sparkles" from the molecule, namely 12, 6, and 3 Å mimicked an increase of solvent polarity.

From the figures it can be seen that energies, as well as geometries of particular states depend strongly on the polarity of environment. In nonpolar media the NMe_2 group is slightly distorted but increase of polarity causes planarization of molecule. Without considering solvation the lowest excited singlet state (HOMO → LUMO + + 1) is of $^1B_1$ character (using C_{2v} symmetry labelling) at 3·51 eV, followed by symmetric $2\,^1A_1$ state (HOMO → LUMO) at 3·60 eV (experimental values are 3·6 and 4·4 eV, respectively[16]). As the polarity of media increases and/or the dimethylamino group twists, the symmetric ^1A state becomes energetically favorable. Anomalous long-wavelength emission come from this state. Experiment also reports considerable decrease of $2\,^1A_2$ emission energy in polar solvents, while the energy of $^1B_2$ emission band changes only slightly[16]. An interesting fact resulted from our calculations is that in polar media "normal" and "anomalous" fluorescence come from planar and perpendicularly twisted conformation, respectively, while in nonpolar media both emitting conformations are twisted, and differ only in the twist angle of NMe_2 group.
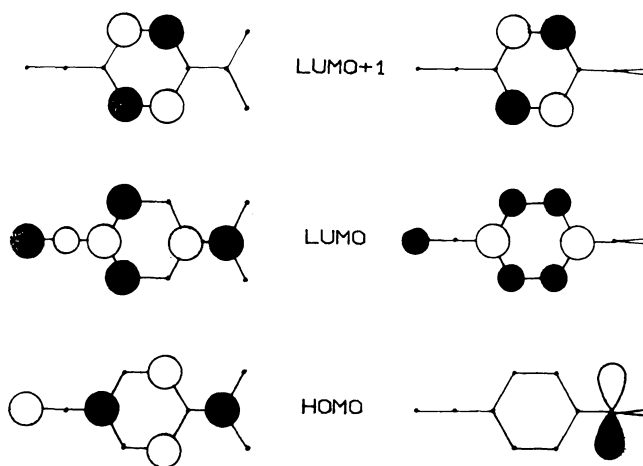

FIG. 1

Schematic drawings of HOMO, LUMO, and LUMO + 1 orbitals of DMABN in planar and perpendicularly twisted conformations

We are aware of the fact that results presented here have only qualitative predictive value. Since the half-electron method was used, the twisted geometries having biradical character were overstabilized relative to the vertical ones. It is also questionable,
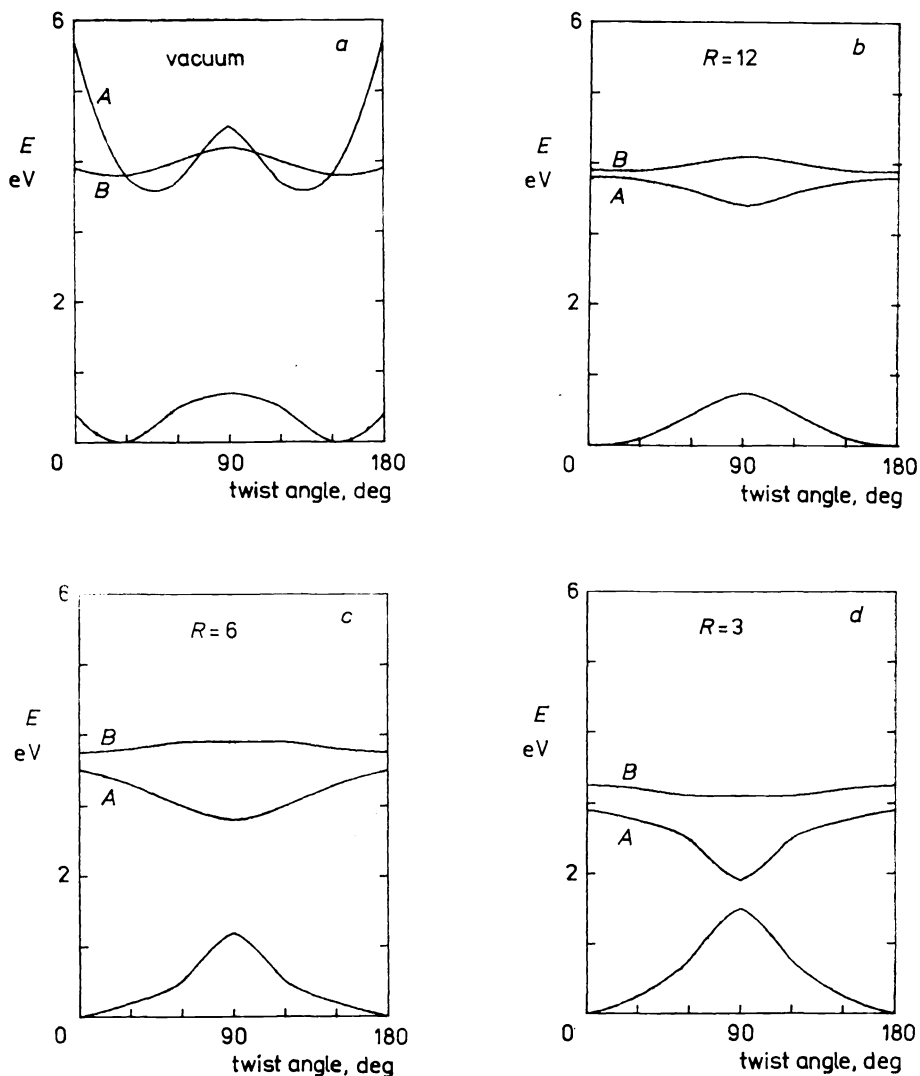

FIG. 2

Energies of the ground and two excited singlet states of DMABN as a function of twist angle. Different distances of sparkles (given at the top of the particular figure) simulate an increase of solvent polarity

whether the barrier in the $2\,^1A$ state in perpendicularly twisted conformation in Fig. 2a is not only an artifact of the method (although AM1 is clearly better than MNDO in describing conformations of arylsubstituted compounds[17]). Results would be probably better by using large extent of CI, though we believe the qualitative conclusions drawn in this paper are correct.

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