

# Dual fluorescence in donor-acceptor molecules

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The quantum chemical study of the fluorescent properties of donor–acceptor molecules has been carried out with the allowance made for the interaction with a polar solvent. The mechanism of formation of dual fluorescence in polar molecules is proposed. It is supposed that, as a polar molecule interacts with a polar solvent, the strong hydrogen bond and the molecule–polar solvent complex are formed, and a radiative state with a large Stokes shift can arise in this complex.

## Introduction

The dual-band fluorescence of 4-dimethylaminobenzonitrile (DMABN) was observed for the first time more than 40 years ago.<sup>1</sup> Since that time this phenomenon was discovered in the fluorescence spectra of some other organic compounds of the donor–acceptor type. Dual fluorescence is observed in the gas phase, and it manifests itself only as interaction of the molecule with a solvent. In all the cases, the molecules are strongly polar, and the abnormal fluorescence is recorded in polar solvents. The DMABN molecule is the most thoroughly studied both theoretically and experimentally. There exist various models for explanation of the dual fluorescence.

Traditionally, the emission in the second fluorescence band located in the long-wave part of the spectrum is attributed to the high intramolecular charge (electron density) transfer in the electronic transition from the locally excited singlet state. The most commonly accepted hypothesis is the so-called TICT (twisted intramolecular charge transfer) model proposed by Grabowski,<sup>2</sup> according to which the charge transfer state is connected with the twist of the dimethyl amino group from the molecular plane to the plane normal to the aromatic ring.

## Methods of investigation

The problem on structure–optical properties has two complementary aspects. Usually, investigators consider the change in the optical properties with variation of the molecular structure (for example, when incorporating various substitutes). This research field is now basic and rather fruitful. However, the opposite consideration is possible as well, namely, revealing the molecular structure from the known spectral characteristics. For the first time, this approach in its clear form was applied by Weller<sup>3</sup> for explanation of the anomalous shift of fluorescence in compounds with the intramolecular hydrogen bond (derivatives of salicylic acid).

With the allowance made for the equivalence of light absorption and emission at a given molecular

structure, the change of the optical property was explained by the change of the molecular geometry in the fluorescent state (proton phototransfer).

Most of the authors considering the dual fluorescence also explain this phenomenon by a possible change of the molecular geometry. The quantum chemical calculations in Ref. 4 has shown that, if the TICT model is chosen, the true nature of the charge transfer state is, in fact, forbidden. As is known from the experiment,<sup>5</sup> the time of fluorescence growth weakly depends on the solvent viscosity, which does not agree with this model. So we decided to consider this phenomenon not invoking the TICT model, but based on the assumption that the molecule form a complex with the polar solvent in the solution. The complexes were calculated within the framework of the "supermolecule" model.

We have studied the quantum chemical electronic structure and the spectral-luminescent properties of some donor–acceptor molecules (Table 1). The calculations have been carried out by the PNDO (partial neglect of differential overlap) method with the use of spectroscopic parameterization.<sup>6,7</sup> To study the proton-accepting properties of the molecules and to determine the probable structures of the molecule–solvent complexes, we used the molecular electrostatic potential (MEP) procedure. The main idea of the MEP procedure is that electric Coulomb forces play the major role in many types of intermolecular interactions (ionic and electron-philic reactions, formation of the hydrogen bond, and donor–acceptor complexes). Having this in mind, MEP is determined as the energy of electrostatic interaction of the molecular electron distribution with the positive point unit charge located at a given point of the molecular ambient space. Proton is a good physical analog of such a "sample" charge. Therefore, this procedure is especially efficient in analysis of the protonation reactions and of the hydrogen bond formation.

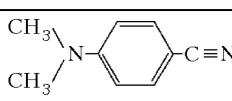
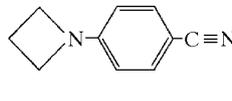
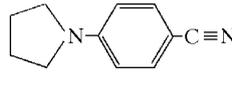
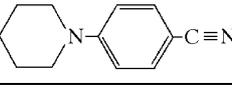
To take into consideration the change of the molecular geometry in the fluorescent state, we used the linear relation between the population of the *A*–*B* chemical bond ( $P_{AB}$ ) calculated according to Ref. 8 and the length of this bond:  $\Delta R_{AB} \approx -0.46 \cdot \Delta P_{AB}$ ,

where  $\Delta R_{AB}$  and  $\Delta P_{AB}$  are the changes in the length and population (electron density) of the chemical bond upon excitation of the molecule. The increase in the population of the bond is indicative of its shortening, while the decrease evidences its elongation. It is assumed that the changes in the valence and torsion angles are caused only by the changes in the bond lengths.

## Results and discussion

The calculation of the molecules in the gas phase has shown that all the studied objects have similar spectral-luminescent characteristics for the states  $S_1$  and  $S_2$  both in the oscillator strength and in the rate constants of the radiative transition (see Table 1). In the oscillator strength, the  $S_1 \rightarrow S_0$  transition is weakly allowed, while the  $S_1 \rightarrow S_2$  transition is allowed. The dipole moment calculated for the molecules in the ground state is 7–8 D, and for the  $S_1$  and  $S_2$  states it is about 10 and 13 D. Thus, the studied molecules are strongly polar, and the molecules in the state  $S_2$  have stronger polarity than those in the state  $S_1$ .

**Table 1. Characteristics of the electronic transitions in the molecules: electronic state energy  $E$  ( $\text{cm}^{-1}$ ), oscillator strength  $f$ , and rate constants of radiative transitions  $k_r$ .**

Molecule	State	$E$	$f$	$k_r, \text{s}^{-1}$
	$S_1(\pi\pi^*)$	34460	0.0328	$3.8 \cdot 10^7$
	$S_2(\pi\pi^*)$	37740	0.5671	$5.7 \cdot 10^8$
	$S_1(\pi\pi^*)$	34060	0.0467	$3.8 \cdot 10^7$
	$S_2(\pi\pi^*)$	37540	0.5791	$5.7 \cdot 10^8$
	$S_1(\pi\pi^*)$	34770	0.0291	$2.5 \cdot 10^7$
	$S_2(\pi\pi^*)$	37950	0.5405	$5.5 \cdot 10^8$
	$S_1(\pi\pi^*)$	34840	0.0279	$2.4 \cdot 10^7$
	$S_2(\pi\pi^*)$	37810	0.5492	$5.5 \cdot 10^8$

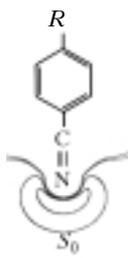
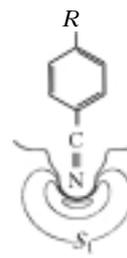
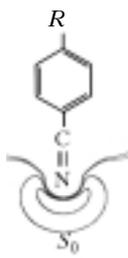
The redistribution of the electron density among the states has shown that, in the excited states, the electron density at atoms and bonds changes considerably. As the molecule is excited, the electron density in the state  $S_1$  redistributes to the benzene ring, and in the state  $S_2$  it flows out to the cyano group.

The calculation of the molecular electrostatic potential has shown that, in the ground state, the minimum of the potential is located on the cyano group in the plane of the benzene ring, and there are also small minima above and below the ring plane. The calculated MEP minima are summarized in Table 2.

In the  $S_1$  state, the potential minimum on the cyano group increases due to the inflow of the electron density, while the minimum above the ring

decreases and disappears. Finally, only one deep minimum on the cyano group remains in the  $S_2$  state (see Table 2). This minimum lies in the molecular plane. From this it follows that in the  $S_1$  and  $S_2$  states the hydrogen bond with the proton-donating solvent is formed through the cyano group.

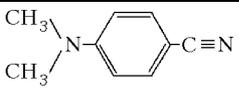
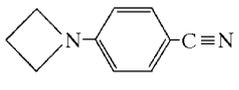
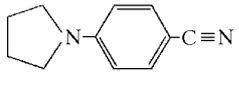
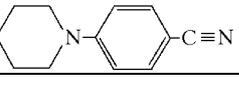
**Table 2. Calculated MEP minima for the molecules on the cyano group in the states  $S_0, S_1, S_2$**

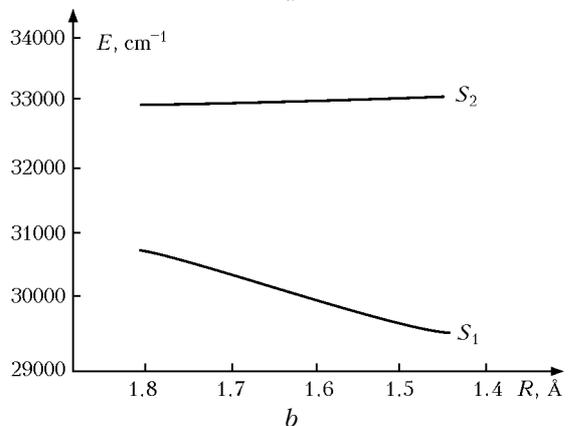
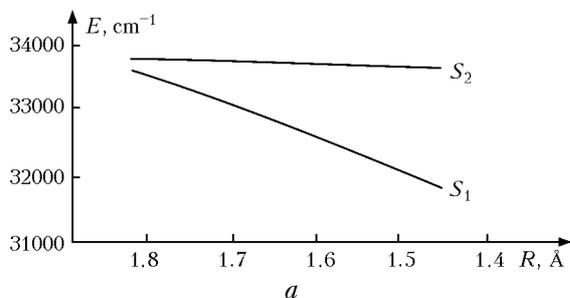
	MEP in the states $S_0 \rightarrow S_1 \rightarrow S_2, \text{kJ/mol}$		
			
R- 			
	-417.8	-452.8	-570.2
	-421.5	-451.29	-572.5
	-412.3	-456.0	-575.2
	-412.2	-455.1	-571.3

Water was taken as a solvent. It is known from the literature that the structures like  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  are formed in water. Thus, we have considered the complex "molecule–polar solvent." The solvent was brought to the cyano group according to the calculated MEP values. As was shown by the calculation, neutral water induces no significant changes in the photophysical processes in the molecules. Therefore, we have considered the complex with the ion forms  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$ . The separation  $R_{(\text{N} \dots \text{O})}$  between nitrogen N and oxygen O was taken equal to 2.8 Å, while the separation  $R_{(\text{N} \dots \text{H})}$  was varied from 1.4 to 1.8 Å. The calculated results (Table 3) indicate that the inversion of the levels  $S_1$  and  $S_2$  occurs at the separations of 1.7–1.8 Å. With the further decrease of  $R_{(\text{N} \dots \text{H})}$ , the energy interval  $\Delta E$  increases (Fig. 1a).

The fluorescence occurs from the equilibrium state  $S_1$ , whose geometry may differ from that of the ground state even for photostable molecules. To take this circumstance into account, we have calculated the changes in the bond lengths for the complex and carried out the calculations for the equilibrium geometry of the  $S_1$  state. The dependence of the energy of the  $S_1$  and  $S_2$  states on the proton position

**Table 3. Characteristics of the electronic transitions in molecule + H<sub>3</sub>O<sup>+</sup> complexes: electronic state energy  $E$  (cm<sup>-1</sup>), oscillator strength  $f$ , and rate constants of radiative transitions  $k_r$ , s<sup>-1</sup>**

Molecule + H <sub>3</sub> O <sup>+</sup> , ( $R_{N-H}$ , Å)	State	$E$	$f$	$k_r$
	$S_1(\pi\pi^*)$	33810	0.627	$5.03 \cdot 10^8$
	$S_2(\pi\pi^*)$	33890	0.025	$2.01 \cdot 10^7$
	$S_1(\pi\pi^*)$	33360	0.669	$5.27 \cdot 10^8$
	$S_2(\pi\pi^*)$	33550	0.033	$2.7 \cdot 10^7$
	$S_1(\pi\pi^*)$	33810	0.603	$4.9 \cdot 10^8$
	$S_2(\pi\pi^*)$	34090	0.021	$1.6 \cdot 10^7$
	$S_1(\pi\pi^*)$	33670	0.624	$5.0 \cdot 10^8$
	$S_2(\pi\pi^*)$	33950	0.021	$1.7 \cdot 10^7$



**Fig. 1.** Energy of the  $S_1$  and  $S_2$  states vs.  $R_{(N-H)}$  at  $R_{(N-O)} = \text{const}$  in the geometry of  $S_0$  (a) and  $S_1$  (b) states.

in the molecule–solvent complex for the geometry of the  $S_1$  state is shown in Fig. 1b. The energy interval for the geometry of the fluorescing state is about  $3000 \text{ cm}^{-1}$ . As the proton was moved from hydroxonium to nitrogen of the cyano group, the energy interval increased.

## Conclusions

Thus, we have carried out the quantum chemical study of the fluorescent properties of donor–acceptor molecules taking into account their interaction with the polar solvent. The possibilities of forming abnormal fluorescence have been analyzed for the polar molecules. The model has been proposed, in which the polar molecule interacts with the polar solvent yielding the formation of strong hydrogen bond and the ionic molecule–solvent complex. The proton transfer from the solvent to the molecule can occur rather fast ( $< 0.1 \text{ ns}$ ) and is almost independent of the solvent viscosity.

Within the framework of the proposed model, the second radiative state with the large Stokes shift can arise in the molecule.

## Acknowledgments

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## References

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