Russian Physics Journal, Vol. 47, No. 11, 2004

COMPLEXING AND PHOTOPROCESSES IN A PRODAN MOLECULE

V. Ya. Artyukhov, O. M. Zharkova, and Yu. P. Morozova

UDC 535.37

The effect of hydrogen bond on the spectral-luminescent properties of the PRODAN molecule – water complexes is studied. Quantum chemical calculations are performed for the ground and fluorescent equilibrium states of a free PRODAN molecule and its complexes with H_3O^+*. It is shown that significant changes occur in the geometry of the molecule in the fluorescent state. To describe the fluorescent state, account was taken of the changes in the electron density (population) on the bonds and atoms in transition of the molecule to an excited state. The rate constants of radiative and nonradiative processes and quantum yields of fluorescence are calculated for the PRODAN molecule and its complexes in water. A significant shift of the fluorescent bands (sensitivity to a solvent) in transition of the molecule from cyclohexane to water is accounted for.*

INTRODUCTION

The fact that the problems facing molecular photophysics become increasingly more involved places new requirements upon the information on the structure of organic molecules, their complexes in solvents , and, in the first place, on the electronic structure, since it is the electron-density distribution that exerts a primary effect on spectral characteristics, and photochemical and biological activity [1].

The effect of complexing on spectral-luminescent characteristics of molecular systems is a currently central problem of molecular photophysics. Complexing can markedly change the relationship between radiative and nonradiative processes.

A PRODAN molecule (6-propionyl-2-dimethylaminnaphtalene) is widely used in biochemical studies as a probe extremely sensitive to the nature of the solvent used. The effect of the solvent is registered by the shift of absorption and fluorescence bands. The properties of the molecule were studied for a number of solvents significantly different in polarity [2, 3]. It was pointed to a low quantum yield of fluorescence for the foregoing molecule, however, its value was not reported. It was also shown that the quantum yield in a nonpolar solvent is much higher than that in water [2].

The present paper studies the PRODAN molecule – hydrogen-bond complexes. The effect of intermolecular interactions between a dissolved molecule and a polar proton-donor solvent on the electron-state positions and photophysical processes is examined.

MOLECULE GEOMETRY

The structure and numeration of atoms of a PRODAN molecule is shown in Fig. 1. The geometric parameters of the molecule (bond lengths and angles) were taken as averaged over related compounds discussed in [4]. Considering a high negative effective charge on a nitrogen atom in the amino group, we suggest that the methyl groups in the amino group will deflect from the molecule plane through an angle of 15°.

Tomsk State University. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 11, pp. 71–75, November, 2004. Original article submitted May 11, 2004.

1064-8887/04/4711-1172

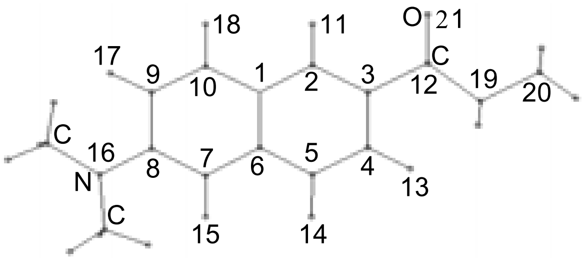

Fig. 1. Structure and numeration of atoms of a PRODAN molecule.

INVESTIGATION TECHNIQUES

A quantum-chemical calculation of a PRODAN molecule was performed using a program package on the basis of the INDO method (Intermediate Neglect of Differential Overlap) with spectroscopic parameterization [5]. The calculated wave functions of electron states were used for evaluating the rate constants of the photophysical processes. The rate constant of the radiative decay was found by means

$$k_{\mathrm{r}} = \frac{f(S_i \to S_0)E_i^2}{\sqrt{2}}, \tag{1}$$

where f is the oscillator strength of the electron $S_i \to S_0$ transition and E_i is the energy of the $S_i \to S_0$ transition in cm^{-1}. The technique for evaluating the rate constants of nonradiative processes (internal conversion – k_{ic}, singlet-triplet conversion – k_{ST}) is described in [6].

To assess the possibility of a specific interaction of the molecule with a polar solvent use was made of the Method of Electrostatic Potential (MEP) [7] whereby the electrostatic energy of nuclear interaction and electron distribution of the molecules with a positive point charge placed at a given point in the space surrounding the molecule are calculated. The MEP values can be used as a basis for determining the geometry of hydrogen-bond complexes [6]. In our work, the MEP was calculated in the deorthogonalized basis.

It is well-known that the calculated energies of electron transitions correspond to the maxima of the respective absorption or luminescence bands (i.e., Franck–Condon transitions). Therefore it is necessary to determine the geometry of the excited state for correct calculation of the radiation spectra. To find changes in the geometry under excitation, the bond populations P_{AB} (according to Mulliken) were calculated in the ground and excited states. A well-known linear dependence between the bond length and population was assumed. The change in the bond length in transition to the excited state is described as

$$\Delta R_{AB}^{*} = -k\Delta P_{AB}^{*}, \tag{2}$$

where ΔP_{AB}^{*} is the change in the bond population in transition of the molecule from the ground state to the excited state. The value of the coefficient k depends on the quantum-chemical technique used for calculating the electronic structure. In our case, $k = 0.46$ was obtained from the change in the length of the C–C bond of benzene for the $S_0 \to S_1$ transition [8]. The change in the bond length usually occurs in the molecule plane. In the case where the effective charge on the atom is highly negative, the geometry can be changed outside the plane. The atom can partially go from the sp^2- to sp^3-hybridization, that is, leave the plane of the molecule. This was taken into account in determining the geometry of the fluorescent state of the molecule.

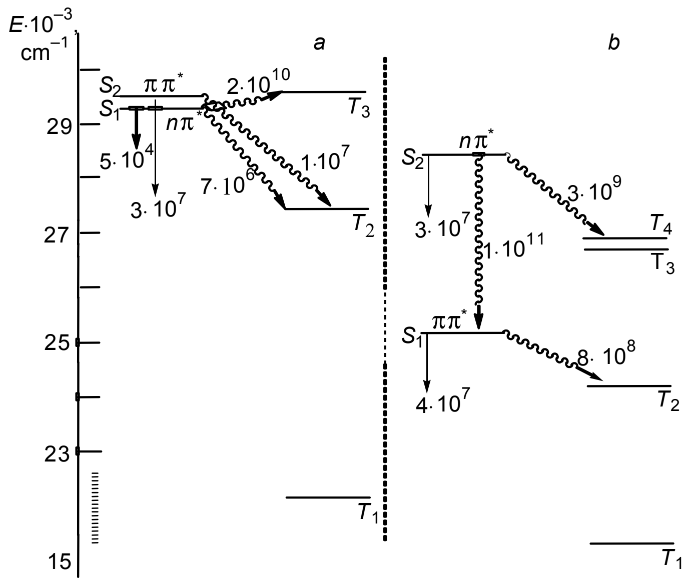

Fig. 2. The energy-level diagram and photoprocess in PRODAN: ground-state geometry (*a*) and equilibrium geometry of the S_1 state (*b*).

CALCULATION RESULTS AND DISCUSSION

The absorption and emission characteristics of the PRODAN molecule in various solvents are reported in [2]. A maximum in the long-wavelength absorption band of PRODAN in cyclohexane corresponds to 29200 cm^{-1}, fluorescence – 24900 cm^{-1}. The highest shifts of the maxima of absorption and fluorescence bands are observed for water. An absorption maximum of the PRODAN molecule in water corresponds to 27500 cm^{-1}, fluorescence – 18800 cm^{-1}.

First we performed quantum-chemical calculations of an isolated PRODAN molecule. Taking into consideration that parametrization of the method used for calculations was derived on the basis of experimental data in "inert" hydrocarbon solvents, we can expect that the results of absorption-spectrum calculations must reproduce an experimental spectrum of PRODAN in cyclohexane. According to the calculation results (Fig. 2 *a*), two lower closely located singlet states have different orbital nature: the S_1 state – $n\pi^*$-type (29350 cm^{-1}) and S_2 state – $\pi\pi^*$-type (29700 cm^{-1}). The $S_0 \rightarrow S_1$ transition is forbidden in orbital nature: the oscillator strength $f = 7 \cdot 10^{-6}$ and the radiation constant $k_r = 5 \cdot 10^4$ s^{-1}. Hence the major absorption in the long-wavelength spectral band of PRODAN is determined by the electron $S_0 \rightarrow S_2$ transition ($f = 0.04$, $k_r = 3 \cdot 10^7$ s^{-1}). The rate constant of internal conversion $k(S_2 \rightarrow S_1) = 10^9$ s^{-1}. Thus the calculation of the isolated molecule allowed the absorption spectrum of PRODAN in cyclohexane to be adequately described. The energy-level diagram of electronic states shown in Fig. 2 *a* corresponds to the ground-state geometry where the methyl groups in the amino group are rotated from the molecule plane through an angle of 15°. We assumed this rotation with regard for a high negative effective charge on the nitrogen atom. In the plane geometry, the S_1 and S_2 states change their places, however, this affects the absorption spectrum but slightly.

In order to study the fluorescent properties of PRODAN, one should calculate the molecule in the excited-state geometry. It was described in the prevous section that for searching such a geometry we must use the change in the electron density (population) on the bonds and atoms in transition of the molecule into the excited state. These calculated data are listed in Table 1. It follows that the greatest changes in the electron density occur on the C_2–C_3, C_4–C_5, C_7–C_8 , and C_9–C_{10} bonds. The bond lengths (with simultaneous correction for the valence angles in cycles) were changed according to Eq. (2). We assume this modified geometry to correspond to the equilibrium geometry of the excited state of the molecule. The calculations of the electronic spectrum of the molecule in the equilibrium geometry show that the energy of the lower (fluorescent) state S_1 ($\pi\pi^*$) is about 27500 cm^{-1}, which does not agree with the experimental value. Therefore, taking into

TABLE 1. Atomic Populations and Charges on Certain Bonds of an Aromatic Nucleus

Bond	$\Delta P^*_{AB}(S_1)$	$\Delta P^*_{AB}(S_2)$	No. atom	$Q(S_1)$	$Q(S_2)$
1–6	0.024	0.041	1	–0.054	0.023
1–10	0.018	0.010	2	–0.040	–0.052
2–3	0.019	0.068	3	0.020	–0.029
3–4	0.006	0.012	4	–0.114	–0.110
3–12	0.070	–0.026	5	–0.094	–0.031
4–5	0.050	0.061	6	–0.031	–0.003
7–8	0.031	0.070	7	–0.163	0.007
8–9	0.020	0.008	8	0.058	0.139
8–16	0.019	–0.026	9	–0.134	–0.076
9–10	0.034	0.054	10	–0.079	–0.052
12–21	–0.045	0.039	12	0.424	0.352

Note. $\Delta P^*_{AB}(S)$ stands for the bond population in transition of the molecule from the ground state to the corresponding excited S_1 or S_2 state and $Q(S)$ is the atomic charge in the corresponding excited S_1 or S_2 state.

TABLE 2. The MEP Minima. Ground-State Geometry

Molecule	z, Å	S_0, kJ/mol		$S_1(n\pi^*)$, kJ/mol		$S_2(\pi\pi^*)$, kJ/mol	
		N	O	N	O	N	O
PRODAN	0	–	–383	–	–	–	–524
	–1.2	–222	–	– 279	–	–	–

Note. z is the distance from the molecule plane.

account high negative charges on C_4 and C_9 of aromatic nucleus, we further assumed that these two atoms can (partially) go from the sp^2-hybridization to the sp^3 one, that is, go outside the plane of an aromatic part of the molecule. The results with such a "non-plane" equilibrium molecule geometry are shown in Fig. 2 *b*. In so doing, the rotation of the C_4 and C_9 atoms from the plane is 0.28 and 0.26 Å, respectively. Analysis of the wave functions of the excited states with a "non-plane" geometry shows that the σ–π-mixing is insignificant and the orbital nature of the S_1 and S_2-states is affected but slightly. This calculation allowed us to describe an experimental fluorescence spectrum of PRODAN in cyclohexane. The quantum yield of fluorescence from the S_1 ($\pi\pi^*$) state is estimated to be 0.05.

Water is a polar solvent. Consequently, investigating the spectral-luminescent properties of PRODAN in water, we must take into account the specific interactions, that is, complexing with water molecules. The MEP calculations show that the PRODAN molecule in the ground state has two proton-acceptor centres (Table 2). The strongest one is closely related with the O_{21} atom of the CO-group and is localized in the molecule plane. The second one is related to the nitrogen atom of the amino group and is localized above the molecule plane. Under excitation, the MEP values change in different electronic states in a different way due to redistribution of the electronic density. The PRODAN – water-molecule complexes were calculated using the foregoing technique. In the ground-state geometry, the interaction with water over the oxygen atom shifts the $\pi\pi^*$-level to the lower frequency region (from 29700 down to 29600 cm^{-1}), and the $n\pi^*$-level – to the level of higher frequency region (from 29350 up to 29560 cm^{-1}), the interaction over the nitrogen atom shifts the $n\pi^*$-level to the lower frequency region (down to 29250 cm^{-1}), and the $\pi\pi^*$-level – to the higher frequency region (up to 29820 cm^{-1}). In the fluorescent state, the shift of the levels as compared with a free molecule is of similar character: in the interaction over the oxygen, the $n\pi^*$- and $\pi\pi^*$-levels correspond to 28900 and 25250 cm^{-1}, in the complex on nitrogen, the $n\pi^*$- and $\pi\pi^*$-levels correspond to 28300 and 25460 cm^{-1}, that is, the interaction with water molecules insignificantly affects the spectrum resulting from the quantum-chemical calculations for a free PRODAN molecule. Thus, such allowing for specific interaction precludes reproduction of experimental data from spectral-luminescent properties of PRODAN in water.

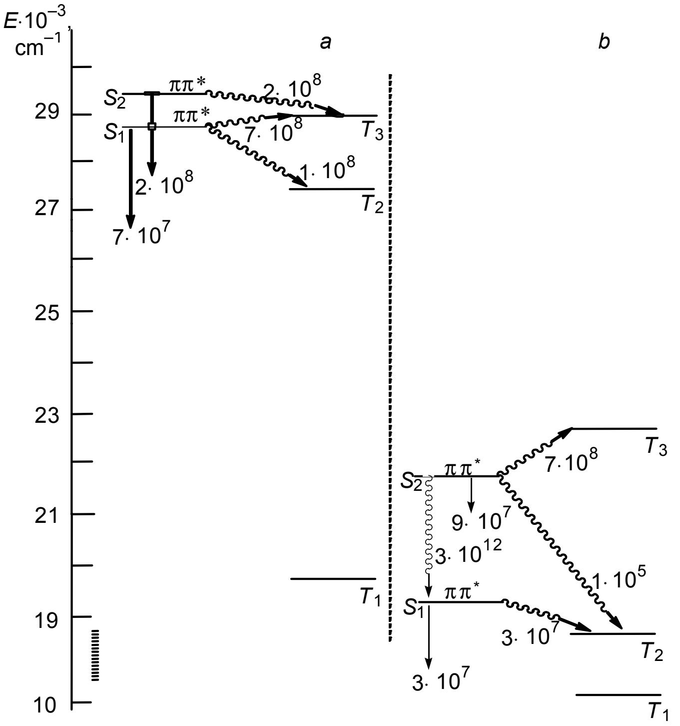

Fig. 3. Energy-level diagram and photoprocesses for the PRODAN – oxygen complex: ground-state geometry (*a*) and equilibrium geometry of the S_1-state (*b*).

It is shown in [9] that there are ionic forms H_3O^+, $H_5O_2^+$, and $H_9O_4^+$ in water, the most stable being $H_2O\cdots H^+\cdots OH_2$. In the case of solution of an organic proton-acceptor molecule (B) in water, there occurs a substitution reaction: the water molecule in $H_5O_2^+$: $H_2O\cdots H^+\cdots OH_2 + B \leftrightarrow H_2O\cdots H^+\cdots B + H_2O$ is substituted by the molecule B, that is, B forms a complex with H_3O^+. Therefore, we decided to examine the PRODAN – H_3O^+ complex. The influence of the PRODAN – H_3O^+ interactions on the oxygen and nitrogen atoms on the shift in the electronic states is similar to the influence of water molecules, however, the shifts are considerably larger in magnitude (6000 cm^{-1}). Taking into account the MEP minima (Table 2), the PRODAN – H_3O^+ complex on the oxygen atom should be considered to be the most stable one. The calculations of the electronic-state energies and photoprocess rate constants determining the spectral luminescent properties of PRODAN in water are shown in Fig. 3. The changes in the electronic density (polulation) on the bonds and atoms in transition of the molecule to the excited state are insignificantly different in this complex model from the data listed in Table 1.

Two lower singlet states are states of the $\pi\pi^*$-type in the geometry of both ground and excited states. Major absorption in the long-wavelength spectral band of PRODAN in water is determined by the $S_0 \to S_1$ transition. The internal-conversion rate for the fluorescent state is estimated to be $k_{ic}(S_1 \to S_0) = 5 \cdot 10^7$ s^{-1}. The calculated quantum yield of fluorescence for the foregoing complex is about 0.24 – far in excess of the experimentally obtained value [2]. This disagreement can result from wrong position of the triplet T_2. It is well-known that significant errors are possible in determination of triplet-state energies [5]. If one assumes energy “degeneracy” of the S_1 and T_2 states, the calculated quantum yield of fluorescence will be about 0.016.

Thus, the results of quantum-chemical calculations of the spectral-luminescent properties of a PRODAN molecule in inert and polar solvents are in good agreement with the available experimental data, provided suitable models are chosen. At the same time, the results must be discussed in a more general context of spectroscopic manifestations of intermolecular interactions.

1. The model structure of complexes proposed in the paper takes no account of the influence of the general (physical, bulk) interaction of the polar solvent on the spectral parameters of the molecule. This influence is generally

described using the so-called solvent function [10–12]. However, the specific (quasi-chemical, structural) interaction of the molecule with the solvent is virtually ignored in such an approach. The problem of distinguishing the contributions from different types of interaction is rather involved and ambiguous and requires further investigation [10].

2. The question on the possible quantity (concentration) of the PRODAN – H_3O^+ complex remains unclear. On the one hand, it is known that the proton concentration in neutral water $[H^+] = 10^{-7}$, that is, much less than the commonly used concentration of the molecule under study. On the other hand, many organic compounds (including PRODAN molecules) are organic bases (alkali). For example, it is shown in the paper that the PRRODAN molecule has two strong proton-acceptor (i.e., base) centers. We believe, that introduction of such molecules into a solution must lead to an increase in ionization of the solvent, at least, in the first coordination sphere. This is in agreement with the interpretation of the water – base interaction made in [9]. The author argues that a number of conditions should be met for the PRODAN – H_3O^+ complex to exist: positively charged proton solvates must occur in the solution; the molecules solvating protons should have unshared electron pairs providing symmetric hydrogen bonding; the heat of proton attachment to the molecule should exceed 170 $\text{kcal}\cdot\text{mol}^{-1}$. This approach allows for mutual influence of the solvent and the compound under study. Hence the formation of an adequate concentration of the PRODAN–H_3O^+ complexes seems quite possible.

CONCLUDING REMARKS

The bands in the long-wavelength absorption spectral bands of the PRODAN molecule are calculated and interpreted. The shifts in the fluorescence bands are due to changes in the molecule geometry in transition from the ground state to the excited one.

A model of PRODAN interaction with the polar proton-donor solvent (water) is proposed. It is shown that the interaction with ionic forms (H_3O^+) results in a pronounced shift of the absorption and fluorescence bands of the molecule.

The major pathway of nonradiative deactivation for the fluorescent state is a singlet-triplet conversion.

The study was supported by the Grant of the Ministry of Education of the Russian Federation (E02-3.2-448).

REFERENCES

1. G. M. Barenboym and A. G. Malenkov, Biologically Active Substances. New Principles of Search [in Russian], Mir, Moscow, 1986.
2. J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic/Plenum Publishers, New York, 1999.
3. G. Weber G and F.G. Farris, Biochemistry, No. 18, 3075 (1979).
4. A. Gordon and R. Ford, The Chemist’s Companion, A Handbook of Practical Data, Techniques, and References, Wiley Interscience, 1972.
5. V. Ya. Artyukhov and A. I. Galeeva, Sov. Phys. J., No. 11, 949 (1986).
6. G. V. Mayer, V. Ya. Artyukhov, O. K. Basyl’, *et al.*, Electronically Excited States and Photochemistry of Organic Compounds [in Russian], Nauka, Novosibirsk, 1997.
7. V. Ya. Artyukhov, J.Struct. Chem., **19**, No. 3, 418 (1978).
8. G. Herzberg, Electronic Spectra and Structure of Polyatomic Molecules, in: Molecular Spectra and Molecular Structure, Van Nostrand, New York, 1966.
9. G. V. Yukhnevich, E. G. Tarakanova, V. D. Mayorov, and N. B. Librovich, Usp. Khim,, **64**, No. 10, 963 (1995).
10. N. G. Bashiev, Spectroscopy of Intermolecular Interactions [in Russian], Nauka, Leningrad, 1972.
11. T. Yoshihara, V. A. Galievsky, S. I. Druzhinin, *et al.*, Photochem. Photobiol. Sci., No. 2, 342 (2003).
12. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Cop. Weinheim, 1988.