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LUMINESCENCE-SPECTRAL CHARACTERISTICS AND CONFORMATIONAL TRANSFORMATIONS IN THE ELECTRONICALLY EXCITED STATE OF THE DIMETHYLAMINOPHENYL DERIVATIVES OF PYRIDINE AND PYRIDINIUM AND PYRYLIUM CATIONS

D. S. Bulgarevich, S. L. Dmitruk,
S. I. Druzhinin, M. I. Knyazhanskii,
E. P. Olekhnovich, B. M. Uzhinov,
and V. A. Kharlanov

The electronic absorption spectra and luminescence-spectral characteristics of the 4-dimethylaminophenyl derivatives of pyridine and pyridinium and pyrylium cations in solutions and polymeric films were studied. The obtained data make it possible to suppose that conformations with the orthogonal arrangement of the donating and accepting fragments (TICT structure) both in the cations and in the neutral molecules are formed as a result of structural relaxation in the excited S_1 *state.*

Study of the conformational behavior in solutions of excited organic molecules containing conjugated fragments capable of rotating about the formal single bonds is of substantial interest for modern photochemistry [1]. During photoexcitation to the nonequilibrium (Frank—Condon) state the balance of the electronic and steric factors determining the equilibrium conformation of the molecule in the S_0 state is destroyed. Structural relaxation is therefore possible both toward greater (TICT structure [2,3]) and toward smaller acoplanarity in the conjugated fragments compared with the ground state (e.g., biphenyl [4], 2,4,6-aryl-substituted pyridinium and pyrylium cations and the isoelectronic pyridines, in which the acoplanarity of the α-aryl rings to the plane of the heterocycle in the S_1 state is reduced [5,6]).

The aim of the present work was to investigate, on the basis of data from the electronic absorption spectra and luminescence-spectral characteristics, the nature of the structural relaxation in compounds for which the two above-mentioned types of relaxation changes in the structure are possible in the excited S_1 state. In this connection we chose the compounds presented below, in which the π-accepting fragments are heterocycles with different accepting ability.

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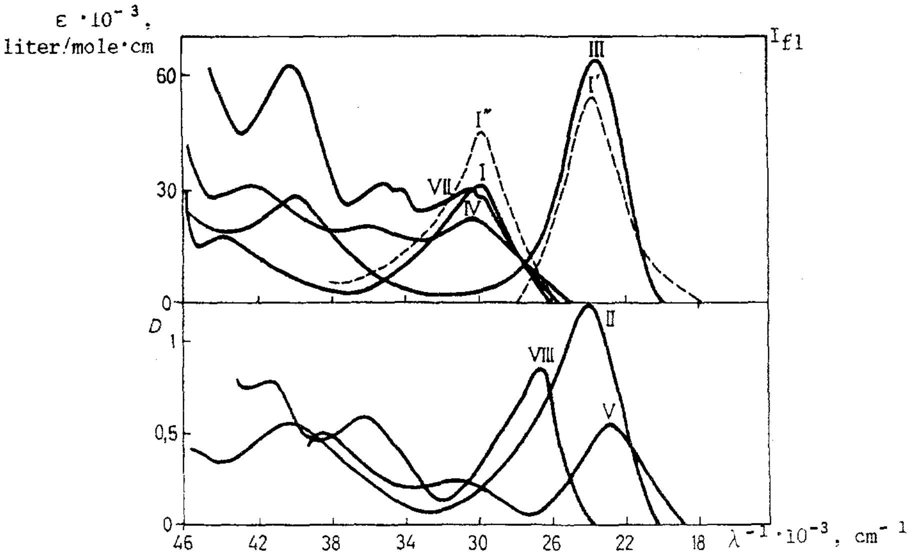
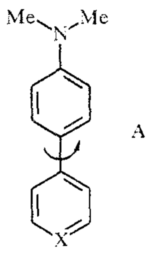
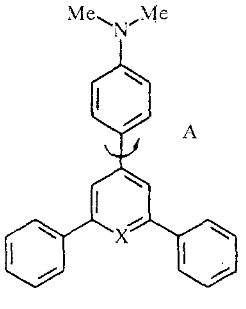


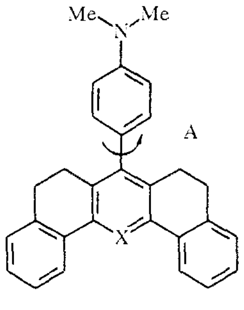
Fig. 1. The UV spectra of compounds (I-V, VII, VIII) (solid line) and the fluorescence (I') and fluorescence excitation (I'') spectra of compound (I) (dotted line) in ethanol at 293 K. II) Sulfuric acid ($C = 1 \cdot 10^{-3}$ M) was added to compound (I) ($C = 2.4 \cdot 10^{-5}$ M). V) Sulfuric acid ($C = 8.2 \cdot 10^{-3}$ M) was added to compound (IV) ($C = 1.8 \cdot 10^{-5}$ M). VIII) Sulfuric acid ($C = 2.9 \cdot 10^{-1}$ M) was added to compound (VII) ($C = 2.5 \cdot 10^{-5}$ M).



I - III



IV - VI



VII -IX

I X=N; II $X=N^+$—H, $A=HSO_4^-$; III $X=N^+$—Me, $A=ClO_4^-$; IV X=N; V $X=N^+$—H, $A=HSO_4^-$; VI $X=O^+$, $A=ClO_4^-$; VII X=N; VIII $X=N^+$—H, $A=HSO_4^-$; IX $X=O^+$, $A=ClO_4^-$

The α-phenyl rings are absent in compounds of the first group (I-III) and are present in the second group (IV-VI). In the third group (VII-IX) the acoplanarity of the α-phenyl substituents is fixed on account of the methylene bridges.

Analysis of the absorption spectra of compounds (I-IX) showed that in the pyridines (I, IV, VII) both with and without α-phenyl rings the positions of the long-wave band in the region of 30 000 cm^{-1} (Table 1, Fig. 1) practically coincide. At the same time in compounds (IV, VII) a new more short-wave band appears in the vicinity of 36 000-34 000 cm^{-1}, and this is close in position to the band for intramolecular charge transfer from the α-phenyl rings for the 2,4,6-triphenylpyridine molecule [6]. In the case of the quaternized forms (V, VIII) [the amount of added sulfuric acid is lower than $1 \cdot 10^{-3}$ M for (II), $8.2 \cdot 10^{-3}$ M for (V), and $2.9 \cdot 10^{-1}$ M for (VIII)] with the introduction of α-phenyl rings into the pyridinium cation (II) a new short-wave band also appears in the region of 31 000 cm^{-1} for compound (V), and this is also close in position to the band for charge transfer from the α-rings for 2,4,6-triphenylpyridinium [6]. The analogous band for compound (VIII) lies in the region of 36 000 cm^{-1}. If the concentration of the added sulfuric acid is higher than the limits indicated above, there is a decrease in the intensity of the absorption in the most long-wave band as a result of protonation of the dimethylamino group. In the case

TABLE 1. The Luminescence-Spectral Characteristics of Compounds (I-IX) in Ethanol and Films of Polymethylmethacrylate (PMMC)

Compound	UV spectrum, λ_{max}^{-1}, cm^{-1}		Fluorescence, λ_{max}^{-1}, cm^{-1}			Stokes shift, cm^{-1}		Quantum yield of fluorescence
	EtOH	PMMC	EtOH		PMMC	EtOH	PMMC	
	293 K		293 K	77 K	293 K	293 K		
I	29900	31000	23800	25300	25300	6100	5700	0,04*; 0,63**
II	24000	24100	20400	21700	21100	3600	3000	10^{-3}*; 0,24***
III	23500	23700	20000	21700	20800	3500	2900	10^{-3}*
IV	30000	29800	21700	24400	25300	8300	4500	0,32*; 0,43**
V	22700	22600	18200	20400	20300	4500	2300	10^{-3}*; 0,33***
VI	18500	18600		16900	16900	—	1700	
VII	30700	31000	20600	25500	25700	10100	5300	10^{-3}*
VIII	26700	26300	23000	23900	23300	3700	3000	0,38*; 0,37***
IX	18000	18100		15300	17000	—	1100	

*The relative quantum yield of fluorescence in ethanol at 293 K.

**At 130 K.

***In a film of PMMC at 293 K.

of the pyrylium salts (VI, IX) the addition of acids leads to a decrease in the intensity of only the most long-wave band [see also data [7] for compound (VI)].

Thus, it can be concluded on the basis of the obtained results that the most long-wave transition in the absorption spectra of all the investigated compounds is due to intramolecular charge transfer from the γ-aryl radical to the heterocycle, while the more short-wave band is determined by charge transfer from the α-phenyl rings. This is also demonstrated by the bathochromic shift of the bands in the series (IV), (V), and (VI), which is probably due to the increase in the accepting ability of the heterocycle, and also by the regular bathochromic shift of the band for charge transfer from the α-aryl radical with increase in its donating capacity, e.g., in the series of 2,4,6-triphenylpyridine [6], 2,6-diphenyl-4-anisylpyridine [6], and compound (IV). From this standpoint the complex nature of the charge-transfer bands for compound (VII) can be explained by the existence, in the solution, of at least two conformers (conrotatory and disrotatory), in which the planes of the α rings are rotated differently in relation to the plane of the heterocycle, and this also determines the different steric hindrances for the α-aryl radical in these conformers.

In fact, as shown for dihydrophenanthrenes and their heterocyclic analogs containing a similar structural fragment [8], conformational flexibility exists for the aryls connected by such an alkyl bridge. The absence of analogous structure in the bands in the spectrum of compound (VIII) and their short-wave shift in relation to the corresponding bands of compounds (II, V) are probably explained by the preponderance of one of the above-mentioned conformers as a result of protonation. Here the conformer with the more acoplanar arrangement of the γ-aryl radical, as in the analogous compounds from [9], may be formed on account of steric hindrances, and this gives rise to the observed short-wave shift of the intramolecular charge-transfer band.

The data obtained on the long-wave absorption spectra and the results from study of the luminescence-spectral characteristics, given below, lead to the conclusion that the observed luminescence-spectral characteristics may be due mainly to the formation of the TICT structure as a result of structural relaxation associated with rotation of the γ-aryl radical. In this case it is supposed that it is the whole γ-aryl radical and not one dimethylamino group that rotates, and this assumption was made by analogy with the conclusion in [10,11].

In fact, the most long-wave transition in the absorption spectra of all the investigated compounds is due to charge transfer from the γ-aryl substituent to the heterocycle, and this is an essential condition for the formation of the TICT state [2,3]. In contrast to the analogs not containing dimethylamino group [6], in the molecules of the pyridines (I, IV, VII) there is a significant increase in the Stokes shift of the fluorescence band with increase in the polarity of the solvent (Table 2), and this is also typical of TICT systems [2,3]. Here the absorption spectra and the excitation spectra of the single fluorescence band observed in all the compounds coincide (Fig. 1).

TABLE 2. The Effect of the Nature of the Solvent on the Luminescence-Spectral Characteristics of Compounds (I, IV, VII)

Solvent	UV spectrum, λ_{max}^{-1}, cm^{-1}*			Fluorescence, λ_{max}^{-1}, cm^{-1}			Stokes shift, cm^{-1}		
	compound			compound			compound		
	I	IV	VII	I	IV	VII	I	IV	VII
Acetonitrile	30700	30000	30800	24300	21200	20600	6400	8800	10200
Ethyl acetate	31000	30100	30900	25300	23500	23300	5700	6600	7600
Hexane	31900	30900	31000	27600	26700	27000	4300	4200	4000

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*The position of the maximum of the most long-wave band.

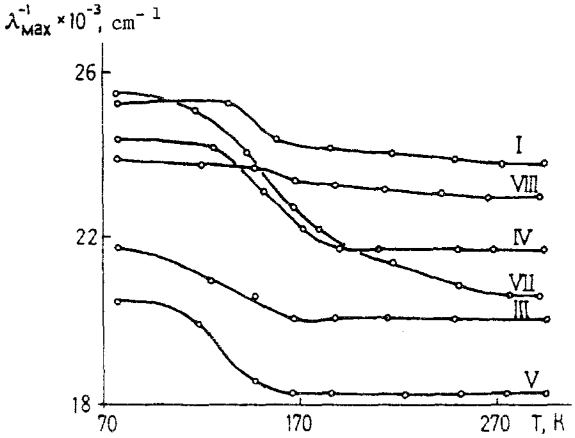

Fig. 2. The dependence of the positions of the maxima in the fluorescence bands of compounds (I, III, IV, V, VII, VIII) in ethanol with variation of temperature.

The following experimental data may indicate realization of the structural relaxation process in the S_1 state and its retardation in media with increased viscosity. Decrease in the temperature of the ethanol solutions of compounds (I, III-V, VII, VIII) (Fig. 2) in the region of high solvent viscosities leads to a short-wave shift of the fluorescence bands and to an increase in the quantum yields of fluorescence [particularly for the quaternized forms of compounds (III, V) and pyridine (I)] and also to the appearance of fluorescence in the pyrylium salts (VI, IX), which is absent in these compounds in nonviscous solvents at 293 K. Increase in the quantum yields of fluorescence and good agreement between the maxima of the fluorescent bands in films and solutions at 77 K are also observed in films of polymethylmethacrylate (PMMC, Table 1). The obtained results also correspond to the theories about the formation of weakly fluorescent or nonfluorescent TICT states in systems with clearly defined acceptor function [3].

As mentioned earlier, in compounds (VII, VIII) even in the ground state the orientation of the γ-radical is close to the TICT structure by virtue of steric interactions. The hypothesis about the attainment of the TICT state after photoexcitation is therefore confirmed by the small increase in the quantum yield of fluorescence with decrease in the temperature of the solution of compound (VII) and in the film of PMMC and also by the presence of phosphorescence in compounds (VII) and (VIII) in ethanol at 77 K with λ_{max} 455, 485, 520 and λ_{max} 480, 510 nm and an inflection at 550 nm. Here the significant hypsochromic shift of the maximum of the fluorescence band of compound (VII) with decrease of temperature (Fig. 2) compared with (VIII) is probably due to the larger contribution from solvent relaxation for compound (VII) and also to a possible conformational transition with decrease in temperature. The fluorescence lifetimes of compounds (IV) and (VIII) in ethanol at 293 K were 2.4 and 3.1 nsec respectively.

Thus, the obtained data give reason to suppose that as a result of photoexcitation and of structural relaxation in the S_1 state a conformation with a close to orthogonal arrangement of the γ-aryl and heteroaromatic rings, which corresponds in its characteristic features to the TICT state, is realized for compounds (I-IX) in solutions (in contrast to the analogous systems without the dimethylamino group). Further evidence for the formation of the TICT state in compounds (I-IX) requires further investigations.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrophotometer for thin layers in Vaseline oil. The PMR spectra of compounds (III, IV) were obtained on a Tesla BS-567A instrument at 100 MHz, and the spectrum of the pyrylium salt (IX) was obtained on a Tesla BS-487C instrument at 80 MHz with HMDS as internal standard.

The elemental analyses agreed with the calculated data.

The absorption spectra were measured on a Shimadzu 3100 spectrophotometer, and the fluorescence spectra on an Élyumin 2M spectrophotometer. The kinetics of fluorescence quenching were studied by counting the single photons on an SP-70 spectrophotometer. The optical density of the working solutions with a layer thickness of 10 mm amounted to 0.1-0.3 and 0.2-0.8 for fluorescence and absorption respectively. The concentrations of the compounds under these conditions were $3 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ M. The quantum yields of fluorescence were determined by the standard procedure [12]. The standard for compounds (I, IV) was a solution of quinine bisulfate in 0.1 N sulfuric acid with a quantum yield of fluorescence of 0.546 [13]. The number of absorbing components in the acid—base equilibrium was determined according to the procedure from [14,15]. For the calculation we used 11-13 solutions with different acid contents and 20-25 wavelengths for each of the solutions. The solvents for the luminescence-spectral measurements were purified by standard procedures [16]. All the compounds except (I) (the industrial reagent) were synthesized specially in the present work.

1-Methyl-4-(4′-dimethylaminophenyl)pyridinium Perchlorate (III) ($C_{14}H_{17}ClN_2O_4$). To a solution of 2 g (6 mmole) of 1-methyl-4-(4′-dimethylaminophenyl)pyridinium iodide (obtained by the method in [17]) in 15 ml of acetonitrile we added a solution of 1.75 g (6 mmole) of sodium triphenylcyanoborate in 5 ml of acetonitrile. The mixture was boiled for 10 min, and the product was filtered off, dried, and recrystallized from isopropyl alcohol. The yield of 1-methyl-4-(4′-dimethylaminophenyl)pyridinium triphenylcyanoborate was 2.1 g (71%), and the product formed light-yellow crystals melting at 192°C (from isopropyl alcohol). IR spectrum, cm^{-1}: 1647, 1593; 2180 ($C \equiv N$). To a solution of 2.1 g (4 mmole) of the obtained pyridinium triphenylcyanoborate in 15 ml of acetic acid in a fume cupboard we added 5 ml (10 mmole) of 57% perchloric acid dehydrated with acetic anhydride. The solution was boiled with a reflux condenser for 30 min, and the precipitate that separated after cooling was filtered off and recrystallized from isopropyl alcohol. The product formed yellow crystals melting at 258°C (from isopropyl alcohol). IR spectrum, cm^{-1}: 1647, 1607, 1567; 1093 (ClO_4^-). PMR spectrum (CD_3CN): 3.27 (6H, s, $2CH_3$); 4.31 (3H, s, CH_3); 7.3-8.3 (8H, m, aromatic protons). The yield was 1 g (80%).

Compounds (IV, VI) are well-known and were obtained by the respective procedures in [18,19]. Their characteristics agreed with published data [7,18].

1,2,7,8-Tetrahydro-9-(4′-dimethylaminophenyl)dibenzo[ch]acridine (VII) ($C_{29}H_{26}N_2$). The compound was obtained by the method in [19] starting from the corresponding pyrylium salt (IX) (described below). The product formed pale-green crystals melting at 277°C (from isopropyl alcohol). IR spectrum, cm^{-1}: 1600, 1520. PMR spectrum (nitrobenzene-d_5): 3.0 (8H, m, $4\text{-}CH_2$); 3.2 (6H, s, $2\text{-}CH_3$); 7.4-8.5 (12H, m, aromatic proton). The yield was 81%.

1,2,7,8-Tetrahydro-9-(4′-dimethylaminophenyl)-dibenzo[ch]xanthylium Perchlorate (IX) ($C_{29}H_{26}ClNO_4$). A mixture of 3 g (20 mmole) of p-dimethylaminobenzaldehyde, 9 ml (60 mmole) of α-tetralone, and 30 ml (60 mmole) of 57% perchloric acid dehydrated with acetic anhydride (the main difference from the method in [18]) was brought to boiling and slowly cooled. The dark-orange crystals that separated were filtered off and recrystallized from isopropyl alcohol; mp >300°C (from isopropyl alcohol). IR spectrum, cm^{-1}: 1606, 1567, 1507; 1100 (ClO_4^-). PMR spectrum (trifluoroacetic acid): 2.6 (8H, m, $4\text{-}CH_2$); 3.1 (6H, d, $2\text{-}CH_3$); 7.3-8.3 (12H, m, aromatic protons). The yield was 4.88 g (50%).

In the working range of added sulfuric acid concentrations [up to $1 \cdot 10^{-3}$ M for (II), $8.2 \cdot 10^{-3}$ M for (V), and $2.9 \cdot 10^{-1}$ M for (VIII)] the formation of compounds (II, V, VIII) protonated only at the nitrogen of the heterocycle and not at the dimethylamino group and the absence of joint protonation at these centers is demonstrated by the more long-wave position of their absorption spectra compared with the initial pyridines (Table 1, Fig. 1), as also in the systems without the dimethylamino group [6]. The absence of joint protonation at the basic centers is confirmed by calculation of the number of absorbing components, not counting the acid in the acid—base equilibrium, which in systems (I-II) and (IV-V) was equal to two (the initial base and the protonated form). Protonation of the dimethylamino group also occurs at acid concentrations above the indicated limits.

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