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SPECTRAL AND QUANTUM-CHEMICAL STUDY OF SOME HETEROANALOGS OF 1,4-BIS(5-PHENYL-2-AZOLYL)BENZENES

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The effect of structural changes in the molecules of thiophene and furan analogs of 1,4-bis(5-phenyl-2-azolyl)benzenes on their electronic spectra was studied by the MO LCAO method within the π-electron approximation.

One of the most effective organic luminophores that are widely used in scintillation technique is 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP, I).

I

The spectral-luminescence properties of POPOP and its various functional substituted derivatives have been investigated quite thoroughly [1].

The aim of the present research was to study the spectral-luminescence properties of our previously synthesized [2] heteroanalogs of I containing alternating oxazole, 1,3,4-oxadiazole, thiophene, and furan residues in various combinations (see Table 1).

The absorption spectrum of POPOP in toluene consists of one intense (ε 52,000) slightly structure band [1]. According to quantum-chemical calculations carried out within the π-electron approximation, this band is formed by a single-configuration $S_0 \rightarrow S_1^*$ transition of the π,π^* type and is associated with transfer of electron density from the oxazole rings and, to a lesser extent, from the terminal phenyl radicals to the central phenylene fragment of the molecule (Table 2). In the ground state the central benzene ring is a weak electron-density donor. A negative charged is shifted to the oxazole rings and to the terminal phenyl radicals. The polarization changes on excitation to the S_1^* state, and the central fragment becomes a π-electron acceptor.

The successive replacement of one and two oxazole rings in the POPOP molecule by 1,3,4-oxadiazole rings (Table 1, II and III) leads to a small degree of redistribution of the electron density: the terminal phenyl radical bonded directly to the oxadiazole ring acquires weakly expressed donor character even in the ground state (Table 2). Nevertheless, this does not affect the principles of the formation of the long-wave band, and the character of the spectrum does not change on passing from I to II and III. Only a short-wave shift of the absorption maxima (Table 1) caused by a decrease in the diene character of the azole heteroring is observed [5].

It must be noted that the $S_0 \rightarrow S_1^*$ transition in all of the examined cases is localized on the three central rings of the molecules with almost no involvement of the terminal phenyl radicals, as evidenced by the number of localizations (see Table 2). As a result, replacement of the outer benzene rings in the II and III molecules by thiophene (IV and V) or furan (VI and VII) rings has little effect on the character and position of the long-wave absorption band (Table 1) and is manifested only in an increase in the extinction coefficient (ε). The small bathochromic shift of this band (4-15 nm) is associated with the stronger (as compared with the phenyl ring) electron

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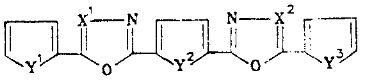
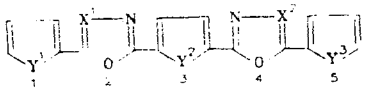
TABLE 1. Characteristics of I-XII



Compound*	X¹	X²	Y¹	Y²	Y³	Absorption (in toluene)		Fluorescence (in toluene)		Δν, cm⁻¹
						λ_{max} nm	$\varepsilon\cdot10^{-3}$	λ_{max} nm	η	
I	CH	CH	CH=CH	CH=CH	CH=CH	365	52,0	415	0,41	3300
II	CH	N	CH=CH	CH=CH	CH=CH	350	44,5	405	0,57	3880
III	N	N	CH=CH	CH=CH	CH=CH	330	—	372	—	3420
IV	CH	N	CH=CH	CH=CH	S	356	46,4	412	0,63	3820
V	N	N	S	CH=CH	S	345	51,8	393	0,50	3540
VI	CH	N	CH=CH	CH=CH	O	354	45,1	410	0,71	3860
VII	N	N	O	CH=CH	O	340	42,5	388	0,67	3640
VIII	CH	CH	CH=CH	S	CH=CH	390	44,5	457	0,29	3760
IX	CH	N	CH=CH	S	CH=CH	375	34,4	443	0,26	4090
X	N	N	CH=CH	S	CH=CH	350	42,2	410	0,25	4180
XI	CH	N	CH=CH	S	S	380	39,9	445	0,29	3840
XII	N	N	S	S	S	365	45,5	425	0,30	3870

*According to the data in [3] for I and II, and according to [4] for III.

TABLE 2. Calculated Characteristics of I, II, and VIII



Compound	$E_{S^*_0\to S^*_1}$, eV*	Fragment	Charges on the fragments		No. of localizations in the fragments, %
			S_0	S^*_1	
I	3,45 (3,40)	1	−0,010	+0,016	8
		2	−0,005	+0,041	28
		3	+0,034	−0,110	28
		4	−0,005	+0,041	28
		5	−0,010	+0,016	8
II	3,54 (3,54)	1	−0,012	+0,030	11
		2	−0,005	+0,080	36
		3	+0,033	−0,086	29
		4	−0,035	−0,045	19
		5	+0,021	+0,021	5
VIII	3,22 (3,18)	1	−0,013	−0,003	7
		2	−0,025	−0,041	27
		3	+0,076	+0,088	32
		4	−0,025	−0,041	27
		5	−0,013	−0,003	7

*The experimental data obtained in toluene are presented in parentheses.

donor effect of the thiophene and furan rings. At the same time, replacement of the central benzene ring in I-III by a thiophene ring (VIII-X) leads to a significantly greater bathochromic shift (20-25 nm) and to a decrease in ε. The long-wave shift of the band in the case of XI and XII is the sum of the effects of replacement of the central and terminal benzene rings by thiophene rings.

Thus the nature of the bathochromic shift of the absorption bands when the aromatic fragments in the 1,4-bis(5-phenyl-2-azolyl)benzene molecules by heterocycles differs.

It is interesting to note that in all of the investigated I-XII with structures of the POPOP type the $S_0 \rightarrow S_1^*$ transition is accompanied by an increase in the order of the C—C (chiefly intercyclic), C—N, and N—N bonds, while the orders of the C=C, C=N, C—O, and C—S bonds decrease. The increase in the double-bond character between the fragments formally attests to flattening of the molecules upon excitation.

TABLE 3. Spectral-Luminescence Characteristics of IV-VII in DMF

Compound	Absorption		Fluorescence		Δ, cm^{-1}
	λ_{max}, nm	$\varepsilon \cdot 10^{-3}$	λ_{max}, nm	η	
IV	350	48,8	428	0,53	5210
V	339	50,6	403	0,60	4680
VI	350	44,4	427	0,57	5150
VII	332	52,9	410	0,65	5730

The emission bands of the investigated compounds by and large are subject to the same principles as the long-wave absorption bands. Replacement of the oxazole rings by oxadiazole rings leads to a hypsochromic shift of the maxima. The introduction of thiophene or furan rings gives rise to an appreciable long-wave shift; the effect from replacement of the central benzene ring is expressed more strongly than in the case of the terminal phenyl radicals.

In connection with the fact that the $S_1^* \rightarrow S_0$ transition responsible for the development of fluorescence is localized primarily on the three central rings, the quantum yield (η) also depends on the location of the thiophene ring. If this heteroring is located in the center of the molecule (VIII-X), the sulfur atom has a quenching effect, while terminal 2-thienyl radicals (IV and V) lead to an increase in the integral intensity of the luminescence. In addition, weak spin-orbital interaction caused by the presence of a "heavy" atom also occurs in this case, as evidenced by the small increase in η when the terminal thiophene rings are replace by furan rings (VI and VII). The "heavy"-atom effect prevails in the XI and XII molecules, and their quantum yields approach those for IX and X (see Table 1).

The fluorescence spectra of IV-XII in toluene are narrower and more structured bands than the absorption curves, which, in conjunction with the somewhat increased Stokesian shifts, attests to flattening of the molecules on passing from the ground state to the excited state.

Smoothing out of the vibrational structure in the electronic spectra, which is probably associated with intensification of the interaction of the luminophore molecules with the solvent, occurs when toluene is replaced by DMF; the increase in the Stokesian shifts (Table 3) is achieved due to a weak hypsochromic shift of the absorption bands and a more pronounced long-wave shift of the fluorescence maxima. Thus the spectral data provide evidence for better solvation of the luminophore molecules in DMF as compared with solvation in toluene; because of the greater polarizability of the molecules in the excited state, the energy of solvation of the S_1^* state is greater than that of the S_0 state.

On the basis of an examination of the spectral-luminescence properties of compounds with chain structures of the POPOP type we singled out the following basic principles of the formation of their electronic spectra.

1. The intense long-wave absorption band corresponds to a single-configuration permitted transition to the first excited singlet state. This transition is polarized along the long axis of the molecule. The short-wave bands have low intensities and are formed by multiconfiguration transitions, which are generally forbidden.

2. In both the ground and first excited state the nitrogen atoms of the azole rings bear significant negative π charge and are capable of serving as electron donors, while the sulfur and oxygen atoms are electron-density impoverished and can act as acceptors. During electron transitions the charges on the heteroatoms and, consequently, their donor or acceptor capacities change only slightly.

3. Excitation to the S_1^* state is accompanied by a pronounced change in the bond orders, particularly of the intercyclic bonds and in the central fragments; the orders of the C—C, C—N, and N—N bonds increase, while the orders of the C=C, C=N, C—O, and C—S bonds decrease.

4. The $S_0 \rightarrow S_1^*$ electron transition is ≈80% localized on the three central rings, and the replacement of the central benzene ring by a heteroring therefore causes a more pronounced bathochromic and bathofluoric shift of the spectra than the replacement of the terminal rings. The presence of a thiophene ring in the center of the molecule gives rise to a decrease in the quantum yield and the molar absorption coefficient, while the presence of outer 2-thienyl radicals increases ε and the integral intensity of the luminescence.

EXPERIMENTAL

The electronic absorption spectra were recorded with an SF-16 spectrophotometer, while the fluorescence spectra and quantum yields were recorded with an apparatus consisting of a ZMR-3 monochromator, an FÉU-18 photoelectron multiplier, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a quartz monochromator. The absolute fluorescence quantum yields were determined by the equal-absorption method [6] and were adjusted by taking into account the coefficients of the spectral sensitivity of the apparatus. The quantum-chemical calculations were made by the Pariser—Parr—Pople method [7, 8]. The number of localizations in the fragments was calculated in accordance with [9]. The purity of the substances was monitored by TLC.

We described the synthesis of III-IX and XI in [2].

2,5-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)thiophene (X). A 0.02-mole sample of thiophene-2,5-dicarboxylic acid dichloride [10] was added slowly with vigorous stirring at 18-22°C to a suspension of 0.04 mole of benzhydrazide in 50 ml of dry pyridine, after which the mixture was stirred for 3 h at 45-50°C and then transferred to 200 ml of water. The resulting precipitate was washed with water until the wash water was neutral, removed by filtration, and dried.

The condensation product obtained was refluxed in 80 ml of phosphorus oxychloride for 4 h, after which the mixture was cooled to 18-22°C and poured over ice. The resulting precipitate was washed until the wash water was neutral, removed by filtration, and dried. The product was chromatographed with a continuous-operation column using Al_2O_3 as the adsorbent (elution with trichloroethylene) and recrystallized from dioxane to give a substance with mp 288-289°C. The yield was 5.2 g (70%).

2,5-Bis[5-(2-thienyl)-1,3,4-oxadiazol-2-yl]thiophene (XII). This compound was obtained in the same way as X using an equimolar amount of thiophene-2-carboxylic acid hydrazide instead of benzhydrazide and had mp 260-262°C. The yield was 9.7 g (86%).

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