SPECTRAL-LUMINESCENCE PROPERTIES OF SOME 2,5-DIHYDROXY-1,4-DI(AZOL-2-YL)BENZENES

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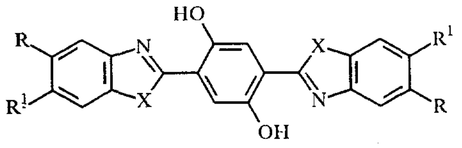
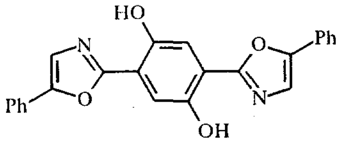
The influence of the type of azole fragments and substituents on the spectral-luminescence properties of a series of 2,5-dihydroxy-1,4-di(azol-2-yl)benzenes, possessing an anomalously high Stokes shift, was investigated.

The 2,5-dihydroxy-1,4-di(benzene-2-yl)benzenes, which are characterized by the presence of intramolecular hydrogen bonds of the hydroxyl groups with the nitrogen atoms of the adjoining heterocycles, possess an anomalously high Stokes shift caused by the intramolecular photo-transfer of the proton of the hydroxyl group to the nitrogen atom of the heterocycle on excitation [1, 2].

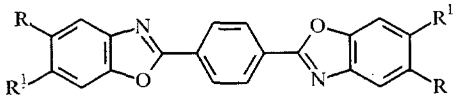
With the object of studying the dependence of the spectral-luminescence properties of different 2,5-dihydroxy-1,4-di(azol-2-yl)benzenes on the type of the azole fragments and the substituents, we synthesized the hydroxyl-containing compounds (Ia-e) and (II) and some of their analogs (IIIa-c) not containing hydroxyl groups.



Ia-e



II



IIIa-c

Ia-c X = O, d X = NH, e X = NMe; Ia, c, IIIa, c R = H, Ib, IIIb R = t-Bu; Ia, b, IIIa, b R^1 = H, Ic, IIIc R^1 = NEt_2; Id, e R = R^1 = H

The 2,5-dihydroxy-1,4-di(6-diethylaminobenzoxazol-2-yl)benzene (Ic), 2,5-dihydroxy-1,4-di(1-methylbenzimidazol-2-yl)benzene (Ie), the benzoxazoles (Ia) and (IIIa, b), and the benzimidazole (Id) were obtained by the condensation of the corresponding o-aminophenols or o-phenylenediamines with 2,5-dihydroxyterephthalic acid or with terephthalic acid in polyphosphoric acid by analogy with the method of [3]. The 2,5-dihydroxy-1,4-di(5-tert-butylbenzoxazol-2-yl)benzene (Ib) and the benzoxazole (IIIb) were obtained by the condensation of 4-tert-butyl-2-aminophenol with diethyl 2,5-dihydroxyterephthalate or with terephthalic acid in chlorobenzene in the presence of boric acid by analogy with the data of the work [4]. The 2,5-dihydroxy-1,4-di(5-phenyloxazol-2-yl)benzene (II) was obtained by the reaction of phenacylamine hydrochloride with 2,5-dihydroxyterephthalic acid in phosphorus oxychloride according to the method of [5].

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TABLE 1. Characteristics of the 1,4-Di(azol-2-yl)benzenes

Compound	X	R	R^1	Empirical formula	mp, °C	Absorption in DMF, λ_{max}, nm (log ε)	Luminescence in DMF		$\Delta\nu_s$, cm^{-1}	Yield, %
							λ_{max}, nm	φ		
Ia*	O	H	H			321 (4,50), 337 (4,54), 392 (4,38), 407 (4,38)	460, 600	0,06	2830, 7900	
Ib	O	*t*-Bu	H	$C_{28}H_{28}N_2O_4$	350	325 (4,57), 342 (4,61), 393 (4,45), 410 (4,46)	460, 600	0,06	2650, 7720	88
Ic	O	H	NEt_2	$C_{28}H_{30}N_4O_4$	288...290	412 sh. (3,58), 447 (4,73), 468 (4,73)	573	0,79	3920	73
Id*	NH	H	H			317 (4,51), 333 (4,66), 386 (4,45), 403 (4,48)	434, 553	0,06	1770, 6730	
Ie	NMe	H	H	$C_{22}H_{18}N_4O_2$	330	310 (4,32), 370 (4,15)	430, 558	0,01	3770, 9110	82
II				$C_{24}H_{16}N_2O_4$	299...301	329 (4,33), 346 (4,35), 392 (4,57), 414 (4,60)	448, 595	0,12	1830, 7350	80
IIIa*		H	H			327, 341**, 358	395**, 413	0,62	4010	
IIIb*		*t*-Bu	H			330, 347**, 364	402**, 421	0,70	3942	
IIIc*		H	NEt_2			430 (4,60), 310 sh. (3,48)	556	0,80	5270	

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*The compounds were obtained according to the methods in [3-5].

**The main maximum.

The investigation of the electronic absorption spectra of the synthesized compounds (Ia-e) and (II) showed that the presence of hydroxyl groups, able to form intramolecular hydrogen bonds with the nitrogen atoms of the heterocycles, in the central benzene fragment changes the character of the spectra by comparison with 1,4-di(azol-2-yl)benzenes and displaces them to the long-wave region (cf. Table 1). Thus, the spectrum of the compound (Ia) in DMF is displaced bathochromically by more than 60 nm in comparison with the spectrum of the substance (IIIa), and agrees with its previously described spectrum [2] in heptane. For the benzimidazole (Id), the character of the spectrum is preserved as for the benzoxazole (Ia); only an insignificant hypsochromic shift is observed. The significant hypsochromic shift of 33 nm for the long-wave absorption maximum of the benzimidazole (Ie) by comparison with (Id) may be explained by the breakdown of the conjugation due to the decrease in the coplanarity of the molecule in consequence of steric hindrance caused by methyl groups in the imidazole fragments. The analogous effect was observed for methyl-substituted p-tert-phenyls [6]. The spectrum of the oxazole (II) has the same character as the spectrum of the benzoxazole (Ia), and shows an insignificant bathochromic shift.

As was to be expected, the introduction of tert-butyl groups at the position 5 of the benzoxazole fragments produces virtually no change in the spectrum of the compound (Ib) by comparison with (Ia), but leads to a significant increase in the solubility in organic solvents. The introduction of the electron-donor diethylamino groups at the position 6 of the benzoxazole fragments leads to the significant bathochromic shift of the long-wave absorption maximums of the benzoxazoles (Ic) and (IIIc) by comparison with the unsubstituted compounds (Ia) and (IIIa) correspondingly.

The luminescence spectra of the azoles (Ia, b, d) and (II) have short-wave (430-460 nm) and stronger long-wave (550-600 nm) luminescence bands in contrast to the single-band spectra, with vibrational structure appearing in (IIIa, b), for compounds of analogous structure, not containing hydroxyl groups. This agrees with the presentations of [2], according to which an equilibrium between the molecules (A) with the intramolecular hydrogen bond and the molecules (B), in which the proton of one hydroxyl group is transferred to the nitrogen atom of the heterocycle, is established in the excited state. In conformity with this, the short-wave luminescence is determined by the emission of molecules occurring in the form A, and is characterized by the Stokes shift of 1770-3770 cm^{-1} not exceeding the usual value for diazolylbenzenes; the long-wave luminescence with the anomalously high Stokes shift (6730-9110 cm^{-1}) is determined by the emission of molecules occurring in the form B. The ratio of the intensities of the short-wave and long-wave luminescence bands is individual for each compound; this indicates the varying ratio of the A and B forms in different compounds.

The luminescence spectra of the oxazoles (Ia, b) and (II) show little mutual difference. The absence of significant differences in the luminescence spectra of the benzimidazoles (Id) and (Ie) indicate the virtual identical degree of coplanarity of their molecules in the excited state. The benzimidazoles (Id, e) luminesce in a region of shorter wavelength than the oxazoles (Ia, b); this is in accord with the literature data for 2-(2-hydroxyphenyl)benzoxazole from 2-(2-hydroxyphenyl)benzimidazole [7, 8].

The introduction of diethylamino groups at the position 6 of the benzoxazole fragments gives a sharp change to the character of the luminescence spectrum of compound (Ic) by comparison with (Ia), making it a single-band spectrum. The disappearance of the short-wave luminescence is probably caused by the fact that the molecules of (Ic) only occur in the form B in the excited state. It is probable that the electron-donor effect of the diethylamino groups, which increases the basicity of the heterocyclic nitrogen atoms significantly, facilitates the intramolecular transfer of the proton in the excitation.

The absolute quantum yields of the luminescence, φ, are insignificant for the majority of the investigated azoles; their value does not exceed 0.06 for the compounds (Ia, b, d, e), and it comprises 0.12 for the oxazole (II), which is significantly less than for their analogs not containing hydroxyl groups. The presence of diethylamino groups at the positions 6 of the benzoxazole fragments in the compound (Ic) leads to an increase of the φ by an order of magnitude in comparison with the unsubstituted (Ia). The quantum yield becomes the same as in the analogously structured compound (IIIc), not containing hydroxyl groups.

EXPERIMENTAL

The electronic absorption spectra of the investigated compounds were measured on a Unicam SP-8000 spectrophotometer. The luminescence spectra were measured on an installation of the SDL-1 type, assembled on the basis of the MDR-1 monochromator. Luminescence was excited by light of the DKSSh-1000 lamp, separated with the MDR-3 monochromator. The spectra were corrected for the spectral sensitivity of the instrument. The Stokes shift was determined as the difference of the strongest long-wave absorption maximum and the main maximum of the luminescence. The absolute quantum yields of the luminescence were determined by the relative method; the standard utilized was the ethanolic solution of 3-aminophthalimide ($\varphi = 0.6$ [9]).

The 2,5-dihydroxy-1,4-di(azol-2-yl)benzenes (Ia-e) and (II) and the 1,4-di(benzazol-2-yl)benzenes (IIIa-c) were synthesized by analogy with known methods for the synthesis of 2-aryl-azoles [3-5]. For the isolation of analytical samples of the compound, (Ia, c-e) and (II) were recrystallized from DMF, and the compound (Ib) was recrystallized from benzene. The data of the elemental analysis for C, H, and N for the compounds (Ib, c, e) and (II) correspond with the calculated data.

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