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STRUCTURE AND SPECTROLUMINESCENCE PROPERTIES OF DERIVATIVES OF 1,8-NAPHTHOYLENE-1′,2-BENZIMIDAZOLE WITH SUBSTITUENTS OF VARIOUS ELECTRONIC TYPES

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A series of quantum-chemical calculations using the CNO SCF CI method were carried out to account for the nontraditional influence of substituents of various electronic types on the spectroluminescence characteristics of naphthoylenebenzimidazole. It is shown that the principal direction of electron-density redistribution during excitation of this molecule is the charge transfer from its benzene fragment to its naphthalene fragment, and the most appreciable change in spectrofluorescence characteristics compared to the unsubstituted compound is achieved by introducing electron-donor substituents into the benzimidazole fragment, and in electron-acceptor characteristics, into the naphthalene fragment of the naphthoylenebenzimidazole molecule.

Derivatives of 1,8-naphthoylene-1′,2′-benzimidazole (I) are known as efficient phosphors whose range extends from 500 nm to 650 nm. Various compounds of this series are used in luminescence flaw detection as fluorescent dyes for various polymeric materials, in scintillation technology, and in biological studies [1]. There also have been synthesized a large number of compounds whose composition, in addition to nucleus I, also includes other heterocycles such as the imidazole, oxazole and pyrazoline heterocycles, etc. [2, 3].

At the same time, despite the large number of publications dealing with the synthesis of derivatives of I, questions related to the spectroscopy of compounds of this series, and in particular, to the influence of the position and electronic type of the introduced substituents or new structural fragments have not been adequately discussed in the literature. Quantum-chemical calculations for the molecule of I were carried out back in the 1960s [4] and are chiefly aimed at studying its reactivity.

The purpose of the present study was to determine the fundamental spectral properties as a function of the structure of naphthoylenebenzimidazole derivatives with substituents of various electronic types. The main emphasis will be placed on the 4, 5, 4′, and 5′ positions, the methods of introduction of substituents into which were elaborated in the greatest detail in [1-3].

The experimental characteristics of the absorption and emission spectra of certain derivatives of I are listed in Table 1. Let us mention a few interesting points in the behavior of the compounds studied that cannot be explained solely on the basis of general considerations regarding the influence of the substituents on the spectra. Thus, the long-wavelength portion of the absorption spectrum of compound II, which contains a strong acceptor substituent, the SO_2CF_3 group, has practically the same position as that of the unsubstituted compound I. The fluorescence spectrum of compound II is shifted to the short-wavelength region by only 1000 cm^{-1} relative to the spectrum of compound I. An analogous effect — the absence of appreciable changes in the spectra — is also observed when an acceptor substituent is introduced into the benzene fragment of compound III (see the spectral characteristics of compounds III and IV). At the same time, the acceptor substituent — an acetyl group, introduced into the naphthalene fragment — causes a shift of the fluorescence spectrum that exceeds the shift due to the introduction of an $N(CH_3)_2$ group. However, the introduction of this distinct electron-donor substituent into the 4 position of the naphthalene fragment has no appreciable effect on the fluorescence spectrum, whereas in the absorption spectrum of compound III, an

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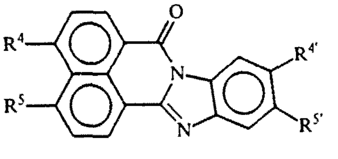
TABLE 1. Spectroluminescence Characteristics of Certain Derivatives of Naphthoylenebenzimidazole in Toluene and Dimethylformamide



Compound	R¹	R²	Toluene			Dimethylformamide		
			ν^a, cm^{-1} λ^a, nm	ν^f, cm^{-1} λ^f, nm	$\Delta\nu_{ST}$, cm^{-1}	ν^a, cm^{-1} λ^a, nm	ν^f, cm^{-1} λ^f, nm	$\Delta\nu_{ST}$, cm^{-1}
I	H	H	25970 385	20410 490	5560	25970 385	19800 505	6170
II	H	5'-SO_2CF_3	25640 390	21510 465	4130	25970 385	21050 475	4920
III	4-$(CH_3)_2N$	H	23260 430	20410 490	2850	22620 442	19610 510	3010
IV	4-$(CH_3)_2N$	5'-SO_2CHF_2	22730 440	19610 510	3120	21980 455	18520 540	3460
V	5-CH_3CO	H	24880 402	19420 515	5460	25320 395	19420 515	5900
VI	H	4'-OC_2H_5	25770 388	18690 535	7080	25910 386	16950 590	8960

appreciable long-wavelength shift is observed. On the other hand, the introduction of a weak donor — a methoxy group into the benzene fragment (compound VI) — has a much more significant effect on the position of the fluorescence spectrum than does the introduction of a dimethylamino group into the naphthalene fragment. Compound VI is also characterized by the most appreciable solvatofluorochromic effect in the investigated series of derivatives of compound I (which can be characterized, for example, by increasing the Stokes fluorescence shift in going from toluene to dimethylformamide, $\Delta\Delta\nu = 1880$ cm^{-1}), which appreciably exceeds the shift for the unsubstituted compound I, as well as for compound IV, which in opposite parts of the molecule contains a strong electron-donor and strong electron-acceptor substituents. Not surprisingly, the smallest solvatofluorochromic effect was observed in dimethylamino derivatives (160 cm^{-1} for compound III and 340 cm^{-1} for compound IV). To account for these facts, we carried out a quantum-chemical calculation of the spectra of naphthoylenebenzimidazole and a series of its derivatives by using special quantum-chemical indices — the localization numbers of electronic excitation on atoms and fragments of the molecule and interfragment ($l\mu\mu$) and intrafragment ($l\mu\nu$) charge transfer numbers [5].

In accordance with the results of the calculations, the absorption of compound I in the near UV is formed by several electronic transitions of different types and intensities. The two longest-wavelength, general molecular and practically single-configuration transitions have a mutually perpendicular polarization and a distinct character of transitions with charge transfer* (Table 2). They are followed by a series of low-intensity transitions, the first of which is localized chiefly on the naphthalene nucleus, and the next on the phenyl fragment. Since the fluorescence properties of the substituted derivatives of the nucleus of I will in all probability be determined by the excited states formed by one of the above long-wavelength transitions, we shall dwell on them in greater detail.

Let us first examine the system of molecular orbitals (MO) of naphthoylenebenzimidazole, shown in Fig. 1. The upper three occupied orbitals of molecule I are localized to a considerable extent on its benzimidazole fragment, and only the orbital which is fourth in energy and which participates in the formation of electronic transitions in the short-wavelength region of the spectrum, is practically a "purely naphthalene" orbital. On the contrary, for the vacant orbitals of molecule I, there is a characteristic high localization on the naphthalene ring, and also on the $-CO-N-CN-$ atomic grouping. This determines

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*The degree of "charge transfer" character of the transition can be estimated from the ratio of local (intrafragment charge transfer numbers) and crossover contributions (interfragment charge transfer numbers) of the individual structurally distinguishable fragments of the molecule to the total localization of electronic excitation.

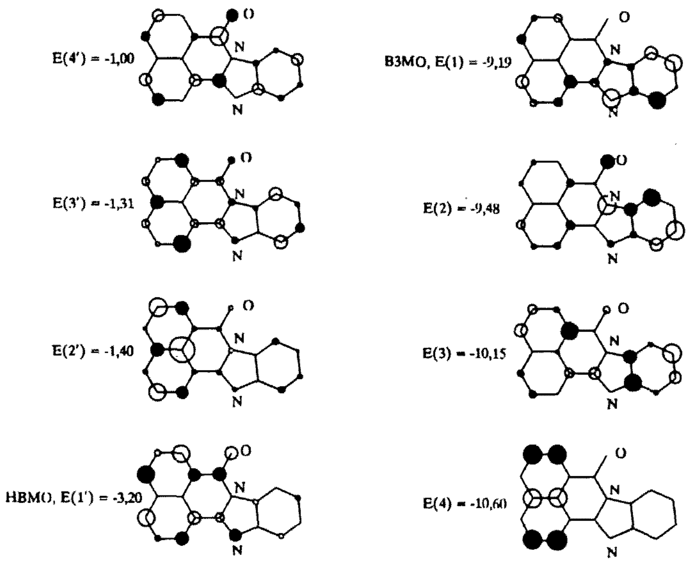

Fig. 1. Molecular orbitals of naphthoylenebenzimidazole (area of circles described around atoms which is proportional to the square of the expansion of the corresponding MO in terms of AO; closed circles denote negative coefficients).

the above charge-transfer character of the majority of the electronic transitions in the spectrum of the molecule studied. We note the very low energy of the first vacant orbital (the energy difference between φ_1, and φ_2, is 1.8 eV, whereas the energy interval between the remaining vacant orbitals, which are higher, is expressed in tenths and hundredths of eV). A similar, though less distinct, pattern is also observed for the filled orbitals: the energy difference between the first two filled MO is 0.3 eV, and between φ_2 and φ_3, almost 0.7 eV. Such appreciable energy intervals between the molecular orbitals forming the electronic transitions in the long-wavelength region of the spectrum accounts for the insignificant mixing of configurations and for the practically single-configuration character of the indicated transitions. As is evident from Fig. 1, the φ_1 and φ_1', orbitals are closer in localization than are φ_2 and φ_1. This is the reason for the high intensity of the transition formed by the $\varphi_1 \rightarrow \varphi_1'$ configuration, in comparison with the transition formed by the $\varphi_2 \rightarrow \varphi_1'$ configuration. We also note that in terms of the simple interpretations of perturbation theory, when the structure of the molecule is varied, the most appreciable shifts in the system of molecular orbitals, which subsequently will result in a change in absorption spectra, will be observed when the substituents are added to positions characterized by high values of the coefficients of expansion of MO in AO. Thus, one should expect the greatest shifts of the lower vacant orbital when substituents are introduced into the 4 and 5 positions, of the upper filled MO — in the 4, 5, and 5' positions, and in the unfilled orbital which follows them — in the 4' position.

The nature of the electronic density redistribution on excitation, represented as numbers of interfragment charge transfer, is shown in Table 2.* It is evident that the chief direction of the electron density displacement for the two long-wavelength transitions is the charge transfer from the benzene to the naphthalene fragment. At the same time, appreciable differences exist between them. Thus, the first long-wavelength transition, localized along the long axis of the molecule (X), is also characterized by an appreciable displacement of electron density to the carbonyl group (a total of 21% in units of charge transfer numbers, with 10% of this number corresponding to the naphthalene fragment, whereas a total of 19% is transferred to the latter). For the transition following it, polarized along the short axis of the molecule (Y), whose charge-transfer character is expressed to a substantially higher degree, the naphthalene ring is also the main acceptor of electron density. We note that in this case, there is even observed a small shift of electron density from the CO group to this ring (5% in units of charge transfer numbers).

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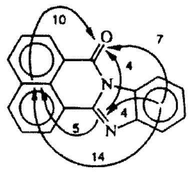
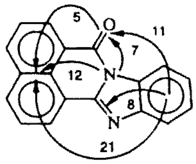
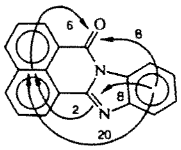
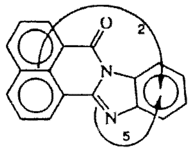
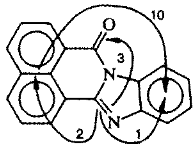
*The sum of the charge transfer numbers given for each of the transitions in Table 2 is not 100%, since in accordance with the conditions of their normalization, all of the local and crossover contributions are taken as 100%, and for the crossover contributions, both the l_{AB} terms and the l_{BA} terms are taken to be of the same sign.

TABLE 2. Characteristics of Long-Wavelength Transitions in the Spectrum of Compound I (Location, Intensity, Polarization, and Vector of Change in Dipole Moment in Passing to an Excited State) and Diagrams of Electron Density Redistribution (charge transfer numbers, %) in Passing to Excited States

Transition No.	ν, cm^{-1}	λ, nm	f	Polarization	$\Delta\mu$, D	Local contribution to excitation	Distribution of charge transfer numbers
1	28307	353,3	0,797	X	6,9	$l_{Nf} = 33$	
2	29409	340,0	0,107	Y	11,7	$l_{Nf} = 8$ $l_{Ph} = 8$	
3	31728	315,2	0,049	Y	1,08	$l_{Nf} = 82$	Absent
4	34663	288,5	0,028	Yx	—	$l_{Nf} = 30$ $l_{Ph} = 3$	
5	38065	262,7	0,093	XY	—	$l_{Nf} = 5$ $l_{Ph} = 55$	
6	40849	244,8	0,173	Yx	—	$l_{Nf} = 27$ $l_{Ph} = 14$	

Thus, it may be postulated on the basis of the results obtained that the most appreciable changes in the spectra of the derivatives of compound I will be observed when substituents of various electronic types are introduced in accordance with the indicated direction of electron-density displacement on excitation: electron-donor substituents into the benzene nucleus and electron-acceptor substituents into the naphthalene nucleus.

To confirm this conclusion, a quantum-chemical calculation was made for mono- and disubstituted derivatives of compound I (Table 3). As the substituents, Table 3 shows the most pronounced donor and acceptor — the amino and nitro groups. Despite the fact that these substituents introduce intrinsic MO into the orbital system of the base molecule, and the electronic transitions involving the participation of these MO may be regarded as "new" in the system of its electronic transitions [6, 7], the results obtained are in complete agreement with the conclusions drawn earlier.

Thus, the spectral shifts due to the introduction of donor substituents into the 4 and 5 positions of the naphthalene fragment were found to be almost one-half as large as those due to the introduction of substituents into the benzene fragment.

TABLE 3. Characteristics of Long-Wavelength Transitions in Calculated Absorption Spectra of Naphthoylene Benzimidazole Derivatives with Donor and Acceptor Substituents (frequency, wavelength, oscillator strength and polarization, $\Delta\mu$ – absolute value of the vector of change in dipole moment in passing to an excited state, $\Delta\nu$ – frequency shift of electronic transition relative to the unsubstituted compound)

R	ν, cm^{-1}	λ, nm	f	Polarization	$\Delta\mu$, D	$\Delta\nu$, cm^{-1}
4-NH_2	25231	396,3	0,919	X	5,45	3076
	30561	327,2	0,011	Y	—	-1152
5-NH_2	23791	420,3	0,748	X	7,62	4516
	30100	332,2	0,027	Y	—	-692
4'-NH_2	21716	460,5	0,073	Y	22,8	7693
	27939	357,9	0,778	X	—	368
5'-NH_2	21921	456,2	0,494	X	20,6	6386
	28694	348,5	0,069	xY	—	715
4-NO_2	26395	378,9	0,711	X	9,76	1912
	27794	359,8	0,088	Y	—	1615
5-NO_2	27067	369,5	0,827	X	9,25	1240
	28114	355,7	0,208	xY	—	1295
4'-NO_2	28900	346,0	0,876	X	4,06	-593
	30967	322,9	0,049	Y	—	-1558
5'-NO_2	28788	347,4	0,955	X	3,41	-481
	30409	328,9	0,097	Y	—	-1000
4-NH_2, 5'-NO_2	24913	401,4	0,917	X	7,43	3394
	30830	324,4	0,002	—	—	-1421
5-NH_2, 5'-NO_2	23956	417,4	0,824	X	8,24	4351
	30513	327,7	0,012	Y	—	-1104
4-NH_2, 4'-NO_2	25133	397,9	0,905	X	6,90	3174
	30875	323,9	0,003	—	—	-14,66
5-NH_2, 4'-NO_2	23980	417,0	0,761	X	8,25	4327
	30520	327,7	0,002	—	—	-1111
4-NO_2, 5'-NH_2	19991	500,2	0,412	X	23,9	8316
	27018	307,1	0,078	xY	—	2391
5-NO_2, 5'-NH_2	20518	487,4	0,545	X	23,9	7789
	27271	366,7	0,082	xY	—	2138
4-NO_2, 4'-NH_2	19990	500,2	0,050	Y	26,6	9419
	25381	387,1	0,709	X	—	1102
5-NO_2, 4'-NH_2	20026	499,4	0,056	Y	26,0	9383
	26561	376,5	0,928	X	—	1746

At the same time, we observed a fundamental difference in the influence exerted on the spectra by the donor substituents introduced into the 4' and 5' positions. Whereas in all the remaining cases, the donor substituent introduced led to an appreciable long-wavelength shift of the more intense first absorption band, polarized along the length of the molecular axis, the introduction of a substituent into the 4' position causes an appreciable shift of the less intense band polarized along the short axis of molecule I. Thus, higher fluorescence characteristics should not be expected of the 4'-substituted derivatives, since the oscillator strength of their long-wavelength transition is smaller than that of the 5' isomers, and this would lead to lower values of the quantum yield of fluorescence. (As a result of the proportionality of the oscillator strength of the $S_0-S_1^*$ transition to the rate constant of fluorescence emission from the S_1^* state, on the condition of an approximately equal efficiency of the nonradiative deactivation of the excited state.)

As expected, the acceptor substituents introduced into the benzene ring either have almost no effect on the positions of the bands in the absorption spectrum or led to hypsochromic shifts, since they hinder the above-mentioned redistribution of electron density on excitation of the naphthoylenebenzimidazole molecule.

A prediction of the magnitude of solvatofluorochormic shifts may be made on the basis of a comparison of the calculated absolute values of change in the dipole moment vector in passing to an excited state. It is evident that the highest values of $\Delta\mu$ characterize compounds in which substituents of diverse electronic nature are introduced in accordance with the above-mentioned chief direction of electron-density redistribution on excitation of molecule I: electron density donors — to the benzene fragment, and acceptors — to the naphthalene fragment.

EXPERIMENTAL

The absorption spectra were measured with a Specord M-40 spectrophotometer, and the fluorescence spectra were taken with a model 850 HITACHI spectrofluorimeter. The quantum-chemical calculations using the CNO SCF CI method allowing for up to 100 singly excited configurations were carried out in accordance with the EASY-PIE program (authors: V. E. Umanskii and E. N. Babich) by use of the set of parameters of [8].

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