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Spectral Characteristics and Scintillation Properties of Some 2-Aryl Derivatives of Benzoxazole and Benzimidazole

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Previously [1,2] we described the synthesis of aryl derivatives of benzoxazole (I) and benzimidazole (II–V).

(I) (benzoxazole derivative with Ar substituent)

(II) $R = H$ (III) $R = CH_3$

(IV) $R = C_6H_5$ (V) $R = CH_2Ar$

where $Ar = C_6H_5$, C_6H_4X ($X = F$, Cl, Br), 4-$C_6H_4CH_3$, 4-$C_6H_4OCH_3$, 3,4-$C_6H_3(OCH_3)_2$, 3,4-$C_6H_3(OCH_2O)$, 4-$C_6H_4NAlk_2$ ($Alk = CH_3$, C_2H_5), 4-$C_6H_4C_6H_5$, 1-$C_{10}H_7$.

In the present communication we set forth some results of measurements of absorption and luminescence spectra, as well as general information on their scintillation properties.

Until now, investigations of these heterocycles in the indicated direction have been sporadic [3]. Aryl derivatives of benzimidazoles have not been studied at all, and only in papers [4,5] are there indications of the scintillation properties of three 2-arylbenzoxazoles, which are of definite interest. Absorption spectra in the ultraviolet were recorded in heptane on an SF-4 spectrophotometer. Luminescence spectra were recorded in benzene solutions on an SF-4 with a special photoelectric attachment [6]. Excitation was produced by the 313 mμ line, isolated from the spectrum of an SVD–120-A mercury-quartz lamp by a combination of UFS-2 and ZhS-3 filters. In the measurements, a correction was made for the spectral sensitivity of the photomultiplier and of the entire apparatus.

The scintillation efficiency was determined in a solution of scintillation toluene relative to 3 g/l of 2,5-diphenyloxazole on a single-channel γ-spectrometer by the constant counting-rate method. A Co^{60} preparation was used as the source of γ-radiation; the γ-ray beam was collimated by a lead block. An FEU-29 spectrometric photomultiplier was used in the measurements.

As was noted earlier [1,2], aryl-substituted benzoxazoles (I) and benzimidazoles (II) possess a characteristic absorption maximum in the region 300–340 mμ,

Fig. 1

Figure 1: Fig. 1

the position of which depends substantially on the presence and nature of the substituent in position 2. Comparison of the absorption spectra of compounds I and II with identical substituents showed that they differ only very slightly both in the position of the principal absorption maximum and in the value of the molar extinction, despite the different nature of their heteroatoms.

A study of the absorption spectra of compounds (III), (IV), and (V), in which the acidic hydrogen atom in NH is replaced by alkyl or aryl groups, made it possible to conclude that the substituent in position 1 of the benzimidazole molecule participates only weakly in conjugation with the π-electron system of the molecule through the pair of p-electrons of the N^1 atom, apparently strongly deflected toward the ring. This is clearly seen when comparing the absorption spectra (Fig. 1) of 1-phenyl- and 1-(n-methoxyphenyl)-benzimidazoles, whose absorption curves are characterized by maxima at about 247 and 277 mμ, i.e., in the same region as that of unsubstituted benzimidazole (curves 1, 2, 4).

In contrast, the absorption maximum of the same derivatives substituted in position 2 (curves 3, 5) is substantially shifted toward longer wavelengths ($\lambda_{\max}$, respectively, 302 and 310 mμ). On introducing methyl, phenyl, or benzyl residues at the ring nitrogen of 2-phenylbenzimidazole, a certain hypsochromic shift of $\lambda_{\max}$ is observed from 302 mμ, respectively, to 295, 295, and 293 mμ, which apparently can be explained by steric hindrance created in position 1,2.

Fig. 1. Absorption spectra of some 1- and 2-substituted benzimidazoles. 1—benzimidazole, 2—1-phenylbenzimidazole, 3—2-phenylbenzimidazole, 4—1-(n-methoxyphenyl)benzimidazole, 5—2-(n-methoxyphenyl)benzimidazole, 6—1-(n-nitrophenyl)benzimidazole, 7—2-(n-nitrophenyl)benzimidazole.

The introduction of an electrophilic nitro group changes the picture somewhat. The absorption spectrum of 1-(n-nitrophenyl)benzimidazole (curve 6), while retaining the general character of the spectrum of 1-phenylbenzimidazole ($\lambda_{\max}$ = 247 and 272 mμ), has one more pronounced maximum at 315 mμ. However, in this case as well, the character of the conjugation differs substantially from 2-(n-nitrophenyl)benzimidazole (curve 7).

All the compounds obtained (I–V) are characterized by an intense luminescence band in solutions in the 320–400 mμ region for phenyl-, n-halophenyl-, n-alkylphenyl-, and alkoxyphenylbenzoxazoles and benzimidazoles, and in the 350–450 mμ region for n-biphenylyl-, 1-naphthyl-, and n-dialkylaminophenyl derivatives. The luminescence spectra of these compounds possess two or three characteristic maxima. The character of the spectra of both classes of compounds in all the cases considered is the same and differs somewhat only in the positions of the maxima and in the intensity of luminescence, which in all cases is somewhat lower for the benzimidazole derivatives.

Fig. 2. Luminescence spectra of n-biphenylyl derivatives of benzoxazole and benzimidazole. 1—2-(n-biphenylyl)benzoxazole, 2—2-(n-biphenylyl)benzimidazole, 3—1-methyl-2-(n-biphenylyl)benzimidazole, 4—1-(n-phenylbenzyl)-2-(n-biphenylyl)benzimidazole, 5—1-phenyl-2-(n-biphenylyl)benzimidazole

Figure 2: Fig. 2. Luminescence spectra of n-biphenylyl derivatives of benzoxazole and benzimidazole. 1—2-(n-biphenylyl)benzoxazole, 2—2-(n-biphenylyl)benzimidazole, 3—1-methyl-2-(n-biphenylyl)benzimidazole, 4—1-(n-phenylbenzyl)-2-(n-biphenylyl)benzimidazole, 5—1-phenyl-2-(n-biphenylyl)benzimidazole

It is noteworthy that the luminescence spectra of the 1,2-substituted compounds III—V differ from their N-unsubstituted analog by an intense emission band in the region of their luminescence. This is seen from the example of the biphenylyl derivatives (Fig. 2 and Table 1).

Measurement of the quantum yield of photoluminescence (B_{ϕ}^{q}) was carried out under conditions of complete absorption relative to 2,5-diphenyloxazole, which has optical characteristics close to those of our compounds, at concentrations of $3 \cdot 10^{-4}$ and $3 \cdot 10^{-3}$ g/cm^3. Comparison of the quantum yields of the benzimidazole compounds once again confirms that in the series of 1,2-substituted benzimidazoles the main influence on the spectra is exerted by the substituent in position 2, whereas the substituent at the ring nitrogen changes only certain physical and chemical properties of the compounds (7). Its influence on the electronic system can more likely be reduced to an induction effect or, in the case of substituents of large volume in positions 1, 2, to steric interaction. This, evidently, can explain the somewhat lowered

quantum yield of the photoluminescence of 1-phenyl-2-(n-biphenylyl)benzimidazole.

The relative quantum yield of 2-(n-biphenylyl)benzoxazole is 1.12, i.e., appreciably higher than for the benzimidazole derivatives. A similar regularity is retained when comparing the results of measuring the spectra of all the compounds obtained. Such an increase in the quantum yield

Fig. 2. Luminescence spectra of n-biphenylyl derivatives of benzoxazole and benzimidazole.
1—2-(n-biphenylyl)benzoxazole, 2—2-(n-biphenylyl)benzimidazole, 3—1-methyl-2-(n-biphenylyl)benzimidazole, 4—1-(n-phenylbenzyl)-2-(n-biphenylyl)benzimidazole, 5—1-phenyl-2-(n-biphenylyl)benzimidazole

of photoluminescence in the case of the benzoxazole derivatives, as compared with the benzimidazole derivatives, is apparently explained by the different nature of their heteroatoms and is connected with the greater electronegativity of the oxygen atom, which, by polarizing the π-electron clouds of the phenyl rings, creates a more stabilized conjugation system having fewer possibilities for loss of excitation energy by a radiationless path than the more mobile system of the

benzimidazole molecule.

All the compounds obtained were tested as primary luminescent additives in liquid scintillators.

The measurements performed showed that a number of benzoxazole derivatives possess a scintillation efficiency (s. e.) of the same order as *n*-terphenyl and 2,5-diphenyloxazole. As for the scintillation properties

Table 1

No.	Compound	Absorption spectra λ_1	Absorption spectra λ_2	Absorption spectra $\lg \varepsilon_1$	Absorption spectra $\lg \varepsilon_2$	Luminescence spectra λ_1	Luminescence spectra λ_2	Luminescence spectra λ_3	Luminescence spectra B_ϕ^{qv}	Relative scintillation efficiency: optimal conc., g/l	Relative scintillation efficiency: % of 2,5-diphenyloxazole	K_v^*	B_{ref}
1	2-(*p*-biphenylyl)-benzoxazole		313		4.73	350	368	385	1.12	5	108	0.93	116
2	2-(*p*-biphenylyl)-benzimidazole	260	315	4.27	4.72	362	375	390	0.99**	0.45***	68	0.94	72
3	1-methyl-2-(*p*-biphenylyl)-benzimidazole	255	306	4.42	4.48	362	375	392	0.99	5	107	0.91	118
4	1-(*p*-phenylbenzyl)-2-(*p*-biphenylyl)-benzimidazole	255	305	4.47	4.55	362	375	395	0.98	5	100	1.0	100

No.	Compound	Absorption spectra λ_1	Absorption spectra λ_2	Absorption spectra $\lg \varepsilon_1$	Absorption spectra $\lg \varepsilon_2$	Luminescence spectra λ_1	Luminescence spectra λ_2	Luminescence spectra λ_3	Luminescence spectra B_ϕ^{qv}	Relative scintillation efficiency: optimal conc., g/l	Relative scintillation efficiency: % of 2,5-diphenyloxazole	K^*	B_{ref}
5	1-phenyl-2-(*p*-biphenylyl)-benzimidazole	255	307	4.48	4.57	362	375	392	0.82	3	90	0.99	91

* Correction for the spectral sensitivity of the FEU-29.
** Comparison of the sample and the standard was carried out only at a concentration of $3 \cdot 10^{-4}$ g/cm^3 because of the poor solubility of the sample.
*** The concentration of the saturated solution is indicated.

benzimidazoles, the poor solubility of 2-aryl derivatives not substituted in position 1 did not make it possible to carry out measurements at the optimal concentrations, which for most known scintillators are 3–5 g/l. However, even at the solubility limit, equal to 0.25–0.5 g/l, most 2-arylbenzimidazoles showed an efficiency of 60–70% of that of 2,5-diphenyloxazole. For the N-substituted benzimidazole compounds III–V, which are readily soluble in nonpolar solvents, the scintillation efficiency is of the same order as that of the benzoxazole derivatives. In a number of cases it exceeds that of 2,5-diphenyloxazole by 8–10%. As a rule, this is observed in those cases where the scintillation solution emits in a longer-wavelength region of the spectrum, i.e., upon the introduction of substituents that cause a strong bathochromic shift (for example, for biphenylyl-, dialkylaminophenyl derivatives). This is explained by better coincidence with the maximum spectral sensitivity of the recording instrument (about 400 mμ).

For the compounds listed in Table 1, the external yield of radioluminescence was determined (7).

Taking into account that the magnitude of the reabsorption coefficient for all the scintillators studied is of the same order, and that the thickness of the sample layer is 8 mm, as a first approximation it may be considered that the external

yield of radioluminescence is equal to the relative energy yield of radioluminescence (B_{rel}).

From the data in Table 1 it is evident that the energy yield of radioluminescence of compounds Nos. 1 and 3 is greater than the energy yield of 2,5-diphenyloxazole by 16 and 18%, respectively.

The comparative study of the absorption, luminescence, and scintillation-efficiency spectra that was carried out showed that among 2-arylbenzoxazoles and benzimidazoles there is a series of compounds that can be used as primary additives in liquid scintillators; moreover, it should be noted that the routes for synthesis of these compounds are uncomplicated (1, 2).

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