BENZINDOLES

X.* SPECTRAL PROPERTIES OF ANGULAR BENZINDOLES

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A large amount of structural similarity between 4,5-benzindole and naphthalene and between 6,7-benzindole and indole was detected on a basis of a comparison of the absorption, fluorescence, and phosphorescence spectra of isomeric benzindoles with the spectra of indole and naphthalene. A great analogy between indole and 6,7-benzindole as compared with 4,5-benzindole is also observed during the formation of hydrogen bonds, as indicated by the shift in the absorption band of the NH group in the IR spectra of the investigated compounds in the presence of various proton acceptors.

Only very scanty information regarding the spectral properties of 4,5- and 6,7-benzindoles is available [1-3], whereas such information is necessary for an understanding of the peculiarities of the chemical behavior of these compounds. The data on the electron density in the 1 and 3 positions obtained by Dewar and co-workers [4] indicate the absence of an appreciable difference between the isomers, but the chemical shifts of the protons in the 1 and 3 positions in the PMR spectra of 4,5- and 6,7-benzindoles are 11.37 and 11.90 ppm and 6.98 and 6.53 ppm, respectively [5].

In order to make a more profound study of the spectral properties of these compounds we investigated the IR, absorption, fluorescence, and phosphorescence spectra of isomeric benzindoles.

The UV absorption spectra of the isomeric benzindoles differ substantially from one another. The spectrum of 6,7-benzindole has one maximum at 259 nm, which is characteristic for indole derivatives. In addition to this band, the spectrum of 4,5-benzindole also contains an intense maximum at 228 nm and a low-intensity maximum at 296-335 nm. A similar difference is characteristic for many 4,5- and 6,7-benzindole derivatives (Table 1). Yet another maximum of very low intensity at 294 nm is observed when the concentration of 6,7-benzindole in alcohol and hexane increases. The appearance of an absorption band in the low-frequency region for 4,5-benzindole derivatives may be associated with an increase in the contribution of the $n-\pi$ transition. To uncover the nature of this band we recorded the spectra of benzindoles in solvents of different polarities (alcohol and n-hexane); however, we did not observe a hypsochromic shift of the low-frequency band. The small (~10 nm) shift to the low-frequency region makes it possible to assign this band to $\pi-\pi^*$ transitions.

We also checked the relationship between the position of the absorption band and the pH of the medium. Measurements made in buffer solutions showed that no changes whatsoever are observed in the absorption spectra of the isomeric benzindoles over a broad range of pH values.

The fluorescence spectrum of 6,7-benzindole is shifted strongly to the longwave region (λ_{max}~361 nm) as compared with the spectrum of indole (λ_{max} ~ 320 nm) [6] and is just as poorly constructed as the

*See [7] for communication IX.

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TABLE 1. UV Absorption Spectra of 4,5- and 6,7-Benzindole Derivatives

4,5-Benzindole derivative	λ_{max}, nm	lg ε	6,7-Benzindole derivative	λ_{max}, nm	lg ε
2,3-Dimethyl	228 250 324 338	4,52 4,38 3,95 3,20	2,3-Dimethyl	270 230	4,65 3,95
2-Carbomethoxy	232 254 278 286 322 328 342	4,62 4,10 4,30 4,26 4,22 4,18 4,16	2-Carbomethoxy	240 246 274 294 306 334 250	4,24 4,28 4,72 4,24 4,19 3,86 3,88
3-Formyl	243 273 316 348	4,10 4,32 3,36 4,14	3-Formyl	252 270 318 333	4,74 4,42 3,77 3,51
3-Benzoyl	238 246 285 342	4,46 4,40 4,30 3,50	3-Benzoyl	254 278 302 322	— — — —
2-Carboxy	232 270 278 310 338	4,58 4,38 4,30 4,10 4,10	2-Carboxy	248 272 304 332 348	4,11 4,69 4,07 3,74 3,73
2-Methyl	228 265 308 324	4,54 4,52 3,88 3,80	2-Methyl	246 264 328	4,45 4,73 3,17

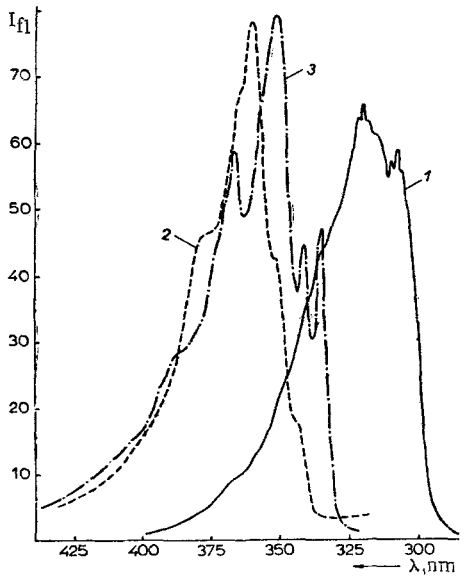

Fig. 1

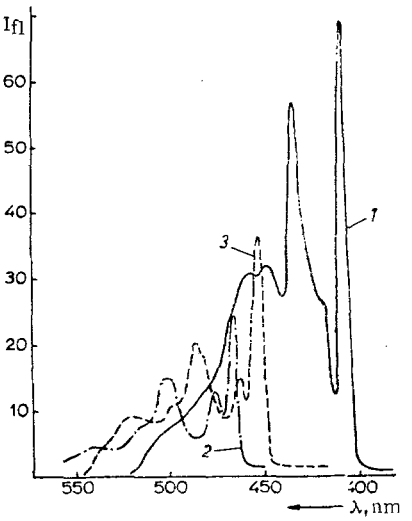

Fig. 2

Fig. 1. Fluorescence spectra: 1) indole; 2) 4,5-benzindole; 3) 6,7-benzindole.

Fig. 2. Phosphorescence spectra: 1) indole; 2) 4,5-benzindole; 3) 6,7-benzindole.

spectrum of indole (Fig. 1). The spectrum of 4,5-benzindole is located in the shorter-wave region as compared with the spectrum of 6,7-benzindole, but it contains a number of narrow bands (335, 340, 352, and 369 nm), which can also be noted in the spectrum of 6,7-benzindole in the form of small shoulders.

As one should have expected, the phosphorescence spectra are less intense than the fluorescence spectra and consist of a number of narrow bands at 400-550 nm (Table 2). A comparison of the phospho-

TABLE 2. Phosphorescence Spectra of Benzindoles

Indole	6,7-Benzindole	4,5-Benzindole	Naphthalene
λ, nm, I	λ, nm, I	λ, nm, I	λ, nm, I
404,5 vs 435,6 s 446,4 w	451 s 463 w 484,7 m	468 s 476 w 501,4 m	471 vs 482 m 504 s 511 s

TABLE 3. Energies of the Singlet and Triplet States

Compound	E, kcal/mole, S_1	E, kcal/mole, T_1
Indole	98,6	70,5
6,7-Benzindole	97,6	64,2
4,5-Benzindole	86,6	61,0
Naphthalene	88,0	61,0

TABLE 4. Absorption Band of the NH Group of Isomeric Benzindoles in the Presence of Some Acceptors

4,5-Benzindole derivatives	ν_{NH}, cm^{-1}			6,7-Benzindole derivatives	ν_{NH}, cm^{-1}		
	$(CH_3)_2CO$ + CCl_4	tetrahydrofuran	CH_3CN + CCl_4		$(CH_3)_2CO$ + CCl_4	tetrahydrofuran	CH_3CN + CCl_4
4,5-Benzindole	3360 3430	3300	3390	6,7-Benzindole	3350 3420	3300	3380
3-Formyl	3320	3250	—	3-Formyl	3330	3250	—
2-Methyl	3400	3330	3380	2-Methyl	3400	3300	3370
2,3-Dimethyl	3380	3300	3380	2,3-Dimethyl	3400	3300	3380
3-Dimethyl-aminomethyl	3380	3330	—	3-Dimethyl-aminomethyl	3380	3310	—

rescence spectra of indole, angular benzindoles, and naphthalene reveals a great deal of similarity between the spectra of the benzindoles and naphthalene. The spectrum of indoles is the shortest-wave spectrum in this group, whereas the spectrum of naphthalene is the longest-wave spectrum. The spectra of the benzindoles occupy an intermediate position, and the spectrum of 4,5-benzindole is somewhat more similar to the spectrum of naphthalene than to the spectrum of 6,7-benzindole (Fig. 2). On the basis of the data obtained in this study, it may be concluded that phosphorescence occurs in the naphthalene ring of the benzindoles and is consequently due to a $\pi - \pi^*$ transition.

On the basis of the absorption and luminescence spectra obtained, we calculated the energy of the first singlet and first triplet states. The results are presented in Table 3. For comparison, data for indole and naphthalene are also presented in Table 3. Although the energies of the singlet and triplet states of all four compounds are close to one another, it is apparent that greater similarity between 4,5-benzindole and naphthalene than between 4,5-benzindole and indole is also observed here, while 6,7-benzindole occupies an intermediate position.

The data from the absorption and luminescence spectra make it possible to assume that the electron pair of the nitrogen atom in 4,5-benzindole is conjugated more strongly with the π electrons of the benzene rings than in 6,7-benzindole. This circumstance suggests a difference in the donor properties of the angular benzindoles during the formation of hydrogen bonds with acceptors. We attempted to confirm the indicated difference by a study of the absorption band of the NH group in the IR spectra of the benzindoles. The spectra of KBr pellets of the benzindoles differ little from one another and from the spectrum of indole. Thus the absorption band of the NH group is found at 3420 cm^{-1} for all three compounds but it is considerably broader and more structured in the case of 4,5-benzindoles. The difference in the nature of the band of the NH group is seen distinctly from its shift in the presence of proton acceptors, as indicated by the data in Table 4. For example, the addition of acetone to a solution of the indole compound in carbon

tetrachloride leads to a decrease in the intensity of the peak of the free NH group and to the appearance of two absorption bands at 3430 and 3360 cm^{-1} for 4,5-benzindole and 3420 and 3350 cm^{-1} for 6,7-benzindole. Considering that the analogous absorption band for indole is found at 3410 cm^{-1}, it may be said that a greater analogy is observed between indole and 6,7-benzindole as compared with 4,5-benzindole in the formation of an $>N-H\ldots O=C<$ hydrogen bond.

The IR spectra were recorded with an UR-10 spectrometer with NaCl and LiF prisms at a spectral slit width of 4 cm and a scanning rate of 60 cm/sec. The UV spectra were recorded with CB-8 and Specord spectrophotometers. The fluorescence and phosphorescence spectra were investigated at 77°K with an SDL-1 luminescence spectrophotometer under monochromatic excitation (λ = 254 nm) or with a photoelectric apparatus with a spark phosphoroscope (W-Fe electrodes).

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