BENZINDOLES.

XV.* SYNTHESIS AND SOME PROPERTIES OF LINEAR BENZINDOLE

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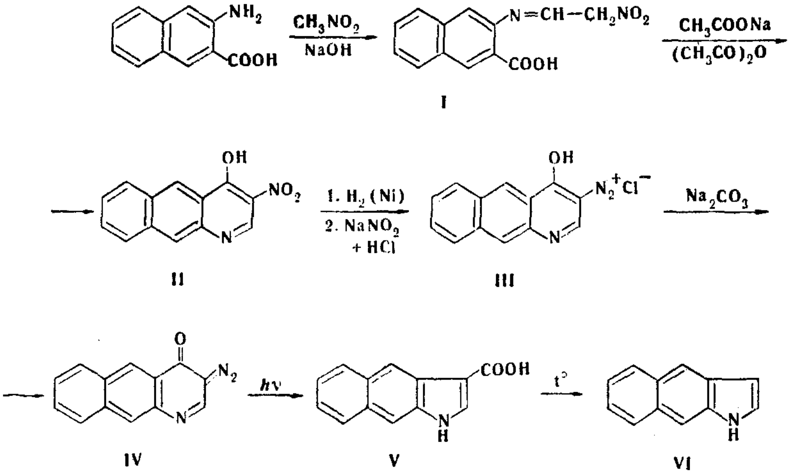
5,6-Benzindole was obtained by the photochemical decomposition of 4-hydroxy-6,7-benzoquinoline-3-diazonium hydrochloride. A substantial difference in the absorption and luminescence spectra of linear benzindole and its angular isomers was observed. It is shown that in the formation of complexes by means of hydrogen bonds the frequency of the associated NH group of linear benzindole is closer to the corresponding value for indole than the frequencies of the angular isomers.

The cyclization of hydrazones under the conditions of the Fischer reaction and numerous variants of this reaction make it possible to obtain a large number of all of the possible indole derivatives. However, it is impossible or very difficult to obtain some of the compounds by the Fischer reaction or by methods based on electrophilic substitution in the benzene ring. Thus 4,5- and 6,7-benzindoles were synthesized by the Fischer reaction [2], whereas for the preparation of 5,6-benzindole we found it necessary to use a scheme including contraction of the ring of o-quinone diazides [3], which has also been successfully used for the synthesis of compounds that are extremely difficult to obtain [4-7].



2-(β-Nitroethylidene)aminonaphthoic acid (I) was obtained by mixing solutions of methazonic and 3-amino-2-naphthoic acids at room temperature. Acid I undergoes cyclization to give 4-hydroxy-3-nitro-6,7-benzoquinoline (II) in low yield (46%); we were unable to raise the yield by modification of the reaction conditions. The reduction of nitrobenzoquinoline (II), the diazotization of aminobenzoquinoline, and the preparation of o-quinone diazide (IV) proceed smoothly to give the products in good yields.

We subjected a 0.04% solution of o-quinone diazide (IV) in water containing a small amount of hydrochloric acid to photochemical decomposition. Irradiation was carried out with a UV-125 lamp in a quartz device with an immersible irradiation source. The highest yield of acid V is obtained at no higher than 20-22°C. An increase in the temperature leads

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*See [1] for communication XIV.

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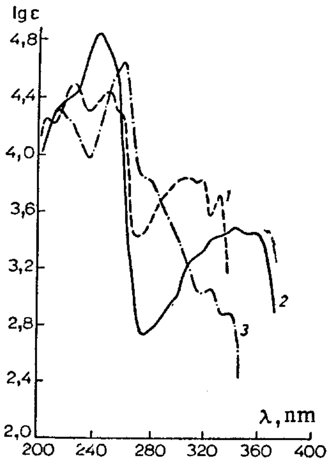

Fig. 1. UV spectra of the benzindoles in ethanol: 1) 4,5-benzindole; 2) 5,6-benzindole; 3) 6,7-benzindole.

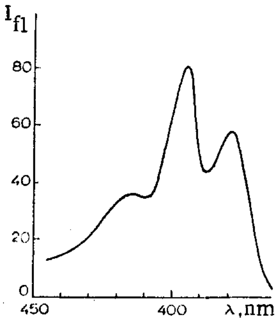

Fig. 2. Fluorescence spectrum of 5,6-benzindole.

to the formation of an unidentified brown substance that is only slightly soluble in organic solvents and does not have a distinct melting point. The same substance is formed when solutions with higher concentrations are used. It was found that the photochemical decomposition of diazonium salt III also leads to the formation of acid V, and the step involving the preparation of the o-quinone diazide can therefore be excluded. The decarboxylation of the thoroughly purified acid was carried out in an apparatus for vacuum sublimation. This procedure gave very pure benzindole VI, which we investigated without further purification.

The absorption spectrum of linear benzindole VI differs substantially from the spectra of the angular isomers [8] (Fig. 1). In addition to two bands at 228 and 259 nm, which are characteristic for 4,5-benzindole, and one band at 259 nm, which is characteristic for 6,7-benzindole, an intense band at 243 nm and a low-intensity band at 320-360 nm are observed. This is in agreement with the changes in the spectrum of anthracene as compared with the spectrum of phenanthrene [9].

The spectra of solutions of the compounds in solvents with different polarities are identical; this indicates the reduced ability of the linear benzindole to form associates with the solvent. The fluorescence spectrum contains one maximum at 410 nm; this maximum is shifted markedly to the long-wave region as compared with the spectra of indole and the angular benzindoles, which have principal maxima at 320, 350, and 360 nm (Fig. 2). An increase in the bathochromic shift in the fluorescence spectra of the benzindoles as compared with the spectrum of indole is observed in the order 5,6-benzindole > 4,5-benzindole > 6,7-benzindole.

We were unable to record the fluorescence spectrum of our sample of linear benzindole. It is possible that the energy of the triplet state of 5,6-benzindole is very low and is

TABLE 1. Absorption Band of the NH Group (ν, cm^{-1}) of Benzindoles and Indole in the Presence of Some Acceptors*

Acceptor	5,6-Benzindole	4,5-Benzindole	6,7-Benzindole	Indole
Carbon tetrachloride	3493 free 3460 assoc.	3490 free 3420 assoc.	3490 free 3430 assoc.	3495 free 3410 assoc.
Nujol	3440	3420	3430	3415
Tetrahydrofuran	3350	3300	3300	3380
Acetone	3420	3430	3420	3410
Dioxane	3345			3345
Acetonitrile	3405	3390	3380	3385
Pyridine	2890			3180

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*The concentration ranged from 0.02 to 0.07 M; this range excludes the possibility of the formation of self-associates.

actively quenched due to emissionless transitions when even very small amounts of impurities are present [10].

In the PMR spectra of benzindole VI the signal of the proton attached to the nitrogen atom, which is observed in the low-field region of the spectrum (11.02 ppm), is closer to the NH signal of indole (10.98) than to the signal of 4,5-benzindole (11.37) or 6,7-benzindole (11.90). The signal of the proton attached to C$_{(2)}$ (7.55) has a somewhat larger chemical shift than the signal of the corresponding proton in the spectra of the angular isomers and indole (7.32, 7.35, and 7.28). In the case of the signal of the proton attached to C$_{(3)}$, which is observed in a higher-field region of the spectrum than the remaining signals, it is interesting to note the agreement between the chemical shift and he corresponding value for 6,7-benzindole (6.53) as compared with 4,5-benzindole (6.98). The assignment of the signals of the protons attached to C$_{(4)}$ and C$_{(7)}$ was made by means of double resonance ($J_{3,7}$ = 0.9 Hz and $J_{4,7}$ = 0.5 Hz). The protons attached to C$_{(8)}$, C$_{(9)}$, C$_{(10)}$, and C$_{(11)}$ have a spectrum close to the spectrum of an AA'XX' system, for which the centers of the multiplets related to the AA' and XX' portions – H_8H_{11} = 7.81 and H_9H_{10} = 7.22 – were determined.

The absorption band of an NH group is observed at 3450 cm^{-1} in the IR spectrum of linear benzindole VI in a KBr pellet, as compared with the band observed at 3440 cm^{-1} in the spectrum of a mineral oil suspension of VI. In the case of the angular benzindoles it is observed at 3420 cm^{-1} (KBr pellet) and 3420 and 3430 cm^{-1} (mineral oil).

A comparison of the donor properties of linear benzindole during the formation of hydrogen bonds with the analogous properties of angular benzindoles and indole shows that the shift of the absorption band of the NH group in the associates of linear benzindole is considerably smaller than in the case of the angular isomers. Thus the shift of the absorption band of the NH group in the self-associates of linear benzindole is 33 cm^{-1}, whereas it reaches 60-85 cm^{-1} for the angular isomers (Table 1). A similar relationship is also observed for the associates with different types of proton acceptors. In the case of dioxane and acetonitrile the absorption band of the associated NH group of linear benzindole approaches the frequency of the NH group for the corresponding associates with indole. In the case of the self-associates and associates with tetrahydrofuran the shift of the absorption band of the NH group is considerably smaller than the shift for indole.

EXPERIMENTAL

The UV spectra of solutions of the compounds in ethanol were recorded with a Specord spectrophotometer. The IR spectra of the compounds were recorded with a UR-20 spectrometer with NaCl and LiF prisms at a spectral slit width of 4 cm^{-1}. The fluorescence and phosphorescence spectra were investigated at 77°K with an SDL-1 luminescence spectrophotometer with monochromatic excitation (λ 325 nm) and with a photoelectric apparatus with a spark phosphoroscope (U–Fe electrodes). The PMR spectra of solutions of the compounds in DMSO were recorded with a Varian HA-100 D spectrometer with hexamethyldisiloxanes as the internal standard. The accuracy in the measurements of the chemical shifts was 0.01 ppm, and the accuracy in the measurement of the spin–spin coupling constants was 0.1 Hz.

2-(β-Nitroethylidene)aminonaphthoic Acid (I) [3]. This compound was obtained in 70% yield. IR spectrum: 1640 and 1680 cm^{-1}. UV spectrum: 224, 247, 312, and 400 nm.

4-Hydroxy-3-nitro-6,7-benzoquinoline (II). This compound, with mp 380°C [3], was obtained in 46% yield. IR spectrum: 1620 and 3480 cm^{-1}. UV spectrum: 217, 244, and 308 nm.

4-Hydroxy-3-amino-6,7-benzoquinoline. A suspension of 18.7 g (0.08 mole) of nitroquinoline II in 350 ml of methanol containing 5 ml of concentrated ammonium hydroxide was reduced over Raney nickel in an autoclave at 50°C until hydrogen absorption ceased, after which the catalyst was removed, and the filtrate was acidified with concentrated hydrochloric acid. The precipitated 4-hydroxy-3-amino-6,7-benzoquinoline hydrochloride was separated to give 11 g (67%) of a product with mp >400°C [3]. UV spectrum: 209, 247, and 274 nm.

4-Hydroxy-6,7-benzoquinoline-3-diazonium Chloride (III). A 3-g (0.017 mole) sample of aminobenzoquinoline hydrochloride was dissolved in 600 ml of water containing 12 ml of concentrated hydrochloride acid as the mixture was heated to 70-80°C. It was then cooled to 40°C, and 8.5 ml of 2 N sodium nitrite solution was added. The mixture was stirred with cooling for 2 h, and the resulting yellow-green crystals of diazonium salt III were removed. The yield was 2.5 g (65%).

5,6-Benzindole-3-carboxylic Acid (V). A 0.2-g sample of diazonium salt III was dissolved in 500 ml of water containing 10 ml of concentrated hydrochloric acid, the mixture was filtered, and the filtrate was irradiated in a quartz apparatus with an immersible irradiation source with a UV-125 lamp at no higher than 22°C. After a few minutes, a flocculent precipitate of the acid formed. The mixture was irradiated for 1 h, after which the precipitate was removed and heated with 20% sodium carbonate solution. The mixture was filtered and acidified to pH 4-5 with 50% acetic acid. The precipitated acid was removed by filtration and dried at room temperature to give 0.1 g of a product with mp 204-206°C [3].

5,6-Benzindole (VI). A 0.1-g sample of acid VI was heated in an apparatus for vacuum sublimation to 210-220°C. Decarboxylation took place very rapidly. Transparent needles of 5,6-benzindole, with mp 190-192°C [3], formed after 5-10 min in a refrigerator. Found: C 86.1; H 5.4; N 8.3%. $C_{12}H_9N$. Calculated: C 86.2; H 5.4; N 8.4%.

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