SYNTHESIS OF BENZO[g]QUINOLINE DERIVATIVES

X.* ELECTRONIC ABSORPTION SPECTRA OF BENZO[g]QUINOLINE DERIVATIVES

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The electronic spectra of linear benzo[g]quinoline, its 4-substituted derivatives, and some hydrogenated derivatives are examined and discussed.

The UV spectrum of benzo[g]quinoline (BQ) has been described in a number of papers [2-5]. The BQ that we investigated has two major absorption maxima (Fig. 1 and Table 2), which correspond to the literature data. A comparison with the spectrum of quinoline demonstrates that linear monoannelation does not alter the general character of the absorption and only shifts the bands to longer wavelengths in connection with an increase in the conjugation chain [5, 6]. However, the magnitudes of the bathochromic shifts of the α and p bands of BQ are different. Therefore, instead of the two separate bands observed for quinoline, in the spectrum of BQ there is one complex long-wave band, in which the more intense forbidden $\pi \rightarrow \pi^*$ transitions mask the absorption associated with $n \rightarrow \pi^*$ transitions. Moreover, the intensity of the short-wave band is almost tripled. A β' absorption band, which is found for other polynuclear aza aromatic compounds [7], additionally appears for BQ.

The information having to do with substituted BQ, especially 4-substituted BQ, is extremely limited. In contrast to the spectra of 4-alkyl(aryl)quinolines, which display a bathochromic shift as compared with unsubstituted quinolines, the introduction of the indicated substituents into the 4 position of the BQ molecule does not lead to an appreciable change in their UV spectra [8, 9].

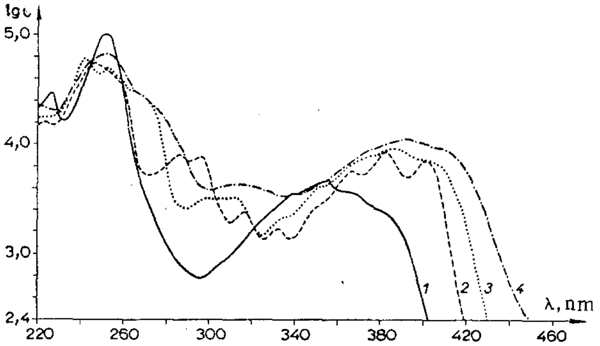
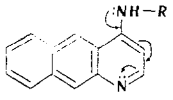


Fig. 1. UV absorption spectra of benzo[g]quinoline derivatives in ethanol: 1) benzo[g]quinoline (I); 2) 4-hydroxybenzo[g]quinoline (II); 3) 4-butylaminobenzo[g]quinoline (IV); 4) 4-anilinobenzo[g]quinoline (V).

We have found that, in accordance with general principles [5, 6, 10, 11], the introduction of electron-donor substituents such as hydroxyl and amino groups into the 4 position of BQ induces a bathochromic shift of the long-wave band with a hyperchromic effect. The shift to the long-wave region is especially appreciable for 4-aminobenzo[g]quinoline (44 nm) and is apparently due to an increase in the electron density in the pyridine ring and intensification of its conjugation with the remainder of the molecule (formula A). The intensity of the short-wave band, which characterizes the energy of the $\pi \rightarrow \pi^*$ transition, is reduced in this case.



A

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[*] See [1] for communication IX.

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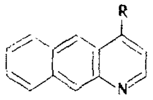
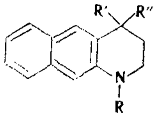
TABLE 1. UV Spectra of Benzo[g]quinoline Derivatives in Ethanol



Compound	R	λ_{max} nm (lg ε)			
		β′	β	p	p, α
I	H	226 (4,47)	252 (5,01)		354 (3,69)
II	OH	222 (4,22)	246 (4,74)	316 (3,38), 332 (3,23)	286 (3,90), 382 (3,93)
III	NH_2		255 (4,80)	297 (3,54), 309 (3,55)	398 (3,84)
IV	NHC_4H_9		242 (4,78), 252 (4,70), ~264 (4,50)	300 (3,51), 312 (3,49)	386 (3,96)
V	NHC_6H_5		252 (4,83), ~264 (4,52)	315 (3,63)	392 (4,05)
VI	$NHC_6H_4OC_2H_5$-*p*		246 (4,81), ~264 (4,50)	308 (3,60)	392 (4,02)

TABLE 2. UV Spectra of 1,2,3,4-Tetrahydrobenzo[g]quinoline Derivatives in Ethanol



Compound	R	R′ R″	λ_{max}, nm (lg ε)		
			β	p	α
VII	H	H_2	248 (4,61)	280 (3,74) 290 (3,88) 300 (3,78)	354 (3,51)
VIII	H	O	238 (4,61) 266 (4,56)	~300 (3,77) ~312 (3,60)	434 (3,28)
IX	$COCH_3$	O	~242 (4,39) 260 (4,65)	294 (3,80) ~304 (3,74)	362 (3,19)
X	H	$NNHC_6H_5$	244 (4,49) 248 (4,51) 268 (4,38)	298 (4,01)	360 (3,63)

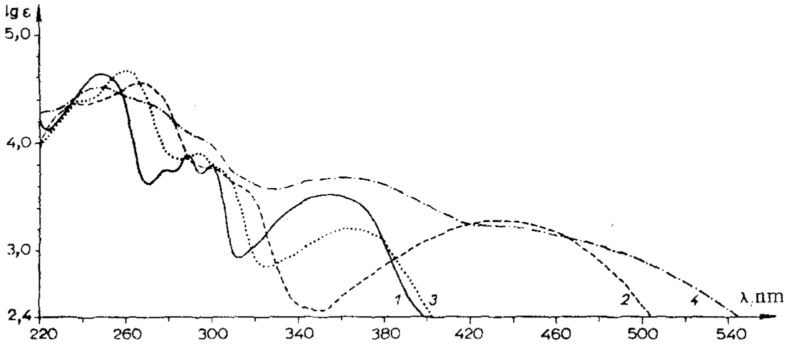
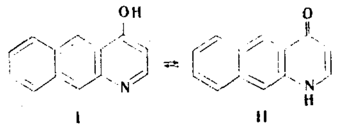


Fig. 2. UV spectra of 1,2,3,4-tetrahydrobenzo[g]quinoline derivatives in ethanol: 1) 1,2,3,4-tetrahydrobenzo[g]quinoline (VII); 2) 4-oxo-1,2,3,4-tetrahydrobenzo[g]quinoline (VIII); 3) 1-acetyl-4-oxo-1,2,3,4-tetrahydrobenzo[g]quinoline (IX); 4) 4-oxo-1,2,3,4-tetrahydrobenzo[g]quinoline phenylhydrazone (X).

The introduction of an alkyl or aryl substituent into the exocyclic amino group (IV-VI) is accompanied by a small hypsochromic shift in the long-wave band. The latter is a composite band, and it is therefore difficult to give an unambiguous explanation relative to the change in energy of the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions.

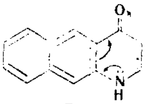
Additional bands at 297-315 nm, which are probably associated with interaction of the $2p_z$ electrons of the exocyclic nitrogen atom with the π-electron system of BQ [6, 12, 13], develop in the spectra of III-VI. The introduction of substituents into the amino group, especially aryl groups (V, VI), causes a bathochromic shift and a certain hyperchromic effect. The presence of an electron-donor ethoxy group (VI) in the phenyl group does not have an appreciable effect on the absorption, which makes it possible to present a single curve for V and VI (Fig. 1). The p band is displayed independently in the spectrum of 4-hydroxybenzo[g]quinoline because of the hypsochromic shift of the benzene bands. The additional bands at 316-332 nm in the spectrum of 4-hydroxybenzoquinoline have much in common with the absorption at 325 nm for 1,4-naphthoquinone, which is due to the quinoid structure of the substance [14]. On the basis of these data and the known analogy with 4-hydroxyquinoline, one can assume the probability of the formation of oxo form II in ethanol. However, this conclusion requires additional investigation.



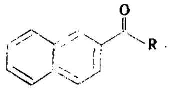
I II

The UV spectra of 1,2,3,4-tetrahydrobenzo[g]quinoline (THBQ, VII) are characterized by three major groups of bands, which, in position and structure, are close to the α, p, and β absorption bands and are hypsochromically shifted as compared with the bands of BQ as a result of a decrease in the conjugation chain (Fig. 2, Table 2).

The long-wave maximum in the spectrum of the 4-oxo derivative of THBQ (VIII) is shifted bathochromically as a result of the development of an amide type of interaction of the p electrons of the cyclic nitrogen atom with the carbonyl group (formula B) [15, 16].



B



C

The acylation of VIII at nitrogen (IX) suppresses the nitrogen–carbonyl interaction and leads to a hypsochromic shift of the long-wave band, which was also observed for the corresponding quinoline derivatives [16]. A band at 260-266 nm, which is apparently associated with $\pi \rightarrow \pi^*$ transitions in fragment C, also appears in the spectra of both 4-oxo derivatives of THBQ (VIII, IX).

EXPERIMENTAL

Compounds I-X were synthesized by known methods [10, 17, 18]. The UV spectra of alcohol solutions were recorded with an SF-4 spectrophotometer.

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