SYNTHESIS OF BENZO[g]QUINOLINE DERIVATIVES

IX.* IR SPECTRA OF BENZO[g]QUINOLINES

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The IR spectra of linear benzoquinoline derivatives at 700-900, 1400-1700, and 2800-3600 cm^{-1} are discussed, and the characteristic frequencies are related to the peculiarities of the structures of the synthesized compounds.

We have previously presented a new method for the synthesis of benzo[g]quinoline derivatives that makes this little-investigated series of compounds accessible [2, 3]. The data on the IR spectra are presented in the literature in extremely limited form and touch upon only the characteristics of groups that enter into the benzo[g]quinoline molecule [4-11]. The goal of the present investigation was a detailed study of the IR spectra of several benzo[g]quinoline derivatives synthesized by us (Tables 1 and 2 and Fig. 1) and exposure of the frequencies that characterize the linear benzoquinolines.

Benzo[g]quinoline (I) as a linear, polynuclear system consisting of three condensed rings is characterized by out-of-plane deformation vibrations at 700-900 cm^{-1} that indicate the order of substitution in the benzene and pyridine rings in the structure of the I molecule.

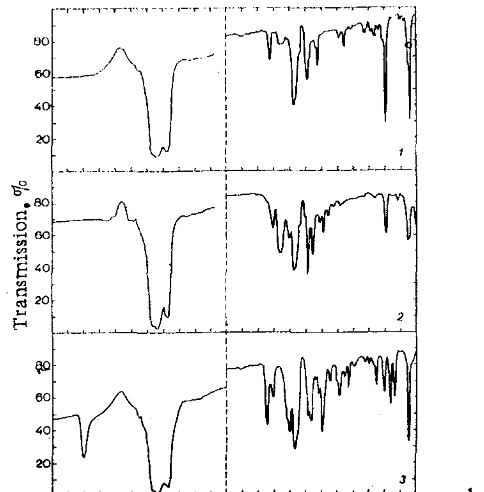
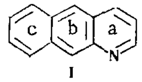


Fig. 1. IR spectra: 1) benzo[g]quinoline (I); 2) 4-anilinobenzo[g]quinoline (III); 3) 1,2,3,4-tetrahydrobenzo[g]quinoline (VI).



I

The c ring can be considered to be an o-disubstituted benzene ring. The absorption band at 735-770 cm^{-1} corresponds to the latter [8, 12-14]. We observed intense absorption at 733-746 cm^{-1} for I derivatives (Table 1). Amino derivatives I also have a band as a shoulder at 723 cm^{-1}. The absorption bands at 740 and 700 cm^{-1} for III should apparently be ascribed to ν_{CH} in the phenyl radical. The frequency of these bands is 741-757 cm^{-1} in a number of 1,2,3,4-tetrahydrobenzo[g]quinoline derivatives (Table 2), and an additional band at 723-728 cm^{-1}, which appears as a satellite of the primary band [12], is more noticeable.

The b ring of I derivatives is a 1,2,4,5-tetrasubstituted benzene ring that has an isolated hydrogen atom [12] and is characterized by a strong band at 887-883 cm^{-1} that retains its position also in solution. The spectra of tetrahydro derivatives contain two absorption bands at 880-918 and 857-910 cm^{-1}, which should be assigned to ν_{CH} of the b ring [15, 17]. In addi-

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* See [1] for communication VIII.

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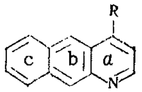
TABLE 1. IR Spectra of Benzo[g]quinoline Derivatives*



Compound	R	State	Absorption frequencies, cm^{-1}																
			ν_{C-H} of the c ring	ν_{C-H} of the b ring	ν_{C-H} of the *a* ring	$\nu_{C=C}$					$\nu_{C=C}$			$\nu_{C=N}$	ν_{C-H}		ν_{N-H}	note	
I	H	cr	733 s	887 s	743 m	1615 m	1589 w	1534 m	1512 w	1488 w	1429 m	—	1386	1553 m		3056 m			
		sol		885		1615	1590	1540	1508	1478	1430	1396		1558	3070	3017, 2982			
II	OH	cr	743 s	863 m 836 m	822 m 787 m	1600 s	1583 s	1543 m†	1492 m	—	—	—	—	1554 s		3070 m	3231 m 3211 m	$\nu_{C=O}$ 1645 m	
III	NHC_6H_5	cr	746 s 723 w†	883 s	887 s	1597 m	1572 m†	1542 m†	1500 m	—	1427 m	1400 m	—	1550 s	3080 m	3050 m	3242 m 3192 m	ν_{CH} (C_6H_5) 700 m 740 s	$\nu_{C_6H_5}$ 1609 m†
		sol		887	870										3087	3028, 2952	3447		
IV	$NHC_6H_4OC_2H_5$-*p*	cr	744 s 723 w†	883 s	887 s	1597 m	1576 m	1543 †	1518 m	—	1434 m	1400 m		1552 s	3076 m	3040 m	3256 m 3226 †, 3208 m	ν_{C-H} (C_6H_4) 823 m 808 m	$\nu_{C_6H_5}$ 1613 m†
		sol		887	872	1592			1515		1433	1392	1382	1550	3092	3022, 2992	3450	δ_{CH_3} 1482	ν_{CH_3} 2950
V	NHC_4H_9	cr	743 s 723 w†	883 s	872 m†	1608 m	1571 s	1583 m†	1488 w†	—	1430 m	1398 m	—	1558 s	3088 m	3056 m	3268 m 3213 m	δ_{CH_3} and CH_2 1381, 1475	ν_{CH_3} and CH_2 2942, 2882
		sol		888	869	1611	1580		1507		1426	1400	1381	1565 1558	3072	3016, 2970	3462		

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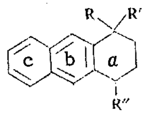
* Abbreviations: cr indicates in crystals, sol indicates in solution in chloroform, s is strong, m is medium, and w weak.

† Shoulder.

TABLE 2. IR Spectra of 1,2,3,4-Tetrahydrobenzo[g]quinoline Derivatives*



Compound	R, R′, R″	State	Absorption frequencies, cm^{-1}																			
			ν_{C-H} of the c ring	ν_{C-H} of the b ring	?	$\nu_{C=C-N}$ of *a* ring	$\nu_{C=C}$					δ_{NH}	δ_{CH_2}	ν_{CH_2}				ν_{CH}			ν_{N-H} cyclic	ν_{N-H} exo-cyclic	note
VI	R=R′=R″=H	cr	741 s 725 w †	897 m 857 m	830 m	1637 s	1603 m	1500 s	—	—	1366 s	1513 m †	—					3051 w	3022 m		3393 m		
		sol		895, 857	830	1640	1604	1493	1437	—	1365	1516	1470	2960	2950	2900	2870 2850	3070	3020	2972 †	3452		
VII	$^{R}_{R'}{>}{=}O$ R″=H	cr	742 s 725 w †	913 m 866 m	838 m	1634 s	1607 m	1497 m	1430 m	1396 m †	1368 s	1506 m †	—					3093 m	3045 m		3420 m		$\nu_{C=O}$ 1681 s
		sol		913, 865	834	1631	1607	1493	1434	1408	1364	1507	1472	2930	2906	2846		3062	3022	2980	3430		1690
VIII	$^{R}_{R'}{>}{=}O$ R″=$COCH_3$	cr	757 s 728 w †	918 m † 910 m	813 w	1633 s	1600 m	1506 m	—	—	—	—	—					3088 m			—		$\nu_{C=O}$ $\nu_{C=O}$ (R″) 1695 m 1663 s
		sol		890, 910	815	1630	1602	1505	1438**	1387	1377	—	1462	2952	2912	2897	2860	3072	3018	2970	—		1692 1663,
IX	$^{R}_{R'}{>}{=}NNHC_6H_5$ R″=H	cr	747 s 723 w †	902 m 880 m 860 m	830 m	1633 s	1603 s	1490 s	—	—	1368 s	1508 m †	—					3060 m			3401 m	3371 w 3313	γ_{CH} (C_6H_5) $\nu_{C=N}$ 690 1560 m 1567
		sol		902, 888, 863	836	1634	1604	1484	1440	1384**	1365	1505	1472	2952	2922	2912	2860—2842	3067	3020	2982	3415	3377 w	$\nu_{C_6H_5}$ 1572 m 1582

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* See the notes to Table 1.

tion, these derivatives display absorption of medium intensity at 830-838 cm^{-1}. Similar bands were found for 1,2,3,4-tetrahydroquinoline [14] and its 4-oxo derivative [18]. However, it is difficult to make an unambiguous assignment on the basis of the available data.

The interpretation of the absorption bands of pyridine ring *a* is a rather difficult task. The band at 743 cm^{-1} corresponds to the ν_{CH} vibrations of the *a* ring of I, which can be considered to be a 1,2,3-trisubstituted benzene ring. The absorption at 873-887 cm^{-1}, which is displayed either as a shoulder or as a difficult-to-distinguish doublet with a band at 883 cm^{-1}, should apparently be assigned to the vibrations of the pyridine ring for 4-amino derivatives III-V, which have two adjacent hydrogen atoms. Two bands at 887 and 872 cm^{-1} are distinctly revealed during the measurement of the spectra of solutions of the substances (for example, IV). It should be noted that the spectrum of IV also contains absorption at 823 and 808 cm^{-1}, which is probably caused by the vibrations of two adjacent hydrogen atoms in the aryl group in the 4 position.

The 1400-1700 cm^{-1} region is important in that it makes it possible to reveal the possibility of the application of correlations established in the quinoline series to the corresponding bonds and structures of derivatives I.

In the indicated region, benzo[g]quinoline is characterized by a series of bands at 1615, 1589, 1553, 1534, and 1512 cm^{-1}, as well as by bands at 1478 and 1430 cm^{-1} and a doublet at 1396 and 1386 cm^{-1}, which are detected in the spectra of a chloroform solution. A comparison with the spectra of quinoline [19] demonstrates that there is much in common with respect to frequency and number of bands; some differences are found only in the absorption intensity.

The interpretation of the bands for 4-arylamino-substituted III and IV is complicated by the fact that $\nu_{C=C}$ of the aromatic ring and δ of the exocyclic NH group are superimposed on $\nu_{C=C}$ of the benzoquinoline system of rings. The presence of an aryl ring is responsible for the appearance of additional bands at 1613 and 1609 cm^{-1}, which are displayed as a shoulder on the primary band at 1579 cm^{-1}. The effect of the δ-exocyclic NH group can be judged from the considerable increase in the $\nu_{C=C}$ intensity at 1571-1580 cm^{-1} in the spectra of III-V [12].

The absorption at 1550-1558 cm^{-1} for I derivatives is probably associated with $\nu_{C=N}$ of the pyridine ring [20, 21], since these bands are not displayed when the latter is hydrogenated.

An intense band at 1645 cm^{-1}, which, in analogy with [10, 22-25], can be assigned to $\nu_{C=O}$, is present in the spectrum of crystals of II. The presence of a band at 3231 cm^{-1}, which corresponds to ν_{NH}, indicates that the compound exists primarily in the oxo form.

The spectra of tetrahydrobenzo[g]quinoline derivatives differ in that there is a strong absorption band at 1630-1637 cm^{-1}, regardless of the character of the substituent in the 4 position and the presence or absence of an acyl group attached to the ring nitrogen. The absorption at 1640-1660 cm^{-1} is characteristic for compounds with an enamine structure [26]. There are only single communications in the literature regarding the presence of this band in hydrogenated nitrogen-containing heterocycles. Bands at 1647, 1640, and 1631 cm^{-1} are found for tetrahydropyridines [19, 27, 28]; 1,2,3,4-tetrahydroquinoline has an intense band at 1610 cm^{-1} [14]. The absorption at 1642 cm^{-1}, which is observed for 1-benzoyl-1,2,3,4-tetrahydro-4-oxoquinoline, has been associated with the vibrations of a tertiary amide group [18]. The band found for tetrahydrobenzo[g]quinoline should apparently be assigned to the vibrations that characterize the enamine double bond in the partially hydrogenated pyridine ring.

Among the bands caused by the aromatic rings of tetrahydrobenzoquinoline, one should note those at 1603, 1500, and 1366 cm^{-1}, as well as the band at 1437 cm^{-1}, which is noticeable only in the spectrum of solutions. The number of these bands is less than for I. One's attention is directed to the absorption as a shoulder at 1506-1513 cm^{-1}, which is observed for all of the tetrahydro derivatives except the N-acetyl derivative, which makes it possible to conjecturally consider it to be due to δ_{NH} in the ring [12].

The spectrum of VIII contains bands at 1695 and 1663 cm^{-1}, which are due to $\nu_{C=O}$ of the ketone group and the N-acetyl carbonyl group [10].

In contrast to I, the IR spectrum of a solution of the tetrahydro derivative has a band at 1462-1472 cm^{-1}, which is associated with the scissors vibrations (δ_{CH_2}) of the pyridine ring.

At 2800-3600 cm^{-1}, the spectra of derivatives of I have a characteristic triplet (as, for example, at 3070, 3017, and 2982 cm^{-1} for I), which is due to ν_{CH}, and the intensity of the latter band is a maximum.

The spectra of crystals of these compounds contain one to two bands, the major band of which is found near 3054 cm^{-1}. The ν_{CH} vibrations of solutions of the tetrahydro derivatives are also characterized by three bands (3070, 3020, and 2972 cm^{-1} for VI), which are sometimes poorly resolved, but the second band has the maximum intensity. In addition, the symmetrical and asymmetrical ν_{CH_2} vibrations are observed as a series of bands at 2842-2870 and 2897-2953 cm^{-1} [29, 30].

A doubled broad band at 3250 cm^{-1} due to association of the exocyclic NH_2 groups [12] is displayed in the spectra of the 4-amino-substituted derivatives of I. In the spectra of solutions, this band has the position of a free NH group at 3450 cm^{-1}. The absorption at 3400 cm^{-1}, which also retains its frequency in solution [23], corresponds to ν_{NH} in the ring of the tetrahydro derivatives. As a consequence of the presence of two secondary amino groups (cyclic and exocyclic), the spectrum of a solution of IX contains two bands at 3415 and 3377 cm^{-1}, respectively.

These investigations have demonstrated that linear benzoquinolines and their hydrogenated analogs can be identified from the absorption in the ν_{CH} region. It was found that bands at 1634 ± 3, 1469 ± 7, and 3403 ± 16 cm^{-1}, which make it possible to distinguish them from derivatives of I, which have specific absorption at 1553 ± 8 cm^{-1}, are characteristic for 1,2,3,4-tetrahydrobenzo[g]quinolines.

EXPERIMENTAL

Compounds I-IX were synthesized by the methods in [2, 3]. The spectra of mineral-oil pastes and 5% chloroform solutions in 0.12-mm-thick cuvettes were recorded with a UR-20 spectrophotometer. Because of its low solubility, the spectrum of III was measured with a 0.62% solution, while the spectrum of IV was measured with a 1.25% solution. The spectrum of a chloroform solution of II could not be recorded.

LITERATURE CITED

1. A. F. Bekhli and N. P. Kozyreva, Khim. Geterotsikl. Soedin., 802 (1970).
2. A. F. Bekhli and N. P. Kozyreva, Khim. Geterotsikl. Soedin., No. 1, 296 (1967).
3. A. F. Bekhli and N. P. Kozyreva, Khim. Geterotsikl. Soedin., 294 (1969).
4. J. T. Braunholtz and F. G. Mann, J. Chem. Soc., 651 (1954).
5. J. T. Braunholtz and F. G. Mann, J. Chem. Soc., 3368 (1958).
6. N. S. Kozlov, V. V. Misenzhnikov, and M. S. Gaisinovich, Khim. Geterotsikl. Soedin., 467 (1965).
7. N. P. Kozyreva, "Investigations of benzo[g]quinoline derivatives," Dissertation [in Russian], Moscow (1969).
8. N. S. Kozlov, 5,6-Benzoquinolines [in Russian], Minsk (1970), p. 16.
9. S. V. Nekrasov and A. V. El'tsov, Zh. Organ. Khim., 7, 188 (1971).
10. A. F. Bekhli, N. P. Kozyreva, and E. M. Peresleni, Khim. Geterotsikl. Soedin., 798 (1970).
11. R. H. Willey, C. H. Jarboe, I. R. Hayes, and F. H. Hayes, J. Org. Chem., 23, 268 (1958).
12. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
13. C. G. Cannon and G. B. B. M. Sutherland, Spectrochim. Acta, 4, 373 (1951).
14. R. A. Heacock and L. Marion, Can. J. Chem., 34, 1782 (1956).
15. V. F. Shner, Zh. Obshch. Khim., 35, 977 (1965).
16. A. R. Katritzky and R. Jones, J. Chem. Soc., 2942 (1960).
17. T. A. Chibisova, A. Ya. Zheltov, V. Ya. Rodionov, and B. I. Stepanov, Zh. Organ. Khim., 7, 143 (1971).
18. J. T. Braunholtz and F. G. Mann, J. Chem. Soc., 4166 (1957).
19. A. R. Katritzky (editor), Physical Methods in Heterocyclic Chemistry, Academic Press (1963).
20. J. T. Kay and P. J. Taylor, J. Chem. Soc., 2656 (1968).
21. M. E. Pudel' and Yu. S. Tsizin, Khim. Geterotsikl. Soedin., 1112 (1970).
22. Yu. N. Sheinker and V. M. Reznikov, Dokl. Akad. Nauk SSSR, 102, 109 (1955).
23. S. F. Mason, J. Chem. Soc., 4874 (1957).
24. M. F. Grundon and N. J. McCorkindale, J. Chem. Soc., 2177 (1957).
25. J. R. Price and J. B. Willis, Austral. J. Chem., 12, 589 (1959).
26. V. I. Minkin, L. N. Olekhnovich, L. E. Nivorozhkin, Yu. A. Zhdanov, and M. I. Knyazhanskii, Zh. Obshch. Khim., 6, 348 (1970).
27. R. Schenker and J. Druey, Helv. Chim. Acta, 42, 1960 (1959).
28. J. W. Lewis and P. A. Major, J. Chem. Soc., 1074 (1970).
29. S. Saeki, Chem. Pharm. Bull. (Tokyo), 9, 226 (1961).
30. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 15.