UDC 547. 832 + 543. 422

RESEARCH ON THE SYNTHESIS OF 5, 6-BENZOQUINOLINE DERIVATIVES. INFRARED SPECTRA OF 2-PHENYL-5, 6-BENZOQUINOLINE DERIVATIVES

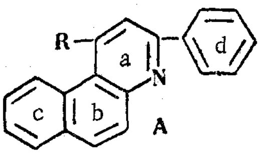
N. S. Kozlov, V. V. Misenzhnikov, and M. S. Gaisinovich

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 3, pp. 467-470, 1965

The infrared spectra of a number of 2-phenyl-5, 6-benzoquinoline derivatives are measured. It is found that in the 690-900 cm^{-1} range, correlations found for benzene homologs and applicable to pyridine and quinoline derivatives also apply to these 2-phenyl-5, 6-benzoquinoline derivatives.

The literature contains comparatively little data on the characteristic absorption bands of aromatic nitrogen heterocyclic systems. The IR spectra of 2-phenyl-5, 6-benzoquinoline and its derivatives have not been described.

In recent years a considerable number of such compounds have been synthesized in this laboratory, and a large amount of material on their IR spectra has been accumulated. The 2-phenyl-5, 6-benzoquinoline molecule comprises three condensed aromatic rings, one a pyridine one with a phenyl group attached to it (A).



A

An absorption band characteristic of aromatic compounds would, first and formost, be expected in the IR spectrum of such a compound. Aromatic type structures are disclosed by the occurrence of bands at 3030 cm^{-1} due to valence vibrations of the C—H bond, and at 1500-1600 cm^{-1}, due to planar vibrations of the C=C skeleton. The nature of the substituent has very little effect on the absorption bands in those regions. The existing data indicate that the C—H valence vibrations in pyridines and quinolines are analogous to the same vibrations in benzene. Pyridine and picolines [1] have C—H absorption bands at 3020-3070 cm^{-1}, the positions and number altering with the presence of substituents, but in every case the band frequencies were close to those for the corresponding benzene homologs. The spectrum of anabasine has an absorption band in the vicinity of 3030 cm^{-1}, which is absent from the spectrum of piperidine, and which belongs to the valence vibrations of C—H in the pyridine ring [2]. Bellamy [3] states that quinoline derivatives also have an absorption band near 3030 cm^{-1}, but these bands can deviate because of the valence vibrations of C—H in the carbon ring. This applies even more to 2-phenyl-5, 6-benzoquinoline derivatives, which have three carbon rings. The spectra of these compounds always have a strong absorption band about 3050 cm^{-1}.

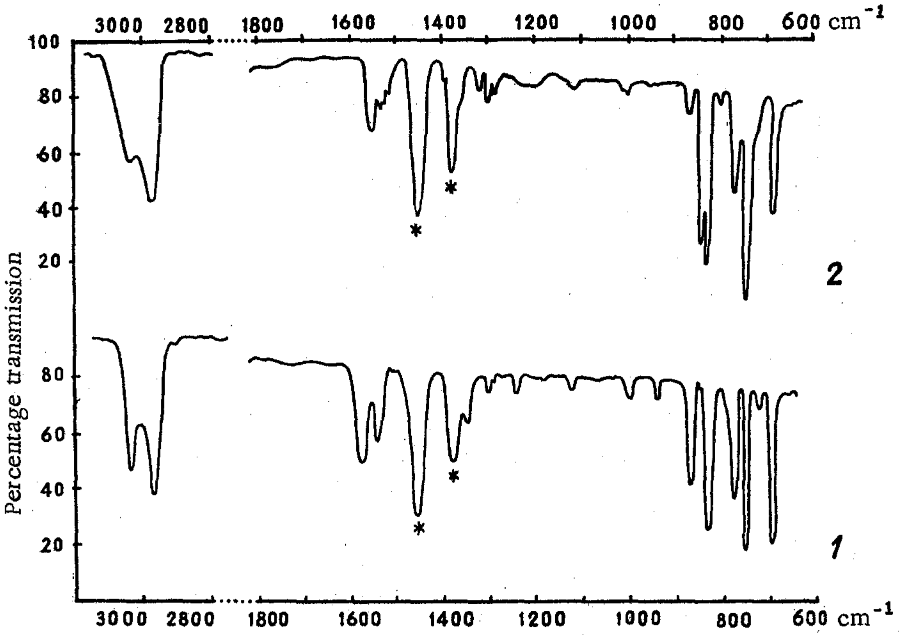
Some authors observed a weak absorption band, frequency 3400 cm^{-1}, in the region of the N—H valence vibrations [4], in the spectra of the pyridine and its derivatives. The spectra of the present compounds have no clear absorption bands in that region.

With pyridine, quinoline, and their derivatives, there are some absorption bands in the 1500-1600 cm^{-1} region, at lower frequencies than the corresponding bands for benzene [2]. The spectra of derivatives of 2-phenyl-5, 6-benzoquinoline have bands in the 1540-1580 cm^{-1} region, but they cannot be used to identify this class of compound.

It can be seen in the figure that the benzoquinolines give some strong absorption bands in the 690-900 cm^{-1} region, a region which usually includes absorption bands corresponding to C—H extraplanar deformation vibrations in aromatic compounds. With substituted benzenes it was shown that the main factor determining the frequencies of these vibrations is the number of mutually contiguous unsubstituted hydrogen atoms in the ring. Hence it is the position and not the nature of these substituents which determines the frequencies of these bands, and they are on excellent means of establishing the type of substituent. The correlations established for substituted benzenes, agree well with those for pyridine and quinoline derivatives. For example, the pyridine spectrum has an absorption band at 750 cm^{-1}. The same band is characteristic of monosubstituted benzenes. The absorption of α-picoline at 755 cm^{-1}, of β-picoline at 790 cm^{-1}, and γ-picoline at 800 cm^{-1}, correspond to the absorptions of ortho-, meta- and para- substituted benzene.

In the case of 4-methyl-2-phenyl-5, 6-benzoquinoline, in order to be able to arrive at a definite conclusion regarding the existence of absorption bands in this region, each ring must be considered separately. Ring a can be regarded as 2, 4, 5, 6-tetrasubstituted pyridine with one isolated unsubstituted hydrogen atom, to which the absorption band in the 860-900 cm^{-1} region must correspond. The spectrum of the present compound has a band at 870 cm^{-1}. Ring b can be represented as a tetrasubstituted benzene with two adjacent unsubstituted hydrogen atoms, and the band in the 800-860 cm^{-1} region must correspond to it. The spectrum has a strong absorption band at 837 cm^{-1}. Ring c can be regarded as an orthosubstituted benzene, with four mutually contiguous hydrogen atoms. The absorption band in the region 735-770 cm^{-1} must correspond to such a compound. The spectrum has an absorption band at 755 cm^{-1}. Apparently the absorption bands at 695 and 770 cm^{-1} are to be ascribed to C—H vibrations in the phenyl group (literature data for a monosubstituted benzene: two bands in the 690-710 cm^{-1} region and the 730-770 cm^{-1} one [5]).

As was to be expected, the spectra of all the 2-phenyl-5, 6-benzoquinoline derivatives with various substituents at position 4, covered in the present work, have the same absorption band in that region as 4-methyl-2-phenyl-5, 6-benzoquinoline, whose spectrum is shown in the figure. 2-Phenyl-5, 6-benzoquinoline itself (see figure) and its derivatives have spectra of a somewhat different character. In those compounds ring a has not one, but two mutually contiguous unsubstituted hydrogen atoms, and this explains the appearance of two absorption bands at 832 and 843 cm^{-1}, along with one band at 837 cm^{-1}, in the spectrum of 4-methyl-2-phenyl-5, 6-benzoquinoline. At the same time the absorption band at 870 cm^{-1} becomes considerably less intense.



IR spectra: 1) 4-Methyl-2-phenyl-5, 6-benzoquinoline; 2) 2-phenyl-5, 6-benzoquinoline. Asterisks denote vaseline absorption bands.

Experimental

The spectra were measured with an IKS-14 infrared spectrophotometer. In the 650-1800 cm^{-1} range a NaCl prism was used, and the specimens used were vasiline mixtures. Above 1800 cm^{-1} a LiF prism was used, and the material was dissolved in chloroform. The layer thickness was 0. 1 mm, concentration of material 10%.

REFERENCES

1. J. Roberts and M. Szwarc, J. Chem. Phys., 16, 981, 1948.
2. L. Marion et al., J. Am. Chem. Soc., 73, 305, 1951.
3. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, 399, 1963.
4. E. Coulson, J. Hales, and C. Herington, J. Chem. Soc., 2125, 1951.
5. A. Cross, Introduction to Practical Infrared Spectroscopy [Russian translation], IL, 88, 1961.