STRETCHING VIBRATIONS OF THE AZOMETHINE GROUP OF 2-AMINOBENZOXAZOLE DERIVATIVES

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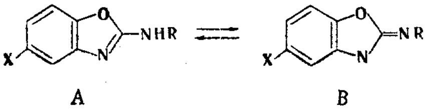
UDC 543.422.4:547.787.3

An analysis of the IR spectra of a series of 2-aminobenzoxazole derivatives in the region of the frequencies of the vibrations of the C=N bond provides evidence for the existence of two tautomeric forms. The position of the tautomeric equilibrium of these types of compounds depends on the medium but is independent of the form of the substituents attached to the nitrogen atoms.

The synthesis of 2-aminobenzoxazole derivatives has been described [1, 2] and it has been noted that the stretching vibrations corresponding to the azomethine group in these compounds show up in a rather high-frequency region (1713-1737 cm^{-1}). It should be noted that the literature does not contain any other data on the absorption of the C=N group at such high frequencies. On the basis of data on the stretching vibrations of the amino group it was concluded [3, 4] that 2-aminobenzoxazoles exist exclusively in the amino form. However, the study of the stretching vibrations of the NH group is complicated considerably because of the fact that the absorption bands of the tautomeric forms lie over a rather narrow range of frequencies.



I-XIV

It seems to us that more reliable results can be obtained by a study of the stretching vibrations of the azomethine group, especially since it has been established [2] that there is a considerable difference between the characteristic frequencies of the C=N groups of these compounds.

In this connection, we obtained alkyl- and aralkyl-2-aminobenzoxazoles and 2-aminobenzoxazole-5-sulfonamides by our previously developed methods [5]. Their IR spectra are presented in Table 1.

The 2-aminobenzoxazole derivatives have an endocyclic azomethine group, while the 2-aminobenzoxazoline derivatives have an exocyclic azomethine group. In conformity with the data in [6], the stretching vibrations are found at 1460-1660 and 1635-1690 cm^{-1}, respectively. These data are in agreement with the previous calculations of the electronic structures of the A and B forms by the Hückel method with the parameters proposed by Streitwieser [7]. In conformity with the established correlations between the characteristic frequencies and bond orders for the endocyclic bond [its order (0.7138) is lower than in the case of the exocyclic bond (0.7432)], the frequency of the vibrations of the C=N group should be lower than in the case of the exocyclic bond. The data in Table 1 show that in the case of the solid state the frequencies of the vibrations of the azomethine group for 2-aminobenzoxazoles with alkyl substituents of the II-IV, VIII, IX, and XI-XIV type are found at 1700 cm^{-1} and that this peak can be assigned to the exocyclic azomethine group. These compounds consequently exist in the solid state primarily in the form of 2-iminobenzoxazolines or in a close structural modification.

The spectra of solutions of the compounds in $CHCl_3$ [I-VII; XI in 1% dimethyl sulfoxide (DMSO)] contain the frequency of the stretching vibrations of the azomethine group at 1645-1660 cm^{-1}, which is in agreement with an endocyclic azomethine group. Thus the indicated compounds exist primarily in the 2-aminobenzoxazole form in dilute solutions.

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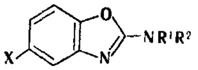
0009-3122/79/1502-0156$07.50

TABLE 1. Stretching Vibrations (ν, cm^{-1}) of the Azomethine Group of 2-Aminobenzoxazoles

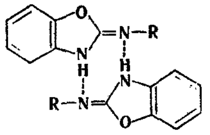


Compound	R¹	R²	X	1% $CHCl_3$	Mineral oil
I	CH_8	H	H	1650	1673
II	C_2H_5	H	H	1652	1700
III	C_3H_7	H	H	1652	1698
IV	C_4H_9	H	H	1653	1703
V	$CH_2C_6H_5$	H	H	1650	1673
VI	C_6H_{11}	H	H	1640	1658
VII	C_6H_5	H	H	1652	1666
VIII	CH_3	H	SO_2NH_2	—	1695
IX	C_2H_5	H	SO_2NH_2	—	1705
X	C_3H_7	H	SO_2NH_2	—	1703
XI	C_4H_9	H	SO_2NH_2	1660 (1% DMSO)	1696
XII	$CH_2C_6H_5$	H	SO_2NH_2	—	1698
XIII	C_6H_{11}	H	SO_2NH_2	—	1692
XIV	C_6H_5	H	SO_2NH_2	—	1700
XV	$(CH_2)_2O(CH_2)_2$		H	1640	1655
XVI	$(CH_2)_5$		H	1643	1646
XVII	CH_3	CH_3	H	1660	1660
XVIII	$(CH_2)_2O(CH_2)_2$		SO_2NH_2	—	1656
XIX	$(CH_2)_5$		SO_2NH_2	1649 (1% DMSO)	1640
XX*	C_2H_5	—	H	1710	1720
XXI*	C_6H_{11}	—	H	1712	1722

*The 3-methyl-2-iminobenzoxazoline derivative.

The data on the frequencies of the azomethine group in the spectra of XV-XXI, for which tautomeric transformations are impossible, confirm the assumption that the change in the frequency of the stretching vibrations of the azomethine group in I-XIV in the solid state and in dilute solutions is associated with a tautomeric transformation (see Table 1).

The change in the characteristic frequencies of the C=N group for compounds of the I and V-VII type in chloroform and mineral oil is slight. The structure of V in the solid state was determined by x-ray diffraction analysis [8], and the electron densities in the case of protonation of the ring and exocyclic nitrogen atoms were calculated. The coefficient of convergence (R) is minimal if one assumes that the ring nitrogen atom is protonated, i.e., in the solid state this compound has an iminobenzoxazoline structure. The formation of intermolecular hydrogen bonds in the solid state was also established by x-ray diffraction analysis [8]:



The IR spectral data presented above are in agreement with the results of x-ray diffraction analysis, i.e., one should assume that V exists in the B form in the solid state and that the formation of hyrogen bonds is the reason for the lower frequencies of the stretching vibrations of the azomethine group. This is evidently also the case for I, VI, and VII.

The IR spectrum of solutions of the examined compounds in chloroform were also investigated. It was established that a significant change in the spectra at 1640-1680 cm^{-1} is observed as the concentration is changed. Only one band at 1658 cm^{-1} is observed in the spectrum of a 1% solution of IV in $CHCl_3$, while two peaks are observed in the spectrum of a 10% solution of this compound in $CHCl_3$: the more intense peak at 1653 cm^{-1} corresponds to an endocyclic azomethine group, and the less intense peak at 1680 cm^{-1} corresponds to an exocyclic group. In addition, a broad band at 3150-3250 cm^{-1}, which corresponds to the hydrogen bonds of the NH groups, is observed.

These data show that IV exists primarily in the A form in a dilute solution in chloroform, whereas an equilibrium between both forms with predominance of the A form is established in concentrated solution. The appearance of the band of an exocyclic azomethine group is associated with the existence of intermolecular hydrogen bonds. The same changes are also characteristic for a 20% solution of IV in $CHCl_3$. Only one peak for the C=N bond at 1652 cm^{-1} is observed in the IR spectrum of a 20% solution of IV in dioxane. Thus the equilibrium is sensitive to the nature of the solvent.

In other words, an analysis of the spectra of the 2-aminobenzoxazole derivatives in the region of the frequencies of the C=N vibrations provides evidence for the existence of two tautomeric forms and that the tautomerism of these types of compounds depends primarily on the medium and is independent of the form of the substituent attached to the nitrogen atoms.

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SPECTRA OF 3-BENZOXAZOLONYLPROPANONES

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UDC 543.422.25.4:547.787.3

The effect of substituents on the vibrational frequencies of oxazolonyl and acetonyl carbonyl groups was studied by means of the IR and PMR spectra of a series of substituted (in the benzene ring) 3-benzoxazolonylpropanones. The experimental data and the results of correlation analysis show that the carbonyl group of the acetonyl grouping is situated along the axis perpendicular to the plane of the benzene and heterocyclic rings and the substituent. The mechanism of transmission of the effect of substituents on the characteristic frequencies and the chemical shifts of the protons of the acetonyl group in the spectra are discussed.

Benzoxazolones have diversified pharmacological activity. 5-Chlorobenzoxazolone (Paraflex or Chloroxazone) and 6-chloro, 5-bromo-, and 6-bromobenzoxazolones [1, 2] are used in medicine as central myorelaxants. The activity of 5-chloro-3-benzoxazolonylpropanone and particularly its oxime surpasses the activity of the preparations Paraflex and Midocalm [3]. A number of N-substituted aryloxazolones have hypnotic, analgesic, anesthetic, anticonvulsive, and antimicrobial activity [4]. A study of the molecular and electronic structures of these compounds is therefore of definite interest, particularly in connection with the establishment of the relationship between the structure and activity. In the present research we investigated the effect of polar substituents on some characteristic vibrational frequencies and chemical shifts, as well as the conformation of substituted 3-benzoxazolonylpropanones. We first desired to thoroughly analyze the effect of substituents in the aromatic ring on the electronic structure of the oxazolone and acetonyl carbonyl groups of these substances, knowing that the IR spectra of such structures satisfactorily explain their reactivities [5, 6].

K. Okhridskii Sofia University, Sofia 1126, Bulgaria. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 191-194, February, 1979. Original article submitted March 9, 1977.

0009-3122/79/1502-0158$07.50