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Abstract

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On the Structure of 2-Aminothiazoline

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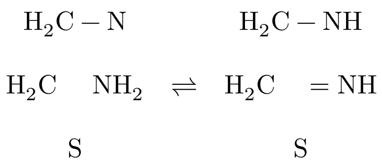
In a number of works it has been shown, by means of spectra ($^{1-5}$), that N-heterocyclic amines of aromatic character in the crystalline state and in solutions have the structure of amines rather than imines. Such a structure is apparently determined primarily by the tendency to preserve the aromaticity of the heterocycle. In this connection, the study of such heterocyclic amines in which the heterocycle cannot possess an aromatic system, and where, consequently, the indicated factor loses its significance, is of particular interest. Among such compounds one should include, in particular, 2-aminothiazoline—an readily accessible compound for which no definite structural data exist, apart from indications of the possibility of amino-imino tautomerism (^{6,7}).



$$\begin{array}{ccc} H_2C - N & & H_2C - NH \\ H_2C \quad NH_2 & \rightleftharpoons & H_2C \quad = NH \\ S & & S \end{array}$$

In the present work we give the results of an investigation of the structure of 2-aminothiazoline by methods of infrared spectroscopy and nuclear magnetic resonance spectroscopy.

In the IR spectra of 2-aminothiazoline* in the crystalline state there is an intense band at 1640 cm^{-1} and a considerably weaker one at 1600 cm^{-1}, appearing as a shoulder on the strong band. In solutions these bands are more clearly separated and have minima at 1663 and 1615 cm^{-1} (in dioxane) (Fig. 1).

We attempted to assign these bands to vibrations of the C=N, NH_2, or C—N—H groups by comparing the spectra of the compound before and after deuteration, as we had already done in similar cases (^{5}). It was found that the strong band at 1640-1663 cm^{-1} remains unchanged upon deuteration, while the comparatively weak band at 1600-1615 cm^{-1} disappears from the region under consideration (Fig. 1).

Consequently, the band at 1640-1663 cm^{-1} can be confidently assigned to $\nu(C{=}N)$; as for the band at 1600-1615 cm^{-1}, it may be due either to deformation vibrations of the NH_2 group (in the amino form) or to the C=N−H and C−N−H groups (in the imino form). Since there are no grounds for one or the other assignment of this band, and the $\nu(C{=}N)$ band should be observed in the spectra of either tautomer, consideration of the IR absorption bands in this region does not permit an unambiguous choice between the two possible forms.

However, the data of the IR spectra in the high-frequency region speak in favor of the existence of the compound in the amino form: in dilute solutions of 2-aminothiazoline in CCl_4 (0.02%) two bands are observed—3507 and 3403 cm^{-1}—which in the literature are usually assigned to the symmetric and antisymmetric stretching vibrations of the NH_2 group ([8]). Substan-

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* The spectra were obtained with an IKS-14 infrared spectrophotometer.

confirmations of the amino structure of 2-aminothiazoline were obtained by the method of nuclear magnetic resonance (NMR).* In the NMR spectra of solutions of the substance under study in chloroform and pyridine, only one peak is observed for both protons bound to nitrogen, which indicates their equivalence; in the imino tautomeric form the protons would have to absorb at different magnetic-field strengths. The result obtained may be due to the amino structure of the compound or to rapid interconversion of tautomeric forms present in commensurable amounts. But in the latter case the spectrum of the protons of the methylene groups $-CH_2-CH_2-$ should be intermediate between the spectra of the amino and imino structures and, generally speaking, should be asymmetric. In the case under investigation, however, the spectrum of the methylene groups of 2-aminothiazoline is strictly symmetric (Fig. 2). This fact rules out the possibility that two tautomeric forms with rapid interconversion exist here.

Fig. 1. IR spectra of 2-aminothiazoline and 3-methyl-2-iminothiazolidine. Dashed lines indicate the spectra of the deuterated compounds. *a*—solutions in CCl_4, *b*—solutions in dioxane.

The chemical shift δ of the peak of the N-protons of 2-aminothiazoline in chloroform at $C = 4$ wt.% is 26; for 2-aminopyridine (which is known to have an amino structure), 28; for 3-methyl-2-iminothiazolidine (a model compound of imino structure), 15.3. In pyridine solution, δ for 2-aminothiazoline is 7, and for 3-methyl-2-iminothiazolidine, 3. In all cases the chemical shift is measured in units of 10^{-7} relative to the proton peak of C_6H_6. The error is $\Delta\delta = 0.5$.

The observed values of the chemical shifts indicate a greater degree of electronic shielding for the N-protons in 3-methyl-2-iminothiazolidine, compared with 2-aminopyridine and the 2-aminothiazoline studied here, which is in good agreement with the imino structure of the first compound and the amino structure of the two latter compounds. In substances modeling the imino tautomeric

Fig. 2. NMR spectra of 2-aminothiazoline, 3-methyl-2-iminothiazolidine, and 2-thiazolidone (solutions in CHCl3)

Figure 1: Fig. 2. NMR spectra of 2-aminothiazoline, 3-methyl-2-iminothiazolidine, and 2-thiazolidone (solutions in CHCl3)

form (3-methyl-2-iminothiazolidine, 2-thiazoline), the spectra of the protons of the $-CH_2-CH_2-$ group, although similar to one another (in the magnitude of δ and the character of the splitting), differ significantly from the corresponding spectrum of 2-aminothiazoline.

Thus, the value of δ (for the center of the entire system of CH_2 peaks) in 2-aminothiazoline is smaller than in compounds of imino structure, which indicates a greater degree of shielding of the protons of the CH_2 groups in the former case. Furthermore, the greater divergence of the peaks of the CH_2 groups from the center of the system in 2-aminothiazoline indicates an enhancement of the nonequivalence of the CH_2 groups in this case compared with models of imino structure. All this is in good agreement with the amino structure of 2-aminothiazoline, in which the double bond in the ring should cause both stronger shielding by the electrons of the protons of the CH_2 groups and an increase in the nonequivalence of the two methylene groups.

* The NMR spectra were obtained using a high-resolution spectrometer of the JNM-3 type.

It is interesting that the value of δ for N-protons in amines (2-aminopyridine, 2-aminothiazoline) depends strongly on the concentration of the solution (in chloroform). The observed increase in the magnitude of the chemical shift upon dilution (from 17 in a 20% solution to 31.5 in a 1% solution for 2-aminothiazoline) is completely analogous to that described in the literature for many hydroxyl-containing compounds and is due to the rupture of hydrogen bonds between associated molecules of these substances when the concentration of the solution is decreased (7). In contrast to these data, the values of δ for the fixed imino model 3-methyl-2-iminothiazolidine practically do not depend on concentration (when the concentration is changed from 100 to 4%, δ changes from 13 to 15.3). These results are in good agreement with IR-spectroscopic data: in the spectra of 2-aminothiazoline (solutions in CCl_4), upon dilution there is a decrease in the intensity of the band at 3100-3200 cm^{-1}, up to its practical disappearance at $C = 0.02$ wt.% (stretching vibrations of bound N—H groups), and the intensity of the bands at 3507 and 3403 cm^{-1}, evidently corresponding to vibrations of free N—H groups, increases. At the same time, for 3-methyl-2-iminothiazolidine such a change is not observed, and the = N—H bond band is localized, independently of dilution, in the region 3340-3360 cm^{-1} (characteristic of imines with the = N—H grouping).

Fig. 2. NMR spectra of 2-aminothiazoline, 3-methyl-2-iminothiazolidine, and 2-thiazolidone (solutions in $CHCl_3$)

All the data obtained make it possible to conclude that 2-aminothiazoline, like N-heteroaromatic amines, has an amine structure, although in this case it is no longer connected with the energetic advantage of preserving the aromaticity of the heterocycle.

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Note: Figure translations are in progress. See original paper for figures.