

IR-SPECTRUM EVIDENCE OF AN INTERACTION
 BETWEEN FUNCTIONAL GROUPS OF
 THE 4-PYRROLIDONES

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The functional groups of the 4-pyrrolidones (Fig. 1) are bound in acyclic system and interact with each other. Of primary interest is the effect of neighboring groups on the methylene group, which corresponds to the greatest number of reactions. As was shown in [1, 2], the extent of the effect depends on the relative arrangement of these groups and on the nature of the functional group in a given position. Various methods have been used to study this problem, but the most useful results have been obtained by procedures based on local changes in the properties of the methylene group, in particular, the method of IR spectroscopy.

We have previously analyzed the effect of position 1 [3], that of position 2 [4], and that of the properties of the rhodanine molecules [5] on the vibration frequencies of the methylene group in the IR absorption spectra of the 4-pyrrolidones. We are concerned here with position 4. We studied the following substances (Fig. 1): isorhodanine, 2,4-iminothiazolidinedione, and 2,4-thiazolidinedione.

Figure 2 shows the IR absorption spectrum of 2,4-iminothiazolidinedione in the range 400-3500 cm^{-1} , recorded on a UR-20 spectrophotometer with samples in tablet form with KBr. The IR spectra of isorhodanine and 2,4-thiazolidinedione have been studied previously [6, 7].

On the basis of a theoretical analysis and a comparison of the spectra of related molecules, we distinguished the frequencies of various vibration modes of the methylene group from the IR spectra (Table 1). The scissors-vibration bands can be identified most easily, because of their intensity, peculiar shape, and

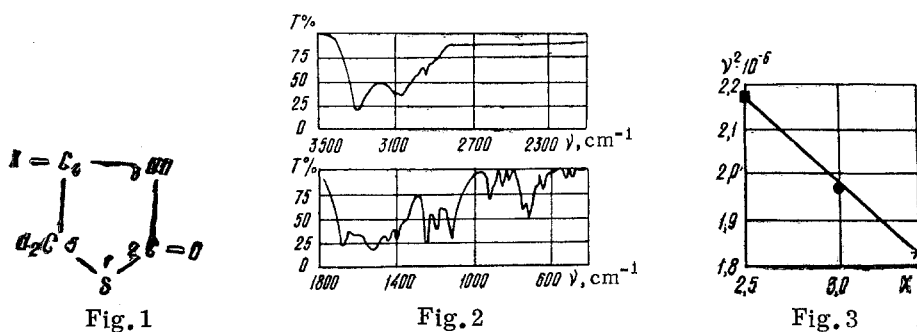


Fig. 1. The 4-pyrrolidones: X = S) isorhodanine; X = NH) 2,4-iminothiazolidinedione; X = O) 2,4-thiazolidinedione.

Fig. 2. IR absorption spectrum of 2,4-iminothiazolidinedione in the range 400-3500 cm^{-1} .

Fig. 3. Dependence of the square scissors-vibration frequency of the methylene group on the electronegativity [10] of heteroatom X: ■) sulfur; ●) nitrogen; *) oxygen.

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TABLE 1. Vibration Frequencies of the Methylene Group in the IR Spectra of the 4-Pyrrolidones (in cm^{-1})

Molecule	Vibration mode					
	scissors, CH_2	pendulum, CH_2	fan, CH_2	twisting, CH_2	symmetric, CH_2	antisymmetric, CH
Isorhodanine	1478 vi	920 vf	1316 m	1190 i	2855 m	2955 m
2,4-Imino-thiazolidinedione	1400 i	906 f	1355 vf	1198 i	2830 vf	2938 f
2,4-thiazolidinedione	1350 i	910 m	1320 vf	1174 i	2827 i	2951 i

Note: Band intensities: vi) very intense; i) intense; m) moderate; f) faint; vf) very faint.

characteristic frequency range. For this type of motion (Table 1) the frequencies decrease in the following order: isorhodanine, 2,4-iminothiazolidinedione, 2,4-thiazolidinedione. An analogous order was found in [3] for position 2 in terms of the frequencies of methylene scissors vibrations and was associated with the order in which other physical properties change; a correspondence between properties was established.

Using the result of [3] in analyzing the effect of position 4 on the properties of the methylene group, we chose the change in the scissors-vibration frequency as a basic indicator.

To explain the observed changes, we compared the square scissors-vibration frequencies (Fig. 3) with the electronegativities of the S, N, and O atoms. We believe the frequency for 2,4-thiazolidinedione is lower than that for isorhodanine because of the low electronegativity of the S atom, whose electronic cloud can become highly deformed. Maximum conjugation and a maximum mobility of the hydrogen atoms in the methylene group are found. The N and O atoms have a polarizability lower than that of the S atom. The activity of the methylene group in 2,4-iminothiazolidinedione is slightly higher than that of 2,4-thiazolidinedione but lower than that of isorhodanine.

An increase in the electronic density of the methylene group should lead to an increase of the force constants of this group and to changes in the frequencies of all modes in the same direction. This behavior was observed in [3-5]. The force constant of cyclopentane, $K_{\alpha} = 0.71 \cdot 10^6 \text{ cm}^{-2}$ [8], was varied; $K_{\alpha} = 0.59 \cdot 10^6 \text{ cm}^{-2}$ was found for 2,4-thiazolidinedione [7], and $K_{\alpha} = 0.765 \cdot 10^6 \text{ cm}^{-2}$ was found for thiorhodanine [5].

On the other hand, analysis of the data in Table 1 shows that the frequencies of the symmetric valence vibrations of the C-H bond change in the same direction with a change in the scissors frequencies. These vibration modes display the greatest frequency change in the transition from 2,4-thiazolidinedione to isorhodanine. An explanation lies in the procedure for taking into account the strict symmetry of the molecules as wholes and the approximate symmetry of the methylene group in the dynamic-coefficient matrix in the theoretical analysis of the frequencies of the completely symmetric vibrations.

For other modes (Table 1) the frequency increase from 2,4-thiazolidinedione to isorhodanine is slight and less clearly expressed, in agreement with the theoretical analysis.

Several bands (Table 1), in particular, those of 2,4-iminothiazolidinedione, are faint and blurred. As in the case of other heterocycles containing nitrogen [9], this behavior can be attributed to the effect of the hydrogen bond on the spectrum. One manifestation of this effect is the relatively high melting point of the heterocycles containing nitrogen.

Replacement of the functional groups in position 4 of the 4-pyrrolidones thus strongly affects the frequencies of symmetric valence deformation vibrations of the methylene group in the IR absorption spectrum, in agreement with the results of [3-5]. However, the changes in the sequence of functional groups in different positions with increasing scissors-vibration frequency needs further study.

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