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INVESTIGATION OF THE STRUCTURE OF 2H,6H-2,6-DIMETHYL-4-AMINO-1,3,5-DITHIAZINE BY IR SPECTROSCOPY

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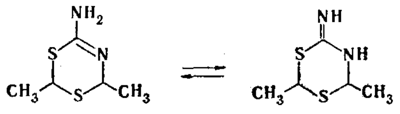
UDC 543.422.4:547.876

It was established by IR spectroscopy that 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine exists in the amino form in carbon tetrachloride at low concentrations.

Cyclic derivatives of thiourea are interesting subjects for the study of amino-imino tautomerism [1]. 2H,6H-2,6-Dimethyl-4-amino-1,3,5-dithiazine (I), which we synthesized by heterocyclization of divinyl sulfide with thiourea [2, 3], can, in principle, also exist in the II form.



I II

Amino form I with equatorially oriented methyl groups was preferred in an analysis of the PMR spectra of this heterocycle and its derivatives [4]. An independent solution of this problem can be obtained by IR spectroscopy.

In the present research we made a thorough analysis of the IR spectra of I and its 4-dideuteroamino derivative (the degree of deuteration was 70-75%), which were obtained in dilute solutions in carbon tetrachloride and chloroform, as well as in the crystalline state. Each form, i.e., I and II, individually gives two absorption bands in the region of NH stretching vibrations in the IR spectrum, whereas the I $\rightleftarrows$ II amino-imino equilibrium should be characterized by at least three (and possibly four) bands [5].

Two intense bands at 3387 and 3491 cm^{-1}, which, on the basis of the information in [5], could be assigned to symmetrical (ν_s) and asymmetrical (ν_{as}) NH vibrations in the NH$_2$ group, appear distinctly in the spectrum recorded in CCl$_4$ at a I concentration of $1 \cdot 10^{-3}$ mole/liter (Fig. 1, spectrum 1).

However, a deviation of 16 cm^{-1} between the experimental ν_s value and the value calculated from the Bellamy dependence $\nu_s = 345.53 + 0.876\ \nu_{as}$, with a mean square error of 4.8 cm^{-1} [6], is observed. Under the condition of the universality of this dependence, its nonfulfillment could constitute evidence for the erroneous selection of the structure.

However, the equation presented above was obtained for amines [6], and its applicability to thiourea fragments requires special proof. In a special case the bands belonging to structures I and II may overlap, but complete coincidence of the frequencies is unlikely, and the simultaneous existence of the two tautomers should therefore be excluded. The choice between structures I and II was made on the basis of an analysis of the position of the intensity (A) and the half width ($\nu_{1/2}$) of the IR absorption bands (Table 1).

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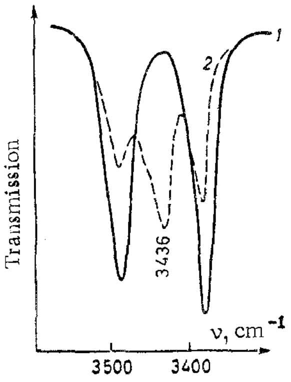


Fig. 1

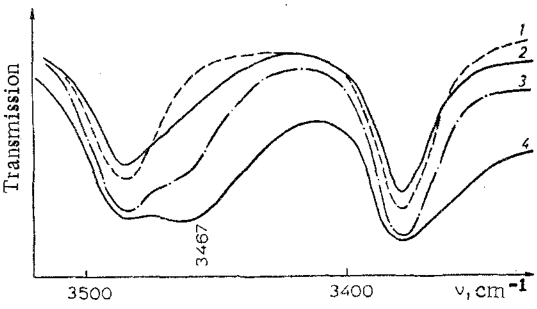


Fig. 2

Fig. 1. IR spectra of solutions 1 and 2 in CCl_4: 1) 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine; 2) 2H,6H-2,6-dimethyl-4-dideuteroamino-1,3,5-dithiazine (C $1 \cdot 10^{-3}$ mole/liter, d = 5 cm).

Fig. 2. Concentration dependence of the absorption curves of the N—H group of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine in CCl_4: 1) $1 \cdot 10^{-3}$ mole/liter, d = 5 cm; 2) $5 \cdot 10^{-2}$ mole/liter, d = 0.1 cm; 3) $1 \cdot 10^{-1}$ mole/liter, d = 0.5 cm; 4) in $CHCl_3$, $95 \cdot 10^{-2}$ mole/liter, d = 0.01 cm.

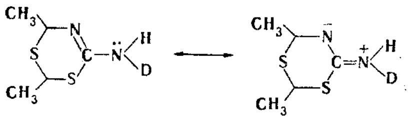
TABLE 1. Spectral Characteristics of the Absorption Bands in the Region of the N—H Stretching Vibrations of I

Concn., mole/liter		c_{Bu_2O}/c_I	ν, cm^{-1}			
			3387		3491	
c_I	c_{Bu_2O}		A·10^{-4} mole·liter/cm^{-2}	ν_{12}, cm^{-1}	A·10^{-4} mole. liter/cm^{-2}	ν_{12}, cm^{-1}
$1 \cdot 10^{-1}$			0,36	19	0,36	25
$5 \cdot 10^{-2}$			0,48	19	0,43	25
$1 \cdot 10^{-2}$			0,51	18	0,50	25
$1 \cdot 10^{-3}$			0,53	18	0,51	26
$2 \cdot 10^{-3}$	$2 \cdot 10^{-1}$	100	0,59	19	0,65	28
$2 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	200	0,67	27	0,80	40

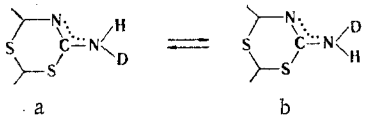
It is apparent from Table 1 that at a I concentration of $1 \cdot 10^{-3}$ mole/liter the integral intensities of the bands at 3387 and 3491 cm^{-1} are almost identical, whereas the half width of the high-frequency band is somewhat greater. This makes it possible to assign these bands to the NH_2 group. In the case of secondary amino groups the intensities of the corresponding bands increase as ν_{max} increases, whereas the $\nu_{1/2}$ value decreases [7].

When a proton acceptor (dibutyl ether) is added, the maxima of both bands remain unshifted, and only their half widths and intensities increase appreciably [8]. However, in the case of secondary amines, on the other hand, contraction and a decrease in the intensities of the bands of the monomers are observed as a result of heteroassociation [9].

Additional evidence for the amino structure of I was obtained during a study of its spectrum in the presence of deutero isomers with respect to the NH_2 group (Fig. 1, spectrum 2). Two bands of undeuterated I (3387 and 3491 cm^{-1}) and a new asymmetrical band at 3436 cm^{-1} are visible in the spectrum. The appearance of a new band indicates that we are actually dealing with a compound with the I structure, since the condition of resonance interaction of the vibrations, which determines the splitting of the frequency by ν_{as} and ν_s, is violated only for primary amino groups in the case of deuteration. In the absence of an interaction of the vibrations the band of the N—H bond should have frequency $\nu_0 = 0.5(\nu_{as} + \nu_s)$, which we also observe. Thus the asymmetrical band at 3436 cm^{-1} corresponds to the vibration of the N—H bond in the partially deuterated amino group (NHD). The weak splitting of this band is the result of slowed down rotation about the C—N bond as a consequence of p—π conjugation:



This resonance should lead to fixation of rotational isomers *a* and b:



The doublet at 3436 cm^{-1} ($\nu_{1/2}$ = 40 cm^{-1}) corresponds to two nonequivalent N—H bonds. The difference in the two frequencies is $\sim$20 cm^{-1}. This nonequivalence also evidently leads to nonfulfillment of the Bellamy dependence [6]. A similar phenomenon is observed in the spectra of amides of carboxylic acids, in which one of the N—H bonds in the amido group is perturbed by the effect of the field of the carbonyl group [10]. Two N—H frequencies of the stretching vibrations of the NHD group are also observed in the case of an even closer analog, viz., partially deuterated trimethylacetic acid thioamide [11], and with virtually the same difference in the frequencies (23 cm^{-1}).

Thus dilute solutions of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine in CCl_4 do not contain the II form. This conclusion cannot be automatically applied to solutions with high concentrations and to the crystalline state, in which the effects of intermolecular association fundamentally distort the entire spectral pattern.

Since 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine has only limited solubility in CCl_4, chloroform was used for the studies with high concentrations.

An appreciable change in the form of the absorption band at 3491 cm^{-1} is observed as the concentration of I in solutions in CCl_4 or $CHCl_3$ is increased. Asymmetry on the low-frequency side is observed for this band at a concentration of $5 \cdot 10^{-2}$ mole/liter, while a new intense band with a maximum at 3467 cm^{-1} is observed at a concentration of $95 \cdot 10^{-2}$ mole/liter (Fig. 2). The intensities of the bands at 3387 and 3491 cm^{-1} decrease as the concentration of I is increased (Table 1), although it is known that a gradual broadening and an increase in the intensities of both bands occur in the case of primary amines as their concentrations are increased [8]. This should not necessarily be observed for I, which has three additional heteroatoms that are capable of accepting the protons of the amino group. The appearance of a new band at 3467 cm^{-1}, the intensity of which increases as the concentration is increased, is evidnetly associated with the existence of a dimer. Open polymeric associates are, of course, also possible.

Unfortunately, because of the limited solubility of I we were unable to follow the changes in the spectrum at concentrations above 1 mole/liter. The number of bands increases in the spectrum of crystals of I, and their assignment becomes even more difficult.

EXPERIMENTAL

The IR spectra of KBr pellets and solutions of the compounds in CCl_4 and $CHCl_3$, as well as in the presence of dibutyl ether, which was used as a proton acceptor, were obtained with a UR-20 spectrometer at 2400-3700 cm^{-1}. The optimal recording conditions were selected. The concentrations of I and dibutyl ether ranged from $1 \cdot 10^{-3}$ to 1 mole/liter and from $1 \cdot 10^{-1}$ to $4 \cdot 10^{-1}$ mole/liter, respectively, and the thickness of the absorbing layer ranged from 0.01 to 5 cm. The error in the determination of the frequencies at the maxima of the bands did not exceed 1 to 2 cm^{-1}, as compared with 3 to 5 cm^{-1} for the "associated" bands. The accuracy in the determination of the integral intensity was 10 to 15% [12].

2H,6H-2,6-Dimethyl-4-amino-1,3,5-dithiazine (I) was synthesized and purified by the method in [2, 3] and had mp 135-137°C (dec., from ethanol).

2H,6H-2,6-Dimethyl-4-dideuteroamino-1,3,5-dithiazine. Three recrystallizations of 2.5 g of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazinium nitrate [2] from D_2O (three 20-ml portions) gave 2.1 g (84%) of 2H,6H-2,6-dimethyl-4-dideuteroamino-1,3,5-dithiazinium nitrate with mp 131.5-133°C (dec.). A solution of 0.38 g of NaOD in 16 ml of D_2O (the NaOD was prepared by dissolving 0.21 g of sodium metal in 16 ml of D_2O) was added with stirring to a solution of 2.1 g of the nitrate obtained in 10 ml of D_2O, and the mixture was maintained at

20-25°C for 4 h. The resulting precipitate was removed by filtration and recrystallized from CCl_4 to give 0.91 g (60%) of 2H,6H-2,6-dimethyl-4-dideuteroamino-1,3,5-dithiazine with mp 105.5-106.5°C. The degree of deuteration (70-75%) was determined from the ratio of the intensities of the absorption bands of the N—H stretching vibrations in the IR spectra of the undeuterated and deuterated samples.

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REACTIONS OF 1-ALKOXYCARBONYLAZIRIDINES WITH NUCLEOPHILIC REAGENTS

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1-Methoxycarbonylaziridines react under mild conditions with a number of nucleophilic reagents such as water, acids, alcohols, and amines with opening of the aziridine ring. In the case of 7-methoxycarbonyl-7-azabicyclo[4.1.0]heptane it was shown by PMR spectroscopy that the ring-opening reaction is realized stereoselectively to give trans-1,2-disubstituted cyclohexanes.

In contrast to epoxides, considerably less study has been devoted to the reactions of aziridines with nucleophilic reagents. This is explained by the substantial differences in the reactivities of epoxides and aziridines that are associated with the presence of a more basic nitrogen atom in the ring and the lower degree of accessibility of the latter. 1-Alkoxycarbonylaziridines are easily obtained compounds [1, 2]; their basicities are close to the basicities of epoxides, and they therefore should have similar reactivities. Individual examples of opening of the rings of 1-alkoxycarbonylaziridines by acids [3, 4], malonic ester [5], and aniline [6] are known.

We have investigated the reaction of 1-methoxycarbonylaziridine (I) and 7-methoxycarbonyl-7-azabicyclo[4.1.0]heptane (III) with various nucleophilic reagents at ~20°C and have found that aziridines that are activated by a methoxycarbonyl group readily react under mild conditions with the most diverse nucleophiles, viz., water, alcohols, acids, hydrogen sulfide, and amines. The reaction with ring opening is realized both in acidic and alkaline media. This makes it possible to obtain various β-functionally substituted carbamates in high yields from 1-alkoxycarbonylaziridines (Table 1).

In the case of the reaction of III with various nucleophiles we showed that the reaction proceeds stereoselectively to give the trans products. This conclusion was drawn on the basis of an analysis of the PMR spectra of IVa-g (Table 2), for which, with the excep-

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