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PMR SPECTRA AND STRUCTURES OF 2H,6H-2,6-DIMETHYL-4-AMINO-1,3,5-DITHIAZINE AND ITS DERIVATIVES

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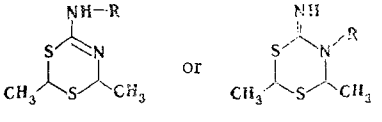
An analysis of the PMR spectra of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine, its acyl derivatives, and 2H,3H,6H-2,6-dimethyl-4-amino-1,3,5-thiadiazine in various solvents and in the presence of $Eu(FOD)_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)$_3$europium] confirms the structure assigned to it and makes it possible to prefer a cis orientation of the methyl substituents in the half-chair conformation.

The heterocyclization of divinyl sulfide with thiourea leads to a nitrogen-containing heterocycle, to which the 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine structure (Ia) was assigned on the basis of IR and PMR spectroscopic data [1].



I-V a I-V b

Ia,b R = H; IIa,b R = $COCH_3$; IIIa,b R = COC_3H_7; IVa,b R = COC_6H_5; Va,b R = $SO_2C_6H_4CH_3$

A great deal of attention is currently being directed to the study of the structure of heterocyclic derivatives of thiourea, which can exist in tautomeric forms [2]. However, the available data are not devoid of contradictions and do not always give an unambiguous answer to the question of the structures of the tautomers [2]. A universal approach to the solution of this problem has not yet been developed.

In the present paper we set forth the results of a study of the structures of heterocycle I and its derivatives II-V, as well as 6H-2,6-dimethyl-4-amino-2,3-dihydro-1,3,5-thiadiazine (VI), by means of PMR spectroscopy (see Table 1). In particular, we studied their tautomerism and cis—trans isomerism.

In examining the question of tautomerism we proceeded from the fact that if two tautomeric forms, viz., amino (a) and imino (b) forms, exist, solvents with different properties should have different effects on the position of the tautomeric equilibrium and, consequently, on the parameters of the PMR spectra of mixture of the tautomers (a and b). The chemical shifts (δ, in parts per million) of the signals of the protons of the methylidyne groups and the methyl groups bonded to them in heterocycles I-VI, the J_{CH-CH_3} spin—spin coupling constants, and the δ values of the signals of the protons bonded to the nitrogen atom are presented in Table 1. The data in Table 1 constitute evidence that replacement of CCl_4 by CD_3OD and d_6-DMSO affects the δ value but only within the limits that are usually produced by a change in the character of the intermolecular interaction of a substance with a solvent [3]; the J_{CH-CH_3} constant remains unchanged in this case.

It also follows from Table 1 that replacement of one of the hydrogen atoms bonded to the nitrogen atom by CO—CH_3 (II), COC_3H_7 (III), COC_6H_5 (IV), and $SO_2C_6H_4CH_3$ (V) groups leads

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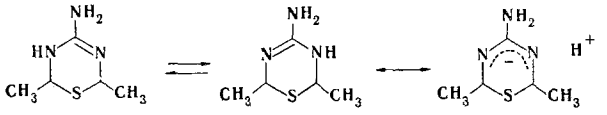
TABLE 1. Parameters of the PMR Spectra of I-VI

Compound	Solvent	δ, ppm			J_{CH-CH_3}, Hz	Compound	Solvent	δ, ppm			J_{CH-CH_3}, Hz
		CH	CH_3	NH				CH	CH_3	NH	
I	CCl_4	4,38 4,60	1,50 1,54	4,34	6,6	III	CCl_4	4,29 4,64	1,54 1,58	7,99	6,5
	CD_3OD	4,55 4,61	1,45 1,47	4,78	6,6	IV	CCl_4	4,48 4,61	1,60	11,18	6,8
	d_6-DMSO	4,55 4,69	1,41 1,44	6,01	6,6	V	d_6-DMSO	4,86	1,44 1,46	9,88	6,8
II	$CDCl_3$	4,41 4,74	1,56	7,95	6,4	VI	d_6-DMSO	4,10 4,26	1,15	3,30 8,06	6,0

to a substantial change in the δ value of the signal of the NH proton. These data, with allowance for the integral intensities of the signals, make it possible to assume that the investigated compounds exist (at least primarily) in a single tautomeric form and that this form is the amino form (a). The spectrum of VI is fundamental in this connection. The protons of two methyl groups turn out to be chemically equivalent, and they therefore give one signal, viz., a doublet because of spin–spin coupling with the methylidyne protons with the same J constant. For the same reason the signals of the methylidyne protons (which turn out to be chemically nonequivalent) are quartets. In addition, the spectrum of VI contains two singlets; the weak-field signal is twice as intense as the strong-field signal, whereas its integral intensity is equal to that of the two methylidyne protons. The position of these singlets depends on the temperature of the investigated sample. This type of spectrum corresponds to the amino form, in agreement with the conclusion drawn during an analysis of the spectra of I-V.

One should note the high lability of the proton attached to the ring nitrogen atom in VI. Evidence for this is provided by the form and magnitude of its singlet, as well as by the fact that the NH and OH protons give one signal when even a small amount of water is present in the solvent. The methylidyne protons in this case become chemically equivalent. A J^3 constant between the NH proton and the adjacent methylidyne proton does not show up in the spectrum of VI evidently for the same reason. The form of the PMR spectrum of VI recorded in d_6-DMSO and its transformation when water is added to the sample may be a consequence of a tautomeric transformation described by the scheme



VI a VI b VI c

In the case of sufficiently rapid interconversion of structures VIa and VIb the N_3 and N_5 atoms become equivalent, which is reflected by structure VIc.

Its stabilization may occur through the formation of a pseudoallyl anion ($-\bar{N}-C=N- \leftrightarrow -N=C-\bar{N}-$). Dimethyl sulfoxide, by forming strong intermolecular hydrogen bonds with the labile protons, stabilizes the VIa, b forms, thereby hindering rapid exchange (on the NMR scale) of the NH and NH_2 protons, as evidenced by the chemical nonequivalence of the methylidyne protons, in this solvent. The addition of H_2O to the sample leads to removal of this nonequivalence due to the development of proton exchange with the medium.

The transformation of the PMR spectrum of I by paramagnetic additives constituted evidence in favor of the amino form (a). In fact, when tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)$_3$europium* is added to the sample, the signal of one of the methylidyne protons undergoes a 2.3 times greater shift than the signal of the other methylidyne proton. The paramagnetic shifts of the signals of the methyl groups differ by just as much; the smaller shift is observed for the signal of the proton of the CH_3 group bonded to the methylidyne group, the signal of which also has a smaller paramagnetic shift.† Taking into account the existing concepts regarding the interaction of lanthanide shift reagents with organic substrates [4], it should be concluded that the observed paramagnetic

*$Eu(FOD)_3$.

†This was established by means of the double-resonance method.

shifts are due to primary coordination of $Eu(FOD)_3$ with the ring nitrogen atom in structure Ia. The conclusion regarding the primary existence of the investigated structures in the amino form makes it possible to conclude that the half-chair conformation is the most stable conformation for them. The absence of doubled signals in the spectra constitutes evidence that these compounds are isomerically homogeneous (they have one variant of orientation of the CH_3 groups relative to the plane of the ring). It is difficult to make an unambiguous choice between the cis and trans isomers. However, an examination of Dreiding models of I with allowance for the observed paramagnetic shifts makes it possible to prefer the cis-axial isomer.

EXPERIMENTAL

The PMR spectra of the compounds at various temperatures and in various solvents were recorded with a BS-487-C spectrometer with hexamethyldisiloxane as the internal standard; the operating frequency of the spectrometer was 80 MHz.

Amides II-V and p-toluenesulfonic acid amide V were obtained by acylation of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine (Ia) with the anhydrides and chlorides of the corresponding acids. 6H-2,6-Dimethyl-4-amino-2,3-dihydro-1,3,5-thiadiazine was synthesized by the method in [5].

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1-ARYLAMINO-3-PHENYL-2,3-DIHYDRO-2-INDOLONES

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α-Chlorodiphenylacetyl chloride reacts with arylhydrazines to give 1-arylamino-3-phenyl-2,3-dihydro-2-indolones, which undergo acetylation at the nitrogen and oxygen and undergo benzoylation at the nitrogen atom.

It is known that α-chlorodiphenylacetyl chloride reacts with 1,1-dimethylhydrazine [1] and 1-methyl-1-benzylhydrazine [2] to give 1-amino-3-phenyl-2,3-dihydro-2-indolone derivatives. We studied this reaction in the case of monosubstituted hydrazines, viz., arylhydrazines Ia-m. In this reaction one may assume the formation of derivatives of diazetidinone, indolone IV, and cinnolone; however, judging from the data from the IR, PMR, and mass spectra, indolones IVa-m are formed, as in the case of 1,1-disubstituted hydrazines.

The occurrence of the reaction through intermediate III is proved by alternative synthesis of IVa, d from phenylhydrazide VIIa [3] and p-tolylhydrazide VIId [4] of benzilic acid. We were unable to isolate intermediate III, which indicates its high reactivity, in contrast to the anilide [5, 6] or 4-methylphenylamide [7] of α-chlorodiphenylacetic acid. The synthesized compounds are presented in Table 1.

In the IR spectrum of derivative IVa the band of the amide C=O group lies at 1725 cm^{-1}, while the NH band is found at 3320 cm^{-1} in the crystalline state and at 3350 cm^{-1} in

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