

PMR OF COMPLEXES OF ORGANOHALOSTANNANES
WITH N-VINYLN-N-ETHYLIMIDAZOLE

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The chemical shifts and spin-spin coupling constants of the protons of the vinyl and ethyl groups and of the imidazole ring in the PMR spectra of complexes $R_{4-n} \cdot SnX_n \cdot mB$, where $R = C_2H_5, C_4H_9$; $X = Cl, Br, I$; B is N-vinylimidazole or N-ethylimidazole; and $n=1$ ($m=1$) and 2 ($m=2$), are compared. The electronic and geometrical structures of these complexes are discussed.

We have previously described new complexes $R_{4-n}SnX_n$ ($n=1-4$, X =halogen) with N-vinyl derivatives of imidazole, benzimidazole, and benzotriazole and also with imidazole and N-ethylimidazole [1]. In this case, it was shown that trialkylhalostannanes ($n=1$) form 1:1 complexes with these heterocycles, while organochlorostannanes ($X=Cl$) with $n=2-4$ give 1:2 complexes. This paper is devoted to a study of complexes $R_{4-n} \cdot SnX_n$ ($R = C_2H_5$ and C_4H_9 , $X = Cl, Br, I$, and $n=1, 2$) of N-vinylimidazole (I) and N-ethylimidazole (II) by PMR spectroscopy.* These investigations are a continuation of the previously initiated study of the hyperfine bond in five-membered nitrogen-containing heterocycles from PMR data [2, 3].

The study of the PMR spectra of complexes of I and II with the alkylhalostannanes was carried out by comparison of the chemical shifts and spin-spin coupling constants (J). The calculated shifts (ω) in the

spectra of the complexes relative to the position of the signals of the protons of the vinyl $\left(\begin{array}{c} & & H_B \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H_X & & H_A \end{array} \right)$

and ethyl (CH_3-CH_2-) groups and of the imidazole ring in the spectrum of the free ligand are presented in Table 1. It follows from Table 1 that the signals of all of the protons are shifted to weak field on coordination of the imidazole derivatives with the alkylhalostannanes. Moreover, the ω values of the protons of the vinyl and ethyl groups are comparable to the shifts of the signals of the ring protons. An exception to this is the signal of the 4-H proton, the chemical shifts of which in the spectrum of the complex and free ligand almost coincide. An increase in the length of the alkyl group (R) in the alkylhalostannane has little reflection on the ω values. An increase in the number of halogen atoms in $R_{4-n} \cdot SnX_n$ from 1 to 2 appreciably raises the ω values of the signals of all of the ring protons but has virtually no effect on the position of the signals of the protons of the vinyl and ethyl groups.

The lowest ω value, observed for the 4-H proton, the signal of which has the greatest paramagnetic shift in the PMR spectra of complexes of I with Mn, Fe, Ni, Co, and Cu [3], is apparently associated with the perturbation action of the unpaired electron in the paramagnetic complex; this perturbation leads to the appreciable contribution of the excited states, the molecular wave functions of which may differ from the wave functions of the ground state.

The vicinal spin-spin coupling constants of the protons of the vinyl (J_{AX} and J_{BX}) and ethyl ($J_{CH_2-CH_3}$) groups in the spectra of the complexes and the free ligand actually coincide. However, the geminal

* The PMR spectra were recorded with a BS487B spectrometer at room temperature. The solvents were carbon tetrachloride and chloroform, and the internal standard was hexamethyldisiloxane.

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TABLE 1. Shifts of the Signals of the Protons of the Vinyl and Ethyl Groups and of the Imidazole Ring in the Spectra of Complexes $R_{4-n}SnX_n \cdot mB$ as Compared with the Spectra of B

Compound	B	R	X	Chemical shifts, ω , ppm									
				ω_2	ω_4	ω_5	ω_A	ω_B	ω_X	ω_{CH_2}	ω_{CH_3}		
			$n=1, m=1$										
III	I	C_2H_5	Cl	0,27	0,01	0,20	0,18	0,17	0,18				
IV	I	C_2H_5	Br	0,22	0,02	0,16	0,18	0,16	0,16				
V	I	C_2H_5	I	0,23	0	0,13	0,15	0,13	0,14				
VI	I	C_4H_9	Cl	0,20	0,01	0,23	0,17	0,15	0,17				
VII	II	C_2H_5	Cl	0,36	0,02	0,24					0,15	0,05	
VIII	II	C_2H_5	Br	0,28	0,04	0,14					0,12	0,05	
IX	II	C_2H_5	I	0,21	0,03	0,10					0,05	0,04	
			$n=2, m=2$										
X	I	C_2H_5	Cl	0,72	0,08	0,38	0,14	0,17	0,17				
XI	I	C_4H_9	Cl	0,66	0,06	0,35	0,14	0,18	0,16				
XII	II	C_2H_5	Cl	0,77	0,08	0,53					0,05	0,07	

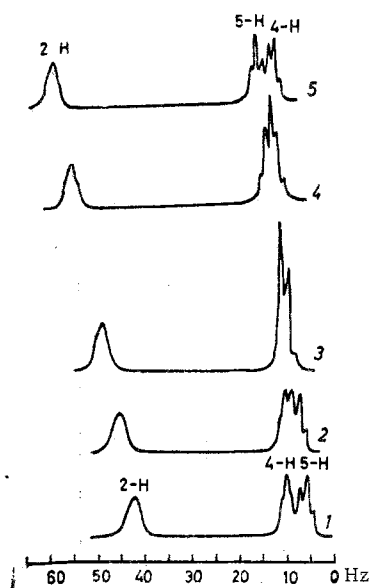


Fig. 1

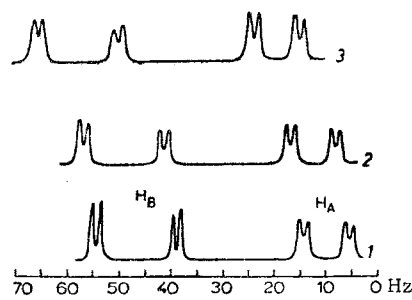


Fig. 2

Fig. 1. Fragment of the PMR spectrum of N-ethylimidazole (1) and of a mixture of it with $(C_2H_5)_3SnCl$ (2-5).

Fig. 2. Signals of the β -olefin protons in the PMR spectrum of N-vinylimidazole (1) and mixtures of it with $(C_2H_5)_3SnCl$ (2, 3).

coupling constant of the β -olefin protons change from 1.5 to 1.9 Hz in the case of 1:1 complexes with trialkylhalostannanes ($n=1$) and up to 2.2 Hz when $n=2$ (1:2). This attests to a change in the character of the C-H bonds of the β -carbon atom of the vinyl group in the complexes [4].

It follows from a comparison of the spectra of the free and coordinated I and II that complexing also affects the J values of the ring protons. The lower spectrum in Fig. 1 pertains to the signals of the ring protons of free II, while the other four upper spectra are the spectra of II containing added trialkylchlorostannane. It is seen from Fig. 1 that the character of the splitting of the signals of the 2-H and 4-H protons, which is due to spin-spin coupling, actually does change. The signal of the ring 4-H proton is shifted slightly as compared with the signals of the 2-H and 5-H protons.

The PMR spectra of I and II (Figs. 1 and 2) show that there is long-range spin-spin coupling (LRSSC) of the 2-H proton with the protons of the vinyl and ethyl groups, which leads to additional broadening of the signals of these protons, since $J^{LRSSC} < 0.5$ Hz. A portion of the PMR spectrum of I pertaining to the β -olefin protons is depicted in Fig. 2. The lower spectrum corresponds to the free ligand, while the other

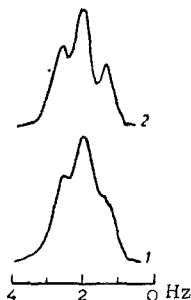
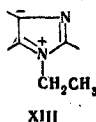


Fig. 3. Shape of the signal of the 2-H proton in the PMR spectrum of complex XII without additional excitation (1) and with additional excitation of the sample at the frequency of the signal of the CH₂ protons (2).

II. In complexes of II, J_{2-CH_2} LRSSC apparently becomes substantially larger than J_{2-CH_3} LRSSC, and the use of the double-resonance method in the analysis of the spectrum of XII is unsuccessful.

To elucidate the structures of the synthesized complexes, we used the assumption [5] that coordination of pyridine with (C₂H₅)₃SnCl and (C₂H₅)₂SnCl₂ brings about an increase in J_{Sn-C-H} and $J_{Sn-C-C-H}$. In our case, the $J_{117Sn-C-C-H}$ constant in complexes III and IX increases as compared with (C₂H₅)₃SnCl (91.8 Hz) to 96.3 and 97.0 Hz. On passing from ethyldichlorostannane to its complex, $J_{117Sn-C-C-H}$ increases from 136.8 to 180.0 Hz. This can be explained by the fact that the tin atom in 1:1 complexes of trialkylhalostannanes has sp³d hybridization, and the three alkyl groups strive to become coplanar, combining with the approximately sp² orbitals of tin. The two other bonds of tin should be of the dp form. However, in 1:2 complexes of dialkyldihalostannanes, in which the tin atom has sp³d² hybridization, the two alkyl groups occupy axial bonds, using the approximately sp orbitals of tin for this. The four other bonds correspond to the d²p² type. The s character of the Sn-C bond increases in the order sp³, sp², sp, and the $J_{Sn-C-C-H}$ constant therefore increases. At the same time, the coordination of I with tin via dp and d²p² bonds has an appreciable effect on the signals of the protons of the vinyl group, which, as quantum-chemical calculations have shown [6], is conjugated with the π system of the heterocycle. This should explain the comparable values of the shifts of the protons of the vinyl group and the protons of the heteroring. Coordination of II with (C₂H₅)_{4-n}SnX_n via the dp and d²p² bonds leads to a change in the contribution of the resonance structures of the XIII type, which describe the participation of the p_z electrons of the 1-N atom in the π system of the ring, i.e., to a change in the electron density on this atom; this is reflected in the electronic environment of the protons of the ethyl group bonded to the 1-N atom. This explains the observed ω values of the protons of the CH₂-CH₃ group in the spectra of complexes of II. The above reasoning relative to the character of the bonds of tin atoms with I and II makes it possible to understand why the 2-H proton has the largest ω value in the case of both 1:1 and 1:2 complexes.



Thus both the π and σ systems of the heterocyclic compounds are involved in the coordination of I and II with alkylhalostannanes.

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