ASSIGNMENT OF THE RESONANCE LINES IN THE PMR
SPECTRA OF N-VINYL- AND N-ETHYLIMIDAZOLE

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The PMR spectra of N-vinyl- and N-ethylimidazole were interpreted on the basis of an esti-
mate of the broadenings and shifts of the resonance lines caused by the effect of an uncom-
pensated electron spin of a paramagnetic complex. The site of coordination of N-vinyl- and
N-ethylimidazole with $NiCl_2$ was established.

A method was proposed in [1] for the determination of the functional groups in molecules of organic
compounds that are capable of forming paramagnetic complexes. The method was based on the use of the
peculiarities of the PMR spectra of paramagnetic compounds. Its application was illustrated by the inter-
pretation of the PMR spectra of some methyl derivatives of pyrazole.

In this paper, this method is used to assign the resonance lines in the PMR spectra of N-vinyl- (I)
and N-ethylimidazole (II). The assignment was based on an estimate of the broadenings (Δ) and shifts (δ)
of the resonance lines caused by the effect of an uncompensated electron spin of a paramagnetic complex.
In the case of labile complexes, the evaluation of Δ and δ reduces to the solution of Bloch equations modi-
fied by MacConnel, who included chemical exchange in them. The analysis of the Bloch−MacConnel equa-
tions for a two-component system reduces to the following expressions that determine the observable Δ and
δ of resonance lines relative to their widths and positions in the spectrum of a diamagnetic compound [2]:

$$\Delta = \frac{P_M}{\tau_M}\left[\frac{(1/T_{2M})^2 + 1/T_{2M}\cdot\tau_M + \omega^2}{(1/T_{2M} + 1/\tau_M)^2 + \omega^2}\right], \tag{1}$$

$$\delta = \delta_c + \delta_p = -\frac{\omega\cdot P_M}{\tau^2_M\left[(1/T_{2M} + 1/\tau_M)^2 + \omega^2\right]}. \tag{2}$$

In expressions (1) and (2), τ_M is the lifetime of a ligand molecule in the first coordination sphere of the
complex, P_M is the molar fraction of the complex in the sample, and $\omega = \omega_c + \omega_p$ is the shift of the reso-
nance line of the nucleus included in the composition of the paramagnetic complex. This shift is caused by
contact (ω_c) and pseudocontact (ω_p) electron−nuclear interactions and depends on the electronic and geo-
metrical structure of the paramagnetic compounds [3]. Here, it should be pointed out that the insignificant
magnitude of the pseudocontact shifts in complexes in which the coordinating atom was nickel was noted in
a number of papers on the PMR of paramagnetic complexes [4-6]; T_{2M} is the transverse relaxation time of
the resonating nucleus in the complex.

In the case of brief electronic relaxation times (for Ni^{2+}, for example), it is determined by the ex-
pression in [1]

$$1/T_{2M} = A\cdot r^{-6} + B\cdot\delta^2_c, \tag{3}$$

where r is the distance from the coordinating ion to the resonating nucleus, δ_c is the observable contact
shift of the resonance line, and A and B are constants for the sample under investigation at a given tempera-
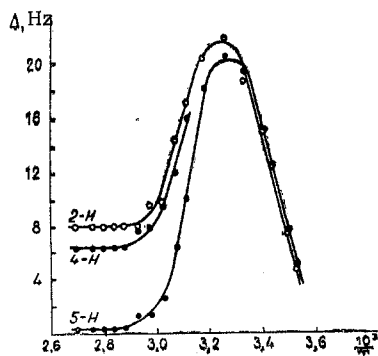ture.

Fig. 1. Dependence of Δ of the resonance lines of ring protons in the PMR spectrum of 1-vinylimidazole on temperature.
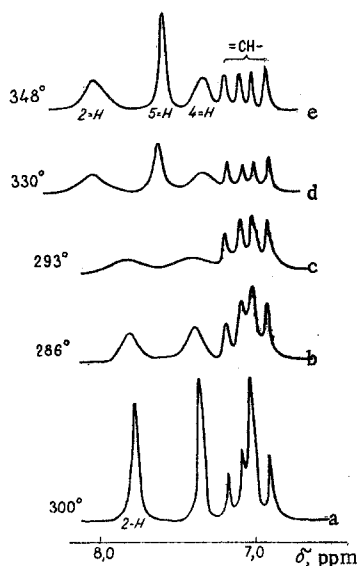

Fig. 2. PMR spectra of I (ring protons and $=$CH proton) without a paramagnetic complex (a) and with paramagnetic complexes (b,c,d,e).
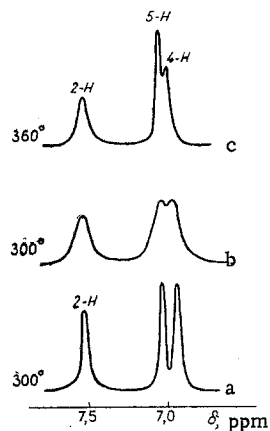

Fig. 3. PMR spectra of II (ring protons) without (a) and with a paramagnetic complex (b, c).

It is apparent that expressions (1) and (2) can be simplified as a function of the relationship between τ_M, T_{2M}, and ω. However, the relationship between these values is determined by the nature of the investigated compounds and also by the conditions used to carry out the experiment. It is simple to demonstrate that expressions (1) and (2) are replaced by more simple expressions [2] in the following cases:

1) Slow exchange (for a low temperature of the sample under investigation:

$$\Delta = \frac{P_M}{\tau_M};$$ (4)

$$\delta = - \frac{P_M}{\tau^2_M \cdot \omega};$$ (5)

2) Rapid exchange (at high temperatures):

$$\Delta = P_M \cdot \tau_M \cdot \omega^2,$$ (6)

or

$$\Delta = \frac{P_M}{T_{2M}};$$ (7)

$$\delta = - \omega \cdot P_M;$$ (8)

3) Intermediate case:

$$\Delta = \frac{P_M}{T_{2M}} + P_M \cdot \tau_M \cdot \omega^2;$$ (9)

$$\delta = - \omega \cdot P_M.$$ (10)

The simplification of expressions (1) and (2) consequently involves obtaining the dependences

$$\Delta = \Delta(T);$$ (11)

$$\delta = \delta(T),$$ (12)

where T is the absolute temperature.

We used the above to assign the signals in the PMR spectra of I and II. The experiments were carried out under conditions involving excess ligand content in the sample. An average spectrum was observed as a result of exchange of molecules between the coordination sphere of the paramagnetic complex and the free ligand. The dependence of the broadening of the resonance lines of the ring protons in the spectrum of I containing the $NiCl_2 \cdot 4Lig$ complex (Lig = I) on temperature is presented in Fig. 1. It is apparent from the graphs that the resonance lines of the two protons of the imidazole ring are broadened identically up to 303°. The resonance line of the third ring proton is superimposed on the signal of the proton of the $-$CH-vinyl group up to ~323°. However, from the form of the signal of this proton, it can be assumed that the resonance line of the third proton is broadened in the same way as the lines of the other two protons up to 303°. Consequently, up to 303°, Δ of the resonance lines of the ring protons is determined by expression (4).

TABLE 1. Dependence of the δ Signals of the Ring Protons of N-Vinylimidazole on Temperature

Temperature, °K	δ, Hz		
	2-H	4-H	5-H
283	1		1
286	1		1
290	1		1
293	4		2
300	10		14
306	14		19
314	23		27
322	24	27	27
325	23	27	25
330	23	26	24
336	22	26	21
342	22	26	21
348	22	25	21
352	21	25	20
357	21	25	19
363	19	23	19
370	18	22	16

Beginning at 313°, two of the lines are compressed approximately identically, while the third is compressed more rapidly than the two others, and the difference involved increases up to about 353° and then remains constant. At temperatures above 353° (Fig. 1), Δ of one of the lines is less than one tenth of Δ for the other two (the experimental accuracy is ±0.8 Hz). It is easy to convince oneself that (beginning at 313°) Δ cannot be determined by expression (6). In fact, in this case, δ should have been determined by expression (8). However, the δ values for all three resonance lines of the ring protons differ only slightly from 313 to 370° (see Table 1).

The ω values (and therefore the Δ values as well) for the three signals should consequently be approximately the same. However, dependence (11) (Fig. 1) does not confirm this. In order to establish the form of approximation (1) at 313-370°, we took into account the fact that (3) for T_{2M} consists of two terms, one of which depends on r^{-6}, the other of which depends on δ_C^2. We estimated the $(r_5/r_2)^6$, $(r_5/r_4)^6$, and $(r_4/r_2)^6$ ratios, for which data on the geometry of imidazole were used along with the ionic radius values of Ni^{2+} and the van der Waals radius of nitrogen.
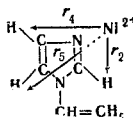
It turned out that $(r_5/r_2)^6 \simeq 24$, $(r_5/r_4)^6 \simeq 14$, and $(r_4/r_2)^6 < 2$. Consequently, if I coordinates with $NiCl_2$ by means of the N-3 nitrogen and Δ of the resonance lines is determined by the first term in expression (3), the following should hold: Δ_2 and $\Delta_4 \gg \Delta_5$; $\Delta_2 > \Delta_4$. Taking this into account, there are two unambiguous conclusions from the graph in Fig. 1:

1) Compound I coordinates with $NiCl_2$ by means of the nitrogen in the 3 position;

2) When the temperature changes from 313 to 353°, the value of the signals of the ring protons is determined by expression (9), and the contribution of the second term decreases as the temperature increases. At temperatures above 353°, Δ is determined by the first term of expression (3).

It is known that the 2-H proton of imidazole resonates at weaker field than the 4-H and 5-H protons, the signals of which in the PMR spectrum of imidazoles are superimposed [8]. In the PMR spectrum of I (Fig. 2a), the signals of the ring protons are therefore arranged in the order: $\delta_2 = 7.71$ ppm, $\delta_4 = 7.05$ ppm, and $\delta_5 = 7.35$ ppm.

When the temperature of the investigated sample containing a $NiCl_2 \cdot 4Lig$ complex is changed, the signals of the protons of the vinyl group remain practically unshifted relative to the position in the spectrum of the diamagnetic compound. And, since these protons are considerably removed from the coordination ion (as compared with the 2-H and 4-H protons), their resonance lines undergo virtually no broadening; i.e., Δ is determined by the first term of expression (3) over the entire range of change in the temperature. The position of the signals of the 2-H, 4-H, 5-H, and $CH{<}$ protons in the spectrum of I with and without added complex at various temperatures is illustrated in Fig. 2.

As in the case of I, we studied the changes in the PMR spectrum of II containing its complex with $NiCl_2$ at various temperatures and determined the position of the signals of the ring protons ($\delta_2 = 7.51$ ppm, $\delta_4 = 6.96$ ppm, and $\delta_5 = 7.05$ ppm) (Fig. 3). It should be noted that the resonance lines of the ring protons in the PMR spectra of I and II are shifted in a different manner when the paramagnetic complex is added to the sample and when the temperature changes. This is apparently a reflection of the difference in the electronic structure of the examined ligands, which is caused by conjugation of the double bond of the vinyl group of I with the π system of the ring.

A comparison of the PMR spectra of I, II, and methyl derivatives of pyrazole [1] indicates that the 4-H protons of imidazoles and the 3-H protons of methylpyrazoles resonate at stronger field than the 5-H proton, despite the effect of the unshared pair of electrons of the adjacent nitrogen atom. This effect should make a contribution to the chemical shifts of the 4-H and 3-H protons (~0.4 ppm) and should shift the signal to weak field [9, 10]. The observed order of the signals in the spectra of N-substituted derivatives of pyrazoles and imidazoles is in agreement with the direction of electrophilic substitution at the 4 position [11].

EXPERIMENTAL

The PMR spectra were recorded with a JNM-4H-100 spectrometer. Nitromethane was used as the solvent and internal standard. The temperature of the samples ranged from 283 to 370°K. The chemical shifts were measured on the δ scale relative to hexamethyldisiloxane. The molar fraction of the paramagnetic complex was varied from $1.1 \cdot 10^{-3}$ to $15 \cdot 10^{-3}$ for a more accurate measurement of Δ and δ (Δ and δ are proportional to P_M). The synthesis of complexes of $NiCl_2$ with I and II is described in [12].

LITERATURE CITED

1. E. E. Zaev, V. K. Voronov, M. S. Shvartsberg, S. F. Vasilevskii (Vasilevsky), Yu. N. Molin, and I. L. Kotlyarevskii (Kotljarevsky), Tetrahedron Lett., 617 (1968).
2. T. J. Swift and R. E. Connick, J. Chem. Phys., 37, 307 (1962).
3. D. E. Eaton and W. D. Philips, Advances in NMR Spectroscopy, Vol. 1, New York (1965).
4. J. A. Happe and R. L. Ward, J. Chem. Phys., 38, 211 (1963).
5. R. H. Holm, G. W. Everett, and W. De W. Horroks, J. Am. Chem. Soc., 88, 1071 (1966).
6. R. J. Fitzgerald and R. S. Drago, J. Am. Chem. Soc., 90, 2523 (1968).
7. S. Martinez-Carrera, Acta Cryst., 20, 783 (1966).
8. NMR Spectra Catalog, Varian Associates, Palo Alto, California, Spectrum No. 91.
9. A. H. Gawer and B. P. Dailey, J. Chem. Phys., 42, 2658 (1965).
10. H. Okuda and M. Nagau, Bull. Chem. Soc. Japan, 40, 1999 (1967).
11. J. Reid, in: Physical Methods in Heterocyclic Chemistry. A. R. Katritzky (editor), Wiley (1971).
12. E. S. Domnina, Yu. N. Ivlev, N. I. Shergina, N. N. Chipanina, L. V. Belousova, Yu. L. Frolov, and G. G. Skvortsova, Zh. Obshch. Khim., 41, 1102 (1971).