PMR SPECTFA OF ALKYL-SUBSTITUTED Δ^1-PYRAZOLINES

N. M. Anodina and B. V. Ioffe

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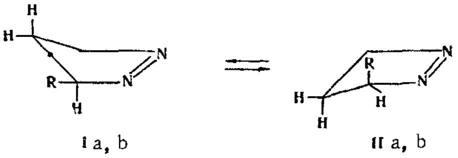
Data from the PMR spectra of Δ^1-pyrazolines and their acyclic analogs – azo compounds – were compared. It is shown that the difference in the chemical shifts of similar fragments in these compounds is due to the peculiarities of the three-dimensional structures, which lead to different contributions to shielding from the unshared electron pairs of nitrogen and the magnetically anisotropic N=N bond.

The literature currently contains PMR spectral data only for a few alkyl-substituted Δ^1-pyrazolines (3-methyl-, 3,5-dimethyl-, and 3,3,5-trimethyl-Δ^1-pyrazolines) [1-4], the spectra of which were interpreted in relationship to the conformation of the pyrazoline ring. It has been shown that the nonequivalence of the 4-H protons of 3-methyl-Δ^1-pyrazoline is due to the preferableness of the Ib form, while in the case of the equilibrium Ia$\rightleftharpoons$IIa the equal populations and rapid transformations from Ia to IIa lead to equivalence of these protons. Functionally, aryl-substituted Δ^1-pyrazolines also exist as mixtures of analogous conformers [5-7], and the fold angle of the envelope flap is ~25°.



I a, b

II a, b

I, II a R=H; b $R=CH_3$

It seems of interest to examine the peculiarities of the PMR spectra of alkyl-substituted Δ^1-pyrazolines in comparison with the spectra of their acyclic analogs – azoalkanes. Insofar as the latter are concerned, the signals of the $CH_3N=N$ and $RCH_2N=N$ groups in the trans forms of the aliphatic azo compounds are observed at quite weak field (δ 3.5-3.8 ppm); this was explained by a change in the state of hybridization of the carbon atoms bonded to the nitrogen and the contribution of mesomeric dipolar structures $CH_3{}^{+}=N-N^{-}-R$ and $RCH_2{}^{+}=N-N^{-}-R$ [8]. The cis forms are characterized by considerably greater shielding of these protons ($\Delta\delta \approx 0.1$-0.4 ppm), but an attempt to arrive at a theoretical explanation of the difference in the chemical shifts of the signals of the stereoisomeric forms of a number of phenylazoalkanes [9] did not give definite results, possibly because of the relative complexity of the subjects of the investigation, which contain phenyl groups. Precisely the simplest Δ^1-pyrazolines are of considerable interest in connection with this problem, inasmuch as they have an azo group that is rigidly fixed in the cis configuration, and they are free of the effects of aromatic rings and rotation of the substituents about the N–C bond.

We have investigated five alkyl-substituted Δ^1-pyrazolines. A summary of the chemical shifts and the spin–spin coupling constants of the protons of these pyrazolines is presented in Table 1 along with the literature data for Δ^1-pyrazoline and three of its homologs. A comparison of the chemical shifts of the ring protons of Δ^1-pyrazolines with the shift of the analogous fragments of the aliphatic azo compounds reveals interesting and substantial differences. As seen from Table 1, the chemical shifts of the signals of the 3-H and 5-H pyrazoline protons lie in the 4.0-4.5 ppm region, which differs markedly from the region of chem-

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TABLE 1. Parameters of the PMR Spectra of Δ^1-Pyrazolines

Compound	Chemical shift, δ, ppm; J, Hz			
	3-*H*	4-*H*	5-*H*	CH_3[a]
Δ^1-Pyrazoline [2]	4,27	1,46	4,27	—
3-Methyl-Δ^1-pyrazoline [3]	4,29; $J_{34}=8,5$, $J_{34'}=7,5$, $J_{35}=2,3$, $J_{35'}=2,0$	0,99, 1,73; $J_{45}=9,6$, $J_{4'5}=5,0$, $J_{44'}=12,3$	4,43, 4,10; $J_{45}=8,0$, $J_{4'5'}=9,3$, $\|J_{55'}\|=16,8$	1,38; $J_{H,CH_3}=6,9$
3,5-Dimethyl-Δ^1-pyrazoline [1] cis	4,20; $J_{34}=8,5$	1,28; $J_{44'}=12,5$	4,20	1,44; $J_{H,CH_3}=7,0$
trans	4,57; $J_{34}=8,5$	1,27	4,57	1,29; $J_{HCH_3}=7,0$
3,3,5-Trimethyl-Δ^1-pyrazoline [3]	—	0,62, 1,78; $\|J_{44'}\|=12,5$	4.40	1,43 (5), 2,40 (3), 1,13 (3)
3,3-Dimethyl-Δ^1-pyrazoline	—	1,30; $J_{45}=8,0$	4,29; $J_{C^{13}H}=141$	1,20
3,3-Diethyl-Δ^1-pyrazoline	—	1,30; $J_{45}=8,0$	4,29; $J_{C^{13}H}=140$	b
3-Methyl-3-ethyl-Δ^1-pyrazoline	—	1,20, 1,41; $\|J_{44'}\|=12,3$	4,32; $J_{45}=J_{4'5}=8$, $J_{C^{13}H}=141$	1,19[c]
4-Methyl-Δ^1-pyrazoline	4,07	2,04	4,07; $J_{C^{13}H}=140$	0,75
4-Ethyl-Δ^1-pyrazoline	3,91	2,78	3,91, $J_{C^{13}H}=141$	—

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[a] The position of the methyl group in the ring is indicated in parentheses.

[b] Ethyl groups: δ CH_2 1.69 ppm, δ CH_3 0.76, J = 7.5 Hz.

[c] Ethyl group: δ CH_2 1.66 ppm, δ CH_3 0.79, J = 7.5 Hz.

ical shifts of the analogous groups in azo compounds (3.7 ppm). This difference cannot be explained by a change in the state of hybridization of the carbon atom, inasmuch as the $J_{NC^{13}H}$ values in both cases are close (140-141 Hz for Δ^1-pyrazolines and 138-139 Hz for azo compounds [8]) and correspond to 28% s character of the hybridized orbital [10]. The reason for these deviations apparently consists in the different shielding of the adjacent pair of unbonded electrons. In the case of Δ^1-pyrazolines, the position of the 3-H and 5-H protons is rigidly fixed relative to the unshared pair of the adjacent nitrogen (which lies in the plane of the ring and is always equidistant from the protons of the methylene group), while rotation of the alkyl groups and more effective shielding of them by the unshared pairs occur in azoalkanes. The relationship between the difference in the chemical shifts of the protons adjacent to the azo group in Δ^1-pyrazolines and in azo compounds and the effect of the unshared pair of the nitrogen atom is also confirmed by the fact that the change in the chemical shifts of the protons of the methylene groups attached to the C=C bond are insignificant (≈ 0.05-0.2 ppm) on passing from olefins to cyclopentene [11].

The resonance signals of the 4-H protons lie at much stronger field (δ 1.3 ppm) than the signals of the 3(5)-H protons, so that they are shielded more strongly by the corresponding groups in azoalkanes (δ 1.6 ppm). This shielding of the 4-H proton is explained by the fact that, as a consequence of bending of the ring of Δ^1-pyrazolines, they fall in the region of increased shielding by the N=N bond. At the same time, the analogous groupings of azoalkanes are situated near the plane of the N=N double bond because of the absence of steric hindrance, and this corresponds to the deshielding region.

EXPERIMENTAL

Preparations obtained by isomerization of Δ^2-pyrazolines [12] were used in this research. The PMR spectra of the pure liquids were recorded with a Varian HA-100D with hexamethyldisiloxane as the internal standard at room temperature. The spectra of the azo compounds, which were prepared from hydrazones [13], were obtained with a JNM-4H-100 spectrometer.

Data from the PMR Spectra of the Azo Compounds. $_d$Azopropane $(\overset{c}{C}H_3\overset{b}{C}H_2\overset{a}{C}H_2N=)_2$ – δ, ppm: CH_3 0.92, CH_2 (a) 3.70, CH_2 (b) 1.70; $J_{ab}=J_{bc}=6.8$ Hz. Azobutane $(\overset{d}{C}H_3\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2N=)_2$ – δ, ppm: CH_3 0.90, CH_2 (a) 3.67, CH_2 (b) 1.65, CH_2 (c) 1.37; $J_{ab}=J_{bc}=J_{cd}=6.8$ Hz.

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