PYRROLES FROM KETOXIMES AND ACETYLENE.

11.* CONFORMATION OF 1-VINYLPYRROLES FROM ^{1}H NMR DATA

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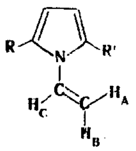
A number of 1-vinylpyrroles were studied by PMR spectroscopy. Bulky substituents in the α position of the pyrrole ring give rise to deshielding of H_B and a decrease in ${}^2J(H_A,H_B)$ and ${}^6J(H_3,H_B)$. The results were interpreted as a decrease in the p,π conjugation in the N-vinyl group due to distortion of the coplanarity. The dihedral angle (φ) between the planes of the pyrrole ring and the double bond was estimated (with an accuracy of ±5°).

During a study of the ^{13}C NMR spectra of 2-alkyl-1-vinylpyrroles [1] we showed that increased branching of the alkyl substituents attached to the C_2 atom leads to disruption of the coplanarity of the system and, as a consequence, to a decrease in the degree of conjugation of the nitrogen atom with the vinyl group. Since the parameters of the PMR spectra, particularly the spin–spin coupling constants (SSCC), are extremely sensitive to the fine details of the three-dimensional structure of the molecules, we made a detailed study of them in the 1-vinylpyrrole series:



I–V

I $R=R'=H$; II $R=CH_3$, $R'=H$; III $R=C_2H_5$, $R'=H$; IV $R=C_4H_9$-*t*, $R'=H$; V $R=CH_3$, $R'=C_6H_5$.

The chemical shifts (CS) and the SSCC of the protons are presented in Table 1.

The H_A and H_C protons of the vinyl group, by virtue of their spatial orientation, are subject to an appreciably greater effect of the magnetic anisotropy of the pyrrole ring and the heteroatom, as well as steric interaction with the ring, than the H_B proton. The chemical shift of the latter should therefore most realistically reflect the electron redistribution in the vinyl group that is associated with the change in the conformation of the

TABLE 1. Chemical Shifts (δ_H) and SSCC of the Protons of 1-Vinylpyrroles I-V

Compound	Chemical shifts, δ_H, ppm (± 0.005)						SSCC, Hz (± 0.05)		
	H_A	H_B	H_C	H_3	H_4	H_5	${}^2J(H_A, H_B)$	${}^6J(H_3, H_B)$*	${}^4J(H_5, H_C)$*
I	4.95	4.47	6.60	6.07	6.07	6.71	−1.2	0.6	0.20
II	4.93	4.50	6.75	5.74	5.99	6.75	−0.8	0.4	0.45
III	4.95	4.52	6.80	5.76	6.97	6.79			
IV	4.95	4.58	7.17	5.79	5.89	6.74	−0.5	0.2	0.60
V	4.90	4.81	6.70	5.85	6.05	—	<0.05	<0.05	—

*The signs of the SSCC were not determined.

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*See [10] for our previous communication [10].

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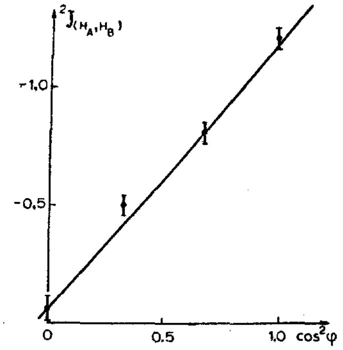
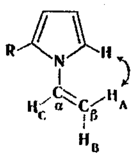


Fig. 1. Dependence of $^2J(H_A,H_B)$ on dihedral angle φ.

molecules due to rotation about the N–vinyl bond. The deshielding of H_B and the shielding of H_4 (the proton that is farthest away from variable substituent R in the ring) follow the tendency previously observed [1] for the chemical shifts of the corresponding ^{13}C nuclei as the volume of R increases. The geminal $^2J(H_A,H_B)$ constant increases (with allowance for the sign) in the same order (I-IV). This SSCC is a reliable criterion of the degree of conjugation in the vinyl group [2], and its increase in the order I-IV once again confirms the conclusions in [1]. There is a linear correlation between the chemical shifts of H_B and C_β:

$$\delta C_\beta = -39.4(\pm 14.8) + 30.2(\pm 3.2)\delta H_B;$$
$$r = 0.998,\ S_0 = 0.32\ (n = 5).$$

The slope of this correlation exceeds the corresponding parameter of the analogous correlation [3] for a series of p-substituted styrenes (ρ = 18) by a factor of almost two. This is a consequence of expansion of the range of the chemical shift of the β-carbon atom due to the variable contribution to its shielding of the steric interactions of the methylene group with the pyrrole ring:



These interactions are maximal in the planar conformations and decrease as the noncoplanarity increases, and this also leads to the observed result.

The long-range $^6J(H_3,H_B)$ constants give additional information regarding the conformation of 1-vinylpyrroles. This sort of interaction is extremely stereospecific [4] and is transmitted primarily through a planar zigzag fragment of the⋁⋁⋁form. A study of styrene derivatives showed [5] that long-range SSCC of this type are subject to the angular dependence

$$^6J = {}^6J_0 \cdot \cos^2\varphi,$$

where φ is the dihedral angle between the planes of the double bond and the ring.

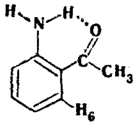
We estimated this angle for 2-methyl-1-vinylpyrrole (II) by means of experiments on the Overhauser nuclear effect (ONE). Increases in the intensities of the H_3 and H_C signals of 6 and 5%, respectively, are observed in the spectrum of a correspondingly prepared sample of II in the case of irradiation of the protons of the CH_3 group with a second radio-frequency field. The absolute values of the ONE in this case cannot be used as a criterion of the geometry of the molecule, since both H_3 and H_C are subject to the additional effect of the relaxation of the adjacent H_4 and H_B protons, respectively [6]. However, their ratio should satisfy the condition [6]:

$$I_1 : I_2 = \frac{1}{r_1^6} : \frac{1}{r_2^6},$$

where I is the absolute value of the ONE, and r is the average distance from a given proton to the protons of the methyl group. Proceeding from the geometry of the pyrrole ring [7], the H_3–CH_3 distance is 3.152 Å. Since the I values for H_3 and H_C coincide within the limits of the integration error, the CH_3–H_C distance is 3.15 (±0.05) Å, which corresponds to dihedral angle $\varphi = 35°$ (±5°). In this case, according to the dependence of the SSCC of $^6J(H_3,H_B)$ on φ, $^6J_0$ for these protons is 0.6 Hz. In the case of I, IV, and V an estimate of the φ values leads to 0, 55, and 90°, respectively. Thus, the maximum disruption of coplanarity occurs only in 2,5-disubstituted 1-vinylpyrrole (V).

A linear dependence is observed between the $^2J(H_A,H_B)$ constant and $\cos^2 \varphi$ (Fig. 1). Since geminal spin–spin coupling (SSC) is a criterion of conjugation in the vinyl group that becomes weaker as noncoplanarity increases, the existence of this dependence is a confirmation of the conclusions drawn relative to the conformation of the investigated compounds.

Long-range SSC (∿0.2 Hz) between H_C and the methyl protons is also observed in the spectrum of II. It may be assumed that in this case coupling through space as a consequence of the sufficient closeness of the indicated protons makes a significant contribution (in V, in which H_C and CH_3 are maximally remote from one another, long-range SSC between them is not observed). This mechanism has been discussed for SSC between the methyl group and H_C in the 2-aminoacetophenone molecule [8], which is isofragmentary with respect to 2-methyl-1-vinylpyrrole:



The $^4J(H_5,H_C)$ constant increases appreciably with branching of the alkyl substituent attached to C_2 (Table 1). In our opinion, this is due to transmission of this SSC via a mechanism involving σ-2p-π-σ interaction [9]. In this case an increase in the noncoplanarity is accompanied by an increase in overlapping of the p orbital of the unshared pair of the nitrogen atom with the H_{C-C_α} σ-bond, which is also reflected in the SSCC.

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EXPERIMENTAL

The PMR spectra of 10% solutions of the compounds in CCl_4 were recorded with a BS-487C spectrometer (80 MHz) with tetramethylsilane as the internal standard. For the measurement of the long-range SSCC and ONE the samples were evacuated by the usual methods [6]. The $^6J(H_3,H_B)$ values were determined from the contraction of the corresponding lines under double resonance conditions; the signs of the $^2J(H_A,H_B)$ constants were determined by the homonuclear INDOR method.

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