PYRROLES FROM KETOXIMES AND ACETYLENE.

V.* STUDY OF THE TRANSMISSION OF SUBSTITUENT EFFECTS IN 1-VINYL-2-ARYLPYRROLES BY ^{13}C NMR SPECTROSCOPY

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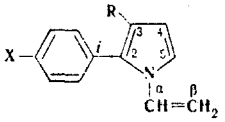
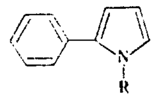
On the basis of a comparative study and analysis of the chemical shifts in the ^{13}C NMR spectra of 1-vinyl-2-arylpyrroles and 3-alkyl-1-vinyl-2-phenylpyrroles, as well as 2-phenyl- and 1-ethyl-2-phenylpyrroles, it was established that the effects of substituents in the investigated series are transmitted via a mechanism involving conjugation and π induction; the conductivity and polarizability of the 2-arylpyrrole system increase when a vinyl group is introduced in the 1 position or, in the case of the 1-vinylpyrrole system, when a phenyl group is introduced in the 2 position; this is due to the increase in the degree of overall conjugation.

During a study of the ^{13}C NMR spectra of 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles we obtained new evidence [2] for conjugation between the double bond and the pyrrole ring; this conjugation is transmitted through the nitrogen atom and depends on the degree of coplanarity of the molecule.

It has recently been shown [3] that in the 5-methyl-2-arylpyrrole series the para substituent of the benzene ring has an appreciable effect on the ^{13}C chemical shifts of the 3-C and 5-C carbon atoms of the pyrrole fragment. The results [2, 3], taken all together, are in agreement with the conclusion, drawn on the basis of UV spectral data [4], that continuous conjugation exists in 1-vinyl-2-phenylpyrrole. We have obtained and thoroughly analyzed the ^{13}C NMR spectra of a number of 1-vinyl-2-arylpyrroles (I-VIII), as well as 2-phenylpyrrole (IX) and 1-ethyl-2-phenylpyrrole (X).



I-VIII



IX, X

IX $R=H$; X $R=C_2H_5$

In contrast to the chemical shifts of the protons, the ^{13}C chemical shifts are relatively insensitive to the effects of magnetic anisotropy, dilution, and solvation [5], and they therefore usually give a more realistic picture of the charge distribution in the aromatic system.

In the ^{13}C NMR spectra of the investigated pyrroles (I-VIII, Table 1) one's attention is drawn to the unexpectedly high sensitivity of the chemical shifts of the β-carbon atom of the vinyl group to the effect of substituents X and R. The range of change of the chemical shift of the β-C atom exceeds the range of change of the chemical shift of 3-C (for pyrroles I-V, which are unsubstituted in this position), 4-C, and 5-C (0.71, 2.14, and 2.39 ppm, respectively), which are closer to the substituents. Formally speaking, the effect of X is transmitted to β-C through eight valence bonds and the effect of R is transmitted through five valence bonds; however, the usual attenuation is not observed in this case. The con-

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*See [1] for communication IV.

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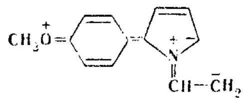
TABLE 1. ^{13}C Chemical Shifts (ppm) of 1-Vinyl-2-arylpyrroles (I-VIII), 2-Phenylpyrrole (IX), and 1-Ethyl-2-phenylpyrrole (X)

Compound	R	X	2-C	3-C	4-C	5-C	i-C	o-C	m-C	p-C	α-C	β-C
I	H	H	133,71	110,00	110,00	117,96	132,26	128,89	127,86	126,60	131,69	97,59
II	H	C_2H_5	134,11	109,90	110,19	117,63	129,90	129,13	127,67	142,67	131,84	97,41
III	H	CH_3O	133,64	109,37	109,97	117,03	124,72	130,19	113,53	158,65	131,68	97,28
IV	H	Cl	132,27	110,08	110,31	118,17	130,58	129,33	128,33	132,79	131,38	98,35
V	H	Br	132,22	110,07	110,28	118,21	130,96	130,00	131,04	121,06	131,35	98,46
VI	CH_3	H	130,21	118,06	112,11	116,06	131,89	130,66	128,01	126,84	131,89	95,97
VII	C_2H_5	H	129,23	124,86	110,02	115,82	131,71	130,54	127,75	126,78	131,61	95,85
VIII	n-C_3H_7	H	129,96	123,32	110,62	115,87	132,10	130,96	128,08	126,96	131,82	95,87
IX			132,12	106,08	106,08	119,84	133,81	123,98	129,27	126,06	—	—
X			133,54	108,87	108,54	121,17	133,87	128,19	128,52	126,06	—	—

jugation nature of this phenomenon also follows from the fact that the electron density on the β-C atom increases on passing from X = H to X = CH_3O (a 0.31 ppm shift to strong field). Being a typical electron acceptor ($\sigma^* = 1.67$), the CH_3O group behaves like a donor only in the case of conjugation with the π system. The resonance structure corresponding to this sort of conjugation also predicts the pronounced shielding of the 5 position of the pyrrole ring that is actually observed experimentally ($C_5^{OCH_3} - C_5^{H} = -0.93$ ppm).

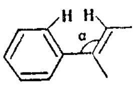


The linear dependence of the relative change in the chemical shift of the terminal carbon atom of the vinyl group ($\Delta C_\beta = C_\beta^X - C_\beta^H$) on the Hammett σ constants is shown in Fig. 1.

$$\Delta C_\beta = 0.65 - (2.6 \pm 0.4)\sigma;\ r = 0.966;\ S_0 = 0.18.$$

Since σ is a combined measure of the resonance and polar effects of a substituent, the correlation found in this research means that X transmits its effect to the β-C atom not only via a conjugation mechanism but also via a π-induction mechanism. The effects of alkyl substituents R also are similar in nature. As in the 2,3-dialkylpyrrole series [2], an alkyl group in the 3 position of the pyrrole ring shifts the β-C signal to strong field, but the conductivity is higher by a factor of ~1.5 in this case: The difference in the β-C chemical shifts between 3-unsubstituted (I) and 3-substituted pyrroles (VI-VIII) is 1.62-1.74 ppm, whereas it is only 1.05-1.16 ppm for the purely alkyl series [2]. Hence it may be concluded that the introduction of a phenyl group in the 2 position increases the polarizability of the π system of N-vinylpyrrole as a whole. This again, in complete agreement with the UV spectral data [4], confirms the development in this molecule of a new low-energy molecular orbital that encompasses all of the unsaturated fragments.

It is known [10, 11] that the intensity of conjugation varies in proportion to $\cos^2 \varphi$ (φ is the dihedral angle between the planes of the π systems). From a comparison of the chemical shifts of the ortho and para carbon atoms (o-C and p-C) in the spectra of pyrroles IX, X, I, and VI-VIII it may be concluded that the benzene and pyrrole rings in 1-vinyl-2-arylpyrroles are noncoplanar. The o-C signal is shifted ~5 ppm to weak field when the NH hydrogen in pyrrole IX is replaced successively by ethyl (X) and vinyl (I) groups. Pronounced deshielding of this type is usually observed in the case of removal of steric strain and conversion of the molecule to another equilibrium conformation (less planar in this case) in order to reduce the destabilizing steric interaction between a bulkier (as compared with hydrogen) substituent (C_2H_5 and $CH_2{=}CH$) and the phenyl group. Steric effects of this sort have also been manifested during the analysis of the UV spectra of analogous pyrroles [4]. The experimental data [12] on trans-stilbene and calculations [13, 14] (CNDO/2 and ab initio) of the geometry of styrene, which are compounds that have a fragment similar to 2-arylpyrroles, show that valence angle α is substantially distorted (it is 8-10° larger than in ethylene). This constitutes an additional argument in favor of steric strain between the phenyl and pyrrole rings. According to the estimates in [15], in α-methyl- and α-tert-butylstyrenes and



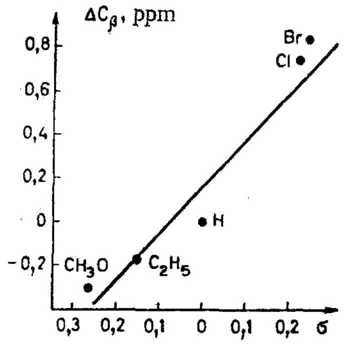
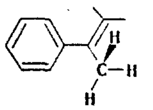
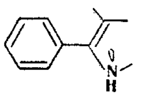


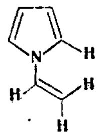
Fig. 1. Dependence of the relative change in the chemical shift of the terminal carbon atom of the vinyl group on the Hammett σ constants.

isofragmentary 2-arylpyrroles the dihedral angle (φ) between the planes of the benzene ring and the double bond are, respectively, 30 and 90°. 2-Phenylpyrrole (IX) is an isostere of α-methylstyrene in the neighborhood of the phenyl group:





It may therefore be assumed that the angle φ in pyrrole IX is also close to 30° and that it increases even more in N-ethyl- (X) and N-vinylpyrroles (I). Insofar as the relative orientation of the planes of the double bond and pyrrole ring is concerned, according to [2, 4, 16, 17], the dihedral angle between these planes is appreciably larger than in 2-unsubstituted 1-vinylpyrroles. An analysis of the stereochemical analogs leads to the same conclusion. Thus the planar forms of the N-vinylpyrrole fragment closely corresponds to the



s-cis conformation of 1,3-butadiene, the population of which at room temperature is, according to the data in [18], only ~1% (the fraction of nonplanar forms due to population of the torsion vibrational levels amounts to 44%). Since the realization of a conformation similar to the s-trans form of 1,3-butadiene is impossible for N-vinylpyrroles, their degree of noncoplanarity should be considerably higher. Nevertheless, a comparison of the 5-C chemical shifts in the spectra of pyrroles I and X (117.96 and 121.17 ppm, respectively) provides evidence for a certain degree of population of the planar conformations of the N-vinyl group. The change in the shielding of the 5-C atom (3.2 ppm) is a consequence of steric interactions of 5-H and one of the vinyl protons in the planar anti conformation of the vinyl group. One is also convinced of this by the invariability (for the given pair of compounds) of the chemical shifts of the 2-C atom, for which this sort steric compression is impossible.

In a conformation in which the benzene ring is already rotated at a certain angle relative to the pyrrole ring under the influence of the substituent attached to the nitrogen atom the introduction of alkyl substituents such as CH_3 (VI), C_2H_5 (VII), and n-C_3H_7 (VIII) in the 3 position of the heteroring should not create substantial steric strain. This is confirmed by the very slight weak-field drift of the o-C signal in the spectra of V-VIII. Independently of this, the distinct and regularly increasing deshielding of the p-C atom on passing from pyrrole IX to X and I, and subsequently to VI-VIII ($C_p^{IX} - C_p^{VIII} = +0.90$ ppm), the reason for which is weakening of the conjugation between the aromatic and heteroaromatic systems, constitutes evidence for the increasing noncoplanarity of the rings. It is known [5] that the p-C chemical shift is a sensitive criterion of the intensity of conjugation in monosubstituted benzenes. On the basis of this criterion, it may be concluded that despite the noncoplanarity, the conjugation between the benzene and pyrrole rings does not disappear entirely: the para position in I and X remains more shielded (to the extent of 1.9-2.4 ppm) than in benzene (128.5 ppm). The comparison would be more nearly correct if one could accurately

TABLE 2. Range of Change in the Charges on the Carbon Atoms

Substituent attached to the nitrogen atom	Range of change in ^{13}C chemical shifts, ppm		
	Δ_3	Δ_4	Δ_5
H	1,55	0,34	1,16
$CH_2{=}CH$	0,71	0,34	1,11

take into account the effect of ethyl- and vinylpyrrole groupings. However, as in the case of all aromatic groupings, it is undoubtedly negative ($\sigma^* \sim 1.06$), i.e., the actual shielding of the para position should be even greater.

Let us now compare the sensitivities of the various positions of the pyrrole ring to the effect of substituents X in N-vinylpyrroles and their N-substituted analogs [3]. We will compare the differences in the ^{13}C chemical shifts for X = Cl and OCH_3 ($\Delta_i = C_i^{Cl} - C_i^{OCH_3}$), which characterize the range of change in the charges on the corresponding carbon nuclei. It follows from Table 2 that the 3-C carbon atom (Δ_3 = 1.55 ppm), which is closest to the substituent, has the greatest sensitivity in NH pyrroles, whereas the most sensitive ring position in N-vinylpyrroles is the most remote 5-C nucleus. It is surprising that despite the twofold decrease in the conductivity in the 3 position, the conductivity in the 4 and 5 positions remains unchanged in both series. The sharp decrease in the conductivity at the 3-C atom on passing to N-vinylpyrroles is completely understandable and is in good agreement with the ^{13}C chemical shifts of 4-substituted styrenes [13] and the α-methyl- and α-tert-butyl derivatives of styrene [15]. However, the retention of the conductivity on the 4-C and 5-C atoms as the noncoplanarity of the system increases must be regarded as reinforcement of the long-range conductivity because of the attachment of an N-vinyl group to the pyrrole ring. To understand the nature of this phenomenon it is expedient to examine how the intensity of the transmission of the effect of a substituent depends on its character. The relative ^{13}C chemical shifts for pyrrole [3] and N-vinylpyrrole series [$\Delta_i' = C_i^H - C_i^X$, where C^H is the chemical shift of the corresponding carbon nucleus in the pyrrole standard (X = H), and C^X is the chemical shift for the substituted compound] are presented in Table 3. It follows primarily from Table 3 that the 3-C and 5-C atoms have the greatest sensitivity to the effect of the substituent (regardless of its character) and vis-à-vis the slight sensitivity of the 4-C atom. This once again confirms the effect of the substituent primarily on the π system and is in agreement with the data in [13] indicating that the σ-inductive effect does not play an important role in compounds of this sort. The methoxy group, which has the greatest ability of the examined substituents to enter into conjugation with the aromatic system, is transmitted with the next greatest intensity. The most important thing to note is that the transmission of the effect of this substituent to the carbon atom that is farthest from it (5-C) is higher by a factor of almost two in the N-vinylpyrrole series than in the series of N-unsubstituted analogs, which are known to have more planar structures. Consequently, the efficiency of transmission of the effect of substituent X along the conjugation system actually increases substantially when an N-vinyl group is introduced in the pyrrole ring: this should be the result of intensification of the overall conjugation in the system.

TABLE 3. Relative ^{13}C Chemical Shifts (Δ_i' in ppm) for Pyrroles and N-Vinylpyrroles

Substituent	Δ'_3		Δ'_4		Δ'_5	
	H	$CH_2{=}CH$	H	$CH_2{=}CH$	H	$CH_2{=}CH$
C_2H_5	−0,49	−0,10	−0,10	+0,19	−0,49	−0,33
CH_3O	−0,87	−0,63	0,00	−0,03	−0,58	−0,93
Cl	+0,68	+0,68	+0,34	+0,31	+0,58	+0,21

EXPERIMENTAL

Pyrroles I-VII were obtained by reaction of the oximes of substituted acetophenones with acetylene, as described in [1, 6]. Pyrrole IX was synthesized by means of the same reaction with insufficient acetylene [7], and pyrrole X was synthesized by hydrogenation of I under the conditions in [8]. The purity of the compounds was always no less than 98% and was monitored by gas—liquid chromatography, thin-layer chromatography, and PMR spectroscopy.

The ^{13}C NMR spectra of 50% (by volume) solutions of the pyrroles in CCl_4 were recorded with a Varian XL-100/12 spectrometer at 25.2 Hz under conditions of complete noise decoupling of the protons at a sample temperature of 25°C with tetramethylsilane as the internal standard. The signals were assigned by means of selective double heteronuclear resonance and from the data in [2, 3, 9].

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