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PYRROLES FROM KETOXIMES AND ACETYLENE.

13.* STUDY OF SOME SUBSTITUTED PYRROLES BY ^{13}C NMR SPECTROSCOPY AND CALCULATIONS WITH THE CNDO/2 APPROXIMATION

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The ^{13}C chemical shifts of six substituted pyrroles are compared with the calculated charges of the corresponding carbon atoms. The correlation is linear only when the charges of the immediate environment are taken into account. The sensitivity of the ^{13}C chemical shift to a change in the charge is increased substantially in 1-vinylpyrroles as compared with their NH analogs. The energetically favorable conformations of the 2-methyl-1-vinyl molecule were established by the CNDO/2 method.

The interrelationship between the conformational and electronic factors in 1-vinylpyrrole molecules was examined qualitatively in [1] by ^{13}C NMR spectroscopy. The electron distribution was discussed on the basis of known data [2-5] on the approximately linear interrelationship between the overall and π-charge densities on the carbon atoms and the chemical shifts of the corresponding nuclei. However, the results of many studies are contradictory. The parameters of the correlation equations always depend on the method by which the charges were calculated. In addition, pyrrole derivatives have not been studied independently in this respect but rather have been examined only in combination with other aromatic heterocycles.

In the present communication we present the results of a joint study of a number of 1-vinylpyrroles and model N-unsubstituted pyrroles by ^{13}C NMR spectroscopy and the CNDO/2 method. The task of this study was to analyze the interrelationship between the ^{13}C chemical shifts and the charge densities on the corresponding carbon atoms in order to quantitatively verify the model of steric inhibition of conjugation developed as applied to 2-substituted 1-vinylpyrroles in [1]. In addition, we set out to ascertain the effect of a vinyl group on the chemical shifts and charges of the ring carbon atoms.

To solve our problem we measured the ^{13}C chemical shifts and calculated the charges of the atoms in pyrrole (I), 2-methylpyrrole (II), 2,3-dimethylpyrrole (III), and their 1-vinyl derivatives (IV-VI, respectively). In addition, we measured the ^{13}C chemical shifts of 2-tert-butyl-1-vinylpyrrole (VII) and 2-methyl-5-phenyl-1-vinylpyrrole (VIII). The results are presented in Tables 1 and 2.

A comparison of the chemical shifts of the ring carbon atoms in I-III and IV-VI (Table 1) shows that C_3 and C_4 are deshielded under the influence of the N-vinyl group, in conformity with the effect of conjugation:

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[*] See [18] for communication 12.

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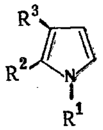
TABLE 1. ^{13}C Chemical Shifts (δ, ppm) of Substituted Pyrroles



Compound	R^1	R^2	R^3	C_2	C_3	C_4	C_5	C_α[a]	C_β[a]
I	H	H	H	118,50	108,16	108,16	118,50	—	—
II	H	CH_3	CH	125,50	106,10	108,57	115,74	—	—
III	H	CH_3	CH_3	123,63	114,38	110,36	115,36	—	—
IV[b]	$CH{=}CH_2$	H	H	118,18	110,14	110,14	118,18	132,83	95,89
V[b]	$CH{=}CH_2$	CH_3	H	127,66	108,38	109,34	115,46	130,33	96,55
VI	$CH{=}CH_2$	CH_3	CH_3	124,18	115,82	111,58	114,39	130,77	95,40
VII[b]	$CH{=}CH_2$	C_4H_9-*t*	H	140,44	106,59	108,41	118,25	133,41	98,48
VIII	$CH{=}CH_2$	CH_3	C_6H_5[c]	131,78	109,52	109,02	129,70	133,60	106,00

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[a] Carbon atoms of the $N{-}C_\alpha H{=}C_\beta H_2$ group. [b] From [1]. [c] Phenyl group attached to the C_5 atom.

TABLE 2. Total Charges on the Carbon Atoms in Substituted Pyrroles

Compound[a]	C_2	C_3	C_4	C_5	C_α	C_β
I	0,0542	−0,0442	−0,0442	0,0542	—	—
II	0,0950	−0,0680	−0,0422	0,0475	—	—
III	0,0709	−0,0202	−0,0571	0,0533	—	—
IVa (0°)[b]	0,0432	−0,0425	−0,0411	0,0464	0,1050	−0,1042
IVb (90°)	0,0475	−0,0454	−0,0454	0,0475	0,1034	−0,0798
Va (0°)	0,0842	−0,0655	−0,0366	0,0384	0,1139	−0,1164
Vb (35°)	0,0846	−0,0657	−0,0394	0,0395	0,1131	−0,1037
Vc (55°)	0,0861	−0,0667	−0,0410	0,0403	0,1127	−0,0946
Vd (90°)	0,0888	−0,0685	−0,0415	0,0399	0,1135	−0,0890
VI (35°)	0,0607	−0,0192	−0,0525	0,0445	0,1127	−0,1037

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[a] The numbering corresponds to the numbering presented in Table 1. [b] The dihedral angles (φ) are given in parentheses.

The C_2 and C_5 chemical shifts, on the other hand, are insensitive to the introduction of a vinyl group. The calculated total charges on the terminal carbon atoms in these compounds (Table 2) constitute evidence that coupling of the nitrogen atom with the vinyl group reduces the electron density on the C_3 and C_4 atoms somewhat and increases it on C_2 and C_5; this increase several times exceeds the loss of charge on the C_3 and C_4 atoms. The slight change in the chemical shifts of C_2 and C_5 in the case of vinyl substitution is evidently due to the compensating β effect, which acts in the opposite direction [6].

For V we calculated the charges in four conformations (Va-d) with a variable orientation of the ring and double bond determined by dihedral angle φ (Table 2); in this case an increase in the noncoplanarity causes a decrease in the electron density on C_β and an increase in the electron density on C_3 and C_4, in complete agreement with the model of steric inhibition of conjugation [1] and the tendency for a change in the ^{13}C chemical shift as branching of the substituent attached to C_2 increases [1].

Thus, a general examination reveals a good qualitative interrelationship between the ^{13}C chemical shifts and the total charges of the corresponding carbon atoms.

In passing to a quantitative evaluation of this dependence let us note that the experimentally determined values of dihedral angles φ (between the planes of the pyrrole ring and the double bond) were used for the calculation of the charges used for the construction of the correlations [7]: 0° for IV, 35° for V, 55° for VII, and 90° for VIII. To simplify the calculations we assumed that the Vc molecule models 2-tert-butyl-1-vinylpyrrole (VII), while the IVb molecule models 2-methyl-5-phenyl-1-vinylpyrrole (VIII); taking into account the assumptions made above, we did not include the chemical shifts of the terminal carbon atoms of these compounds in the correlation but used only the C_β chemical shifts (for an individual correlation).

The dependence of the chemical shifts of the ring carbon atoms on the total charge is unsatisfactory:

$$\delta C_i = 114.3(\pm 1.2) + 101.2(\pm 21.9)q_i,$$
$$r = 0.908,\ S_0 = 2.66\ (n = 22).$$

Moreover, separation of the total number of points into two sorts, viz., pyrroles and vinylpyrroles, does not improve the correlation:

$$\delta C_i^{NH} = 113.8(\pm 1.8) + 102.2(\pm 32.1)q_i,$$
$$r = 0.930,\ S_0 = 2.59\ (n = 10).$$
$$\delta C_i^{NCH=CH_2} = 114.8(\pm 1.8) + 101.8(\pm 36.1)q_i,$$
$$r = 0.891,\ S_0 = 2.87\ (n = 12).$$

As demonstrated in [8], taking into account the charges of even the atoms that are closest to the atom under consideration makes it possible to achieve considerable success in the description of the interrelationship between the chemical shifts and the charge. On the basis of these data we obtained a dependence in which the chemical shift of each atom is a function of its own charge and the charges of the adjacent atoms (separately for pyrroles and vinylpyrroles):

$$\delta C_i^{NH} = 118.7(\pm 0.6) + 220.5(\pm 15.3)q_i + 66.5(\pm 9.2)q_{i-1} + 84.7(\pm 9.2)q_{i+1},$$
$$R = 0.996,\ S_0 = 0.71\ (n = 10).$$

$$\delta C_i^{NCH=CH_2} = 121.1(\pm 1.2) + 266.7(\pm 30.4)q_i + 132.4(\pm 24.0)q_{i-1} + + 151.0(\pm 27.5)q_{i+1},$$
$$R = 0.979,\ S_0 = 1.44\ (n = 12).$$

It follows from these equations that the charge of the atom itself has the dominant effect on the ^{13}C chemical shift; however, the immediate environment also plays a substantial role. The appreciably larger values of the coefficients of the equation for vinylpyrroles constitutes evidence for an increase in the sensitivity of the ^{13}C chemical shift to a change in the charge. In addition, in the vinylpyrrole series the electron density on the adjacent atoms has a much greater effect on the ^{13}C chemical shift than in the N-unsubstituted pyrrole series (the corresponding coefficients are doubled on the average). This actually means that the introduction of a 1-vinyl group increases the ability of the pyrrole ring to transmit the effects of the substituents. This corresponds to an increase in delocalization and is in agreement with the concept of intensification of the overall conjugation in the system. In a previous study of the ^{13}C NMR spectra of 2-aryl-1-vinylpyrroles [9] we showed that the vinyl group actually intensifies transmission of the substituent's effect.

The lower quality of the correlation for the vinyl derivatives (the large values of the overall dispersion and the dispersions of the coefficients) shows that the contribution of the steric interactions of the double bond with the ring, which is not taken into account by the calculation, is manifested in this case.

A comparison of the correlation equations reveals another interesting feature. The correlation line for 1-vinylpyrroles is shifted by a value on the order of 2 ppm to the lower-shielding region. The most likely reason for this shift is the effect of the ring current in the pyrrole ring. According to the data from many investigations (see [10, 11] and the literature cited therein), this effect is rather significant for the ring carbon atoms. In benzene, for example, the diamagnetic shielding of ^{13}C due to the ring current is 6 ppm. In 1-vinylpyrroles the conjugation of the double bond with the nitrogen atom reduces the degree of participation of its unshared pair of electrons in the formation of the ring current; this should be expressed in terms of a decrease in the diamagnetic contribution of the latter to the resonance of the ring carbon atoms. There is no doubt that this hypothesis requires quantitative verification. Let us note only two cases. The aromatic character of the pyrrole ring is substantially lower than that of the benzene ring (∿60% according to the data in [12]). The application of several criteria of aromatic character (the effect of the CH_3 group attached to C_2 on the proton chemical shifts, and the sum of the bond orders) [13] shows that the introduction of an N-vinyl group actually somewhat reduces the aromatic character of the pyrrole ring. Thus, the observed shift of

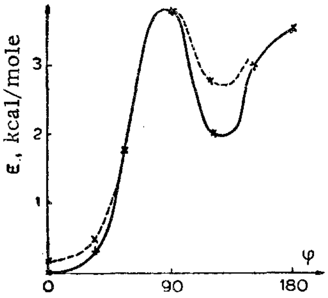


Fig. 1. Dependence of the energy of the 2-methyl-1-vinylpyrrole molecule on dihedral angle φ and the rotational state of the methyl group (see the explanation in the text).

the correlation lines both with respect to sign and magnitude is, in our opinion, logically explained by these reasons.

The C_β chemical shift correlates with the total charge:

$$\delta C_\beta = 137.6 + 400.2(\pm 31.4) q_\beta,$$

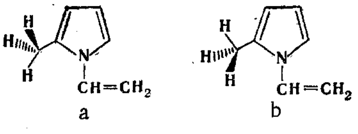
$$r = 0.987,\ S_0 = 0.96\ (n = 4).$$

The slope of this dependence is anomalously high. The reason for this is the doubling of the C_β chemical shift due to the variable contribution of the steric interactions of the vinyl group with the pyrrole ring [7]. The change in the C_β chemical shift due to an increase in the charge on C_β (which is due in turn to steric disruption of coplanarity) is therefore half the observed value of the slope, and this is in good agreement with the known [14] data (160-200 ppm per electron).

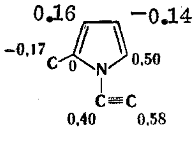
As regards the α-carbon atoms of the double bond, there is no relationship between their chemical shifts and the charge. The total charge on C_α is virtually constant for any φ values (Table 2), whereas the chemical shift changes abruptly on passing from IV to V and then to VII and VIII (Table 1). This is in agreement with the previously noted observation [1] that steric compression has the principal effect on the C_α chemical shift.

In order to study the conformational structure of 1-vinylpyrroles we calculated the total energy of the 1-vinyl-2-methylpyrrole molecule with variation of dihedral angle φ from 0° (the planar anti conformation) to 90° (the planar syn form). Fig. 1 shows the dependence of the relative energy (E) on φ. This dependence has an overall minimum at 0°, and the energy remains virtually unchanged as dihedral angle φ is varied from 0 to 35°, i.e., all of the conformers that are characterized by the corresponding dihedral angles should have an identical population. The second minimum on the curve corresponds to the nonplanar gauche conformation with an angle of 120-130°.

According to the calculation, the conformers with the same φ angle but a different rotational state of the methyl group differ with respect to energy, and the energy of form b is somewhat higher (Fig. 1, dashed line). The most substantial difference is observed for φ = 120°.



The shape of the energy curve is in satisfactory agreement with the temperature dependence of the ^{13}C chemical shift of 1-vinyl-2-methylpyrrole. The changes in the chemical shifts of the atoms of this compound when a sample is heated from 25 to 100°C are presented in the scheme (a positive shift corresponds to deshielding).



All of the temperature shifts correspond to an increase in the population of the conformation with $\varphi = 120°$ (the second minimum on the curve). The deshielding of C_β and the shielding of C_4 constitute evidence for weakening of the p, π conjugation in the N-vinyl fragment, and the fact that the changes in their chemical shifts are not equal to one another is in complete agreement with nonidentical sensitivities of the chemical shifts of the ring and vinyl carbon atoms to a change in their charge; the deshielding of C_5 and C_α is due to a decrease in the nonbonding interactions as a consequence of the increased noncoplanarity. At the same time, the shielding of the methyl carbon atom and the weak-field shift of C_3 are evidently associated with an increase in the percentage of rotamer a.

EXPERIMENTAL

The ^{13}C NMR spectra of 10% solutions in CCl_4 (I-III) and the undiluted liquid compounds (IV-VIII) were obtained with an XL-100/12 spectrometer. The methods used to record the spectra and assign the signals were presented in [1]. All of the calculations* were performed with a BÉSM-6 computer by the self-consistent-field (SCF) MO LCAO method within the CNDO/2 approximation in the original parametrization [15]. The bond lengths and angles were taken from [16, 17].

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