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^{1}H AND ^{13}C NMR STUDY OF CONFORMATIONAL AND ELECTRONIC STRUCTURE OF 1-VINYLPYRROLES

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Abstract—The ^{1}H and ^{13}C NMR spectra of some 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles as well as model 1-unsubstituted pyrroles were studied. Alkyl substituents affect electronic structures of the compounds through steric inhibition of p,π-conjugation and π-induction. Correlations of the ^{13}C chemical shifts of the pyrrole ring carbon atoms with the total charge density (CNDO/2) of these atoms are established.

Previously unknown 1-vinylpyrroles have now become readily available due to the development of their direct one-pot synthesis from ketoximes and acetylene in the dimethylsulfoxide—KOH system.[1-3] These new monomers and intermediates for the synthesis of other substituted pyrroles are now under systematic synthetic[4,5] and physico-chemical[6-10] investigation.

In this work, NMR (^{1}H, ^{13}C) spectra of a set of 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles, as well as model 1-unsubstituted pyrroles have been analysed to gain a clearer understanding of their conformational and electronic structures. Special attention was paid to the following questions: the extent of p,π-conjugation in 1-vinylpyrroles and its dependence on rotation of the vinyl group around the N–C sp^{2} bond and on the ring substitutents, and whether the pyrrole ring substituents can influence the vinyl-pyrrole co-planarity.

The ^{1}H and ^{13}C NMR parameters of 1-vinylpyrroles are listed in Tables 1 and 2. The ^{1}H and ^{13}C shielding of the terminal methylene group of the double bond in all the compounds studied is higher than that of ethylene (δ^{1}H = 5.28 ppm, δ^{13}C = 123.3 ppm) and 3-methyl-1-butene (δ^{13}C = 111.4 ppm), which is isosteric with 1-vinylpyrrole around the vinyl group. This fact, noticed earlier in studying the ^{1}H and ^{13}C NMR spectra of some α,β-unsaturated ethers,[11-15] sulfides,[16-20] and amines,[21,22] is related to p,π-conjugation of the lone electron pair of the heteroatom with an adjacent double bond. However, the delocalization of the nitrogen lone pair over the pyrrole ring decreases the charge transfer from the nitrogen atom onto the double bond as it follows from the C_β shielding in 1-vinylpyrrole (95.9 ppm) as compared with 1-vinylpyrrolidine (79.9 ppm).[22]

The 1-vinylpyrrole molecule conformation is mostly determined by two contrasting factors: (i) p,π-conjugation of the double bond and the nitrogen atom and (ii) steric hindrance to coplanarity (for bulky substituents).

2-*Alkyl*-1-*vinylpyrroles*. Compounds I–V are interesting mainly for the analysis of the susceptibility of the ^{1}H and ^{13}C chemical shifts of the ring and vinyl group to electronic and steric effects of alkyl substituents.

Due to its spatial disposition, the H_A proton is subjected to an essentially greater influence of magnetic anisotropy of the pyrrole ring and the H_B proton. An approximate estimation of this influence shows that when the vinyl group goes out of the ring plane by 90°, the anisotropy contribution to the H_A chemical shifts changes from 0.34 to 0.04 ppm, whereas for H_B such a contribution is practically unchanged (0.16 and 0.14 ppm, respectively). Moreover, H_B is free of steric interaction with the pyrrole ring. Therefore the chemical shifts of the latter can most reliably reflect an electronic redistribution in the vinyl group invoked by the conformational change due to rotation around the N–C sp^{2} bond. The H_4 proton is remote from the vinyl group and substituents in the ring and reflects the π-donative ability of the nitrogen atom to the pyrrole ring better than any other ring protons.

It is seen from Tables 1 and 2 that the introduction of bulky substituents into position 2 uniformly deshields the H_B and C_β nuclei, the greatest shift being displayed by these nuclei in 2,5-disubstituted pyrrole V. Simultaneously, the H_4 and C_4 nuclei in compounds I–IV are shielded to the same degree. The H_B and C_β chemical shifts are linearly related to steric constants of substituent R^{1}:

$$\delta H_B = 4.50 - 0.04(\pm 0.008)E_s^{\circ},\ r = 0.96,\ S_0 = 0.005$$

$$\delta C_\beta = 96.46 - 0.98(\pm 0.08)E_s^{\circ},\ r = 0.98,\ S_0 = 0.24$$

In terms of correlation of chemical shifts (^{1}H and especially ^{13}C) with the charge densities of the corresponding atoms, this means that the p,π-conjugation intensity falls in the sequence I–V.

The ground for that is, as in the case of other heterovinylic derivatives,[14-20] an increase in non-coplanarity of the π-systems.

A long-range coupling (through six bonds) between H_B and H_3 is observed (Table 1). Such an interaction is highly stereospecific[23] and is preferably transmitted through a planar zig-zag pathway. Thus, the existance of such a coupling shows the predominance of anti-conformation with respect to the double bond and substituent R^{1}:

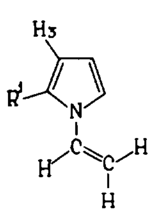
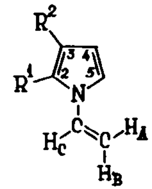


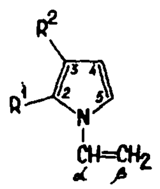
Table 1. The proton chemical shifts and coupling constants of 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles



Compound	R^1	R^2	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	H	H	4.96	4.47	6.60	6.07	6.07	6.71	-1.2	0.6	0.20
II	CH_3	H	4.93	4.50	6.75	5.74	5.99	6.75	-0.8	0.4	0.45
III	C_2H_5	H	4.95	4.52	6.80	5.76	5.97	6.79	-0.7[b]	0.4[b]	0.4[b]
IV	C_4H_9-t	H	4.96	4.58	7.17	5.79	5.89	6.74	-0.5	0.2	0.60
V[c]	CH_3	H	4.90	4.81	6.70	5.85	6.05	-	<0.05	<0.05	-
VI	CH_3	CH_3	4.87	4.45	6.71	-	5.80	6.70	-0.8[b]	-	
VII	C_2H_5	CH_3	4.90	4.45	6.75	-	5.90	6.70	-0.8[b]	-	
VIII	C_3H_7-i	CH_3	4.90	4.49	6.90	-	5.80	6.63	-0.6	-	
IX	CH_3	C_2H_5	4.88	4.46	6.72	-	5.86	6.70	-0.8	-	
X	CH_3	C_3H_7-n	4.89	4.45	6.75	-	5.84	6.70	-0.8	-	
XI	CH_3	C_5H_{11}-n	4.87	4.46	6.77	-	5.87	6.72	-0.8	-	
XII	CH_3	C_3H_7-i	4.85	4.45	6.74	-	5.90	6.70	-0.8	-	
XIII	C_4H_9-n	C_3H_7-n	4.85	4.46	6.75	-	5.96	6.75			
XIV	$-(CH_2)_4-$		4.88	4.42	6.70	-	5.80	6.65	-0.8		
XV	$-(CH_2)_5-$		4.91	4.50	6.80	-	5.78	6.59	-0.6		

[a] In all compounds: $^3J(H_A,H_C)$=15.8 Hz, $^3J(H_B,H_C)$=8.9 Hz; [b] The accuracy is $\pm$0.1 Hz; [c] In this compound the H_5 is replaced by phenyl group (2-methyl-5-phenyl-1-vinylpyrrole)

Table 2. The ^{13}C chemical shifts of 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles



Compound	R^1	R^2	C_2	C_3	C_4	C_5	C_α	C_β
I	H	H	118.18	110.14	110.14	118.18	132.83	95.89
II	CH_3	H	127.66	108.38	109.34	115.46	130.33	96.55
III	C_2H_5	H	134.12	106.92	109.62	115.88	130.55	97.01
IV	C_4H_9-t	H	140.44	106.59	108.41	118.25	133.41	98.48
V*	CH_3	H	131.78	109.52	109.02	129.70	133.60	106.00
VI	CH_3	CH_3	124.18	115.79	111.58	114.39	130.77	95.40
VII	C_2H_5	CH_3	130.73	115.26	111.72	114.45	130.22	95.50
VIII	C_3H_7-i	CH_3	132.74	115.09	112.61	114.78	131.48	96.79
IX	CH_3	C_2H_5	123.02	123.02	109.79	114.61	130.74	95.58
X	CH_3	C_3H_7-n	123.77	121.41	110.55	114.65	130.85	95.62
XI	CH_3	C_5H_{11}-n	123.41	121.50	110.24	114.53	130.78	95.54
XII	CH_3	C_3H_7-i	122.31	128.06	107.33	114.63	130.65	95.67
XIII	C_4H_9-n	C_3H_7-n	128.50	121.34	110.37	114.69	130.86	95.39
XIV	$-(CH_2)_4-$		127.21	118.86	109.65	114.46	130.41	94.75
XV	$-(CH_2)_5-$		130.12	123.56	111.32	113.55	130.68	96.55

*In this compound the H_5 is replaced by phenyl (2-methyl-5-phenyl-1-vinylpyrrole).

Quantum-mechanical calculations of the styrene derivatives predict the existence of an angular dependence for such coupling constants, which is expressed approximately by the equation:[24]

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

where φ is the dihedral angle between the planes of the double bond and the ring. Such an expression obviously fits our case as well, since the pyrrole ring is an aromatic one and 1-vinylpyrrole is therefore a close analog of styrene. This allows the same mechanism for long-range coupling to be assumed.

We estimated the φ angle value for 2-methyl-1-vinylpyrrole(II) by the nuclear Overhauser effect (NOE) experiments. In the spectrum of a degassed sample of pyrrole II an increase in the H_3 and H_C signal intensity by 6 and 5% is observed when the CH_3 protons are irradiated by a second radiofrequency. In this case, the absolute NOE values cannot be used as a criterion of the molecular geometry since both H_3 and H_C are subjected to an additional relaxation influence of the neighboring protons H_4 and H_B, respectively. However their ratio should meet the equation:[25]

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

where I is the absolute NOE value, r—the distance from the given proton to the centre of a circle, drawn by methyl protons upon their rotation. From the pyrrole geometry, the H_3–CH_3 distance equals 3.152 Å. Since the I-values for H_3 and H_C are the same within the integration error, the H_C–CH_3 distance is estimated as 3.15($\pm$0.05) Å that corresponds to the dihedral angle $\varphi = 35°(\pm 5)$. In this case, according to the $^{6}J(H_3, H_B)$ angular dependence, $^{6}J_0$ for these protons amounts to 0.6 Hz and the φ values in compounds I, IV and V are 0°, 55° and 90°, respectively. Therefore the maximum coplanarity distortion takes place only in 2,5-disubstituted 1-vinylpyrrole (V).

We have carried out a CNDO/2 calculation of the total energy of the 2-methyl-1-vinylpyrrole molecule varying the dihedral angle from 0° (planar anti-conformation) to 180° (planar syn-conformation). The angular energy dependence is shown in Fig. 1. This dependence has a

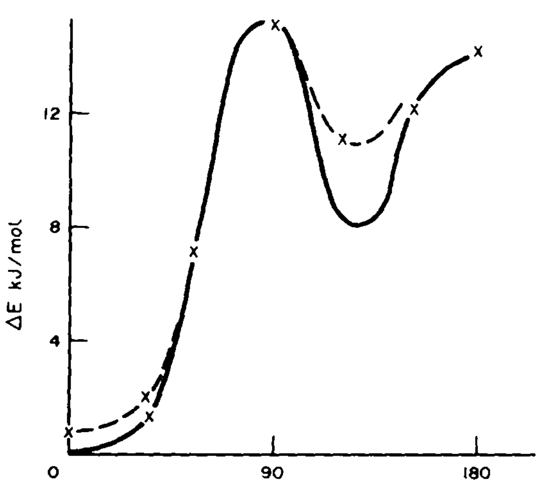


Fig. 1. Angular dependence of the relative energy of 2-methyl-1-vinylpyrrole molecule: rotamer "a" (dashed line); rotamer "b" (solid line).

main minimum at 0° and the energy value is practically unchanged in the 0–35° range, i.e. all the conformers with such angles should have approximately the same population. The second minimum on the curve is related to the nonplanar (gauche) conformation with $\varphi = 120$–$130°$.

We attempted to estimate the population ratio for two conformations of the 2-methyl-1-vinylpyrrole molecule using the experimental δC_β values and the energy curve. The estimation was carried out by the following equation:[26]

$$\delta_{exp} = \delta_1 N_1 + \delta_2 N_2$$

where N_1 and N_2 are population of the two conformers, δ_{exp} is the δC_β experimental chemical shift value of 2-methyl-1-vinylpyrrole(II), δ_1 and δ_2—chemical shifts of C_β in the molecules having the only conformation with $\varphi = 0$ and 120°. We took as δ_1 the C_β chemical shift in 1-vinylpyrrole(I) and as δ_2—the C_β chemical shift in 2-tert-butyl-1-vinylpyrrole(IV), characterized by a conformation with $\varphi = 55°$ being nearest to the 120° conformation. The N_1 and N_2 values proved to be 0.745 and 0.255, respectively, i.e. the population ratio of conformers with $\varphi = 0$ and 120° is approximately 3 : 1. Certainly, this estimation is rough because of the above assumptions. However, the average dihedral angle of 30° determined by this ratio is in good agreement with the experimental value (35°).

The $^2J(H_A, H_B)$ values of pyrroles I, II, IV and V are linearly dependent on $\cos^2 \varphi$, where φ is the angle estimated above (Fig. 2). This dependence proves that our conclusions concerning the geometry of the compounds studied are correct here.

The $^4J(H_5, H_C)$ values increase as the alkyl substituents at C_2 branch (Table 1) that seems to be related to the coupling transmission by the $\sigma - 2p(\pi) - \sigma$ interaction mechanism.[27] In this case the non-coplanarity growth is accompanied by an increase in the overlap of the nitrogen lone electron pair with the H_C–C_α bond that affects the coupling constants values.

The H_B and C_β chemical shifts are linearly related:

$$\delta C_\beta = -39.4(\pm 14.8) + 30.2(\pm 0.1)\delta H_B,$$

$$r = 0.996, \; S_0 = 0.31.$$

The slope of this line is twice as higher as that in para-substituted 2-aryl-1-vinylpyrroles.[28] However, independently of the mechanism by which the electron density at C_β changes, the δC_β–δH_B plot should have the slope in the 10–20 range based on the ratio of the $\delta^{13}C$ (160–200 ppm) and δ^1H (10–15 ppm) ranges provided that there are no other factors influencing the δC_β.

The increase in the slope seems to occur for the following reason. The steric interaction of vinylic methylene with a pyrrole cycle reaches its maximum in conformations having small dihedral angles. These interactions result in a considerable diamagnetic contribution to the δC_β and a contribution of the opposite sign to the δH_A.[29] The steric strain becomes weaker as the non-coplanarity increases, thus diminishing these two contributions and widening the δC_β range.

The value of steric shifts can be approximately estimated as follows. The slope ratio of the $\delta C_\beta = f(\delta H_B)$ correlation in the alkyl- and 2-aryl-1-vinylpyrroles series (the latter is of the invariable geometry set) is equal to 2. Therefore, half of the δC_β range is due to the steric effects. It is possible to assume that 2-methyl-5-phenyl-1-vinylpyrrole has no steric interactions of this kind. So the $\delta C_\beta - \delta H_B$ plot free of steric compression contribution, should have a twice less slope and intersect the experimental one in the point belonging to 2-methyl-5-phenyl-1-vinylpyrrole (Fig. 3). The steric contribution values estimated from this plot for $R^1 = H$, CH_3, C_2H_5 and C_4H_9-t are −5.0, −4.6, −4.5, and −4.0 ppm, respectively, i.e. the increase in non-coplanarity decreases the steric effects.

Substracting these values from the experimental δC_β ones we obtain "true" chemical shifts values (δ^1), which may be considered as a measure of p,π-conjugation in the N-vinyl group:

Substituent	δ^1	ω
None	100.9	0
2-CH_3	101.2	0.3
2-C_2H_5	101.5	0.6
2-C_4H_9-t	102.5	1.6
2-CH_3,5-C_6H_5	106.0	5.1

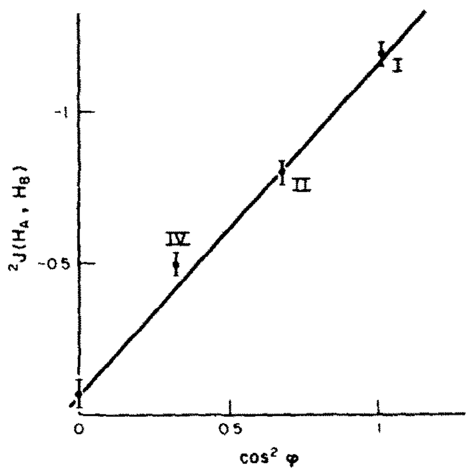


Fig. 2. A $\cos^2 \varphi$ dependence of $^2J(H_A, H_B)$.

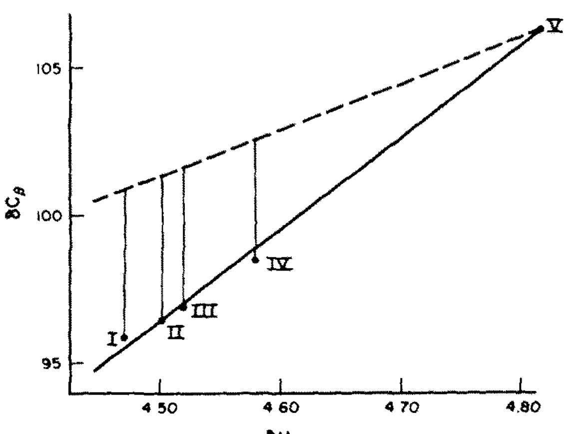


Fig. 3. Estimation of steric contribution to the δC_β: experimental dependence of δC_β on δH_B (solid line); dependence of δC_β on δH_B free of steric interactions (dashed line).

From the ω values (the difference between δ^1C_β of unsubstituted and substituted pyrroles) it is seen that the p,π-conjugation distortion occurs gradually and the most noticeable effect appears in only 2-tert-butyl. Here one can see some analogy with the alkylvinyl ethers CH_2=CHOR in which the alkyl branching influences the p,π-conjugation mostly at $R = C_4H_9$-t.[14,15] However, there is also a marked difference; if, according to IR[30] and dipole moment[31] data, tert-butoxy-ethene has mainly a non-planar gauche-conformation with $\varphi = 90°$, the effective conformation of 2-tert-butyl-1-vinylpyrrole, as determined by ^{1}H NMR spectral analysis, displays φ = 55°. In this case a noticeable conjugation distortion takes place at a lesser non-coplanarity. This difference follows from the fact that the oxygen atom possesses two lone pairs capable of conjugating with a double bond, whereas the nitrogen atom has only one electron pair.

Comparing the δC_β values for 2,5-disubstituted vinylpyrroles V, ethylene and 3-methyl-1-butene, one can conclude that p,π-conjugation in the N-vinyl group remains slightly changes even at a full non-coplanarity and that the pyrrole ring is a rather powerful electron donor even under these conditions. This is confirmed by CNDO/2 calculated charge densities of vinylic β-carbons in 1-vinylpyrrole: -0.10 and -0.08 for $\varphi = 0°$ and 90°, respectively, i.e. there is a considerable excessive charge on the vinylic β-carbons in both cases.

2,3-Dialkyl-1-vinylpyrroles. A stronger shielding of the C_5 and C_β nuclei distinguishes these compounds from 2-alkyl-1-vinylpyrroles. The most remote C_β separated from the substituent at C_3 by five bonds is more sensitive than the C_5 carbon. This shows that the alkyl substituents at C_3 operate through the π-inductive mechanism involving polarisation of the π-system.[32] One could suppose that the degree of coplanarity of the pyrrole ring and the double bond in substituted 1-vinylpyrroles should depend not only on the steric effects but on the intensity of p,π-conjugation as well (the more intensive conjugation leads to a more coplanar system). In such a case alkyl substituents at C_3 of the pyrrole ring influencing the intensity of conjugation (through inductive and mesomeric mechanisms) can, in spite of their remoteness, affect the steric interactions between the vinyl group and the heterocycle. This suggestion may be checked by comparison of chemical shifts (or their differences) for some positions of the pyrrole ring and the vinyl group in compounds with and without alkyl substituents at C_3 (Table 3).

As it is seen from Table 3, the methyl group in position 3 influences the sensitivity of the δ^{13}C to the structural change of the alkyl at C_2 for only C_5, C_α and C_β. This phenomenon seems to be caused by a higher "rigidity" of more planar conformations due to the conjugation increase in the 1-vinylpyrrole system when the methyl group is introduced into position 3.

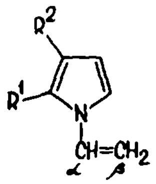
Especially illustrative is this effect for chemical shifts of the C_α. In the first pair of compounds (R^2=H) a small enlargement of the substituent size (CH_3 to C_2H_5) accompanied by non-coplanarity growth deshields by 0.2 ppm the C_α. In the second pair (R^2=CH_3) the same increase in the substituent size cannot make the vinyl group deviate by an identical angle. As a result, the increasing steric compression leads to the observed C_α shielding. A comparison of the ΔC_β also gives evidence for less coplanarity differences at $R^2 = CH_3$ than at R^2 = H.

The model proposed is also supported by observation that the rotation barrier of the acetyl group in the 1-acetyl-3,4-dimethylpyrrole is about 4 kJ/mol higher than that in unsubstituted 1-acetylpyrrole.[33]

A comparison of the δ^{13}C values in 1-vinylpyrroles and the relevant pyrroles (Tables 4 and 5) makes it possible to evaluate a contribution of the vinyl group to chemical shifts of the ring carbon atoms, providing some additional information on the 1-vinylpyrrole molecule structure.

The Δ' values of C_3 and C_4 (Table 5) being remote from the vinyl group, mostly reflect the electronic influence of the latter. On the other hand, the $\Delta' C_2$ and $\Delta' C_5$ values should depend on other factors as well, that makes the analysis and discussion rather difficult. The $\Delta' C_3$ and $\Delta' C_4$ values are always positive, i.e. the vinyl group deshields these nuclei. This is common consequence of the competitive conjugation of p-electron of the nitrogen atom with the π-systems of the ring and the double bond. So the coplanarity distortion is expected to diminish the deshielding influence of the vinyl group really observed for $\Delta' C_4$ in 2-alkyl-1-vinylpyrroles. On

Table 3. The ^{13}C chemical shifts of 2-alkyl- and 2-alkyl-3-methyl-1-vinylpyrroles



R^1	R^2	C_2	C_3	C_4	C_5	C_α	C_β
CH_3	H	127.66	108.38	109.34	115.46	130.33	96.55
C_2H_5	H	134.12	106.92	109.62	115.88	130.55	97.01
Δ		6.46	-1.46	0.28	0.42	0.22	0.46
CH_3	CH_3	124.18	115.79	111.58	114.39	130.77	95.40
C_2H_5	CH_3	130.73	115.26	111.72	114.45	130.22	95.50
Δ		6.55	-0.53	0.14	0.06	-0.55	0.10

the other hand, the mutual orientation of unsaturated fragments in 2-methyl-3-alkyl-1-vinylpyrroles is undoubtedly constant which is reflected in a fairly small change in the $\Delta'C_3$ and $\Delta'C_4$ values.

However, in compounds with variable coplanarity (I–IV) the $\Delta'C_3$ values increase and in the case of VI–VIII the same is also observed for the $\Delta'C_4$ values.

This "anomaly" is believed to be caused by a different population of rotational states of alkyl radicals around the C_{sp^2}–C_{sp^3} bonds in 1-vinylpyrroles and their NH-analogs.

In 2-alkyl pyrroles the environment of the substituent at the C_2 from both sides is practically the same (NH and H_3 protons), but in 1-vinylpyrroles it is not the same (vinyl group and H_3). Therefore, corresponding rotamers of pyrroles and vinylpyrroles should differ in their energies.

As recent *ab initio* calculations shows,[34] in conformational equilibrium of 2-methylpyrrole (X = H) the

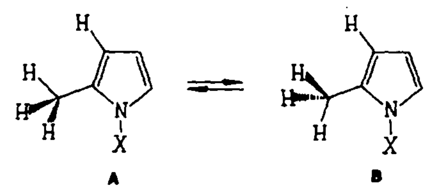
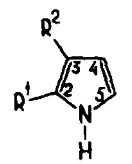


Table 4. The ^{13}C chemical shifts of alkylpyrroles



Compound	R^1	R^2	C_2	C_3	C_4	C_5
XVI	H	H	118.50	108.16	108.16	118.50
XVII	CH_3	H	126.24	106.10	108.57	115.74
XVIII	C_4H_9-t	H	141.09	102.54	107.95	115.51
XIX	CH_3	CH_3	125.65	113.74	110.18	114.50
XX	C_2H_5	CH_3	128.90	112.96	110.14	114.45
XXI	C_3H_7-i	CH_3	132.64	112.09	110.29	114.09
XXII	CH_3	C_2H_5	122.16	120.94	108.29	114.58
XXIII	CH_3	C_3H_7-n	122.44	119.28	108.98	114.57
XXIV	CH_3	C_5H_{11}-n	122.19	119.40	108.86	114.48
XXV	CH_3	C_3H_7-i	121.13	126.06	105.97	114.54
XXVI	C_4H_9-n	C_3H_7-n	127.55	119.05	108.80	114.66
XXVII	$-(CH_2)_4-$		126.28	116.67	107.40	115.32
XXVIII	$-(CH_2)_5-$		129.48	120.99	110.29	112.82

Table 5. Relative the ^{13}C shifts of the ring carbon atoms ($\Delta'C_i$, ppm)* in 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles

Compound	R^1	R^2	C_2	C_3	C_4	C_5
I	H	H	-0.32	1.98	1.98	-0.32
II	CH_3	H	1.42	2.28	0.77	-0.28
IV	C_4H_9-t	H	-0.65	4.05	0.46	2.74
VI	CH_3	CH_3	1.47	2.05	1.40	-0.10
VII	C_2H_5	CH_3	1.83	2.30	1.58	0.00
VIII	C_3H_7-i	CH_3	0.10	3.00	2.32	0.69
IX	CH_3	C_2H_5	0.86	2.08	1.50	0.03
X	CH_3	C_3H_7-n	1.33	2.13	1.57	0.08
XI	CH_3	C_5H_{11}-n	1.22	2.10	1.38	0.05
XII	CH_3	C_3H_7-i	1.18	2.00	1.36	0.09

* $\Delta'C_i = \delta C_i^{NCH=CH_2} - \delta C_i^{NH}$

rotamer "A" is more preferred by 3.0 kJ/mol. In such a conformation, the H_3 proton is involved in a considerable steric interaction with the methyl proton lying in the ring plane. From our CNDO/2 calculations, in the 2-methyl-1-vinylpyrrole ($X = CH{=}CH_2$) the energy of rotamer "A" is higher than that of rotamer "B" (Fig. 1, dashed line), and the latter is therefore more populated. These considerations seem to be true also for the 2-tert-butyl analogs. In such a case, an introduction of the vinyl group to the nitrogen atom of the pyrrole ring, the steric substituents effects on the C_3 atom should become weaker which is expressed in the C_3 deshielding. Thus, the C_3 chemical shifts are subjected to two deshielding effects: an electron acceptor influence of the vinyl group (i) and a weaking of the steric compression by the alkyl substituent (ii). The latter effect is stronger with a bulkier alkyl radical. So, it is not occasional that the highest $\Delta' C_3$ is observed for the 2-tert-butyl derivative.

The second explanation is based on the assumption that in 1-unsubstituted pyrroles, the $\delta^{13}C_{3,4}$ values are more sensitive to the σ-inductive effect.

In compounds VI–VIII the situation is more complicated. The growth of size of R^1 increases both $\Delta' C_3$ and $\Delta' C_4$. The reason for the $\Delta' C_3$ increasiing seems to be the same as in the former case. The $\Delta' C_4$ behavior has not found yet a reasonable rationalisation.

As it was already stated, the analysis of relative C_2 and C_5 chemical shifts is rather difficult. Perhaps, the only noteworthy thing here are the fairly close $\Delta' C_5$ values in the 2-methyl-3-alkyl-1-vinylpyrroles. This again might be connected with the conformational homogeneity of this series of compounds.

The ^{13}C chemical shifts are known to be a well-justified criterion of the electron molecular structure only when a reliable correlation with the charge of relevant atoms is established. To verify qualitatively the model of the steric inhibition of the resonance developed here for the 1-vinylpyrroles, we have analyzed interrelation of ^{13}C chemicals shifts and charge densities at the relevant atoms. Besides, it was intended to estimate the influence of vinyl group on the $\delta^{13}C$ values and the carbon charge of the cycle. With this goal in view, we have undertaken CNDO/2 calculations of the carbon atom charges in molecules of pyrrole (XVI), 2-methylpyrrole (XVII), 2,3,-dimethylpyrrole (XVIII) and their 1-vinyl derivatives (I, II, VI). The results obtained are listed in Table 6. In the case of pyrrole (I) the charge calculation for two conformations (Ia, b) was carried out by changing mutual orientation of the ring and double bond which is defined by the dihedral angle φ(Table 6). The same was done for four conformations (IIa–d) of pyrrole II.

It is seen that the non-coplanarity growth decreases the electron density on the C_β atom and increases that on the C_3 and C_4 atoms. This is consistent with the model of a steric distortion of conjugation and the trend of the $\delta^{13}C$ when the alkyl substituents at the C_2 atoms are progressively branching.

The δC_β are linearly correlated with the total charge:

$$\delta C_\beta = 137.6 + 400(\pm 31) q C_\beta,$$
$$r = 0.986, \qquad S_0 = 0.96$$

The slope value of this dependence is unusually high. This, as shown above, is a consequence of the two-fold widening of the δC_β range due to the varying contribution of steric compression. If the charges on the C_β atom are correlated with the $\delta^{13}C$ values corrected for this contribution (δ'), the slope value obtained (199 ppm/e) agrees well with the known data (160–200 ppm per electron).[35]

The dependence of the $\delta^{13}C$ values of the ring atoms on the total charge may be expressed satisfactorily as:

$$\delta C_i = 113.8(\pm 1.9) + 102.2(\pm 32.1) q_i,$$
$$r = 0.930, \qquad S_0 = 2.59 (n = 22)$$

where i is the atom number the chemical shift of which (δC_i) is correlated with the charge (q_i).

As has been shown,[36] accounting for charges of atoms nearest to the atom in question allows one to obtain a closer $\delta^{13}C$-charge dependence. Based on this conclusion we have relations in which $\delta^{13}C$ of each atom is a

Table 6. Total charges of the carbon atom in pyrroles

Compound	C_2	C_3	C_4	C_5	C_α	C_β
Ia (0°)*	0.0532	-0.0424	-0.0411	0.0464	0.1050	-0.1042
Ib (90°)	0.0475	-0.0454	-0.0454	0.0475	0.1034	-0.0798
IIa(0°)	0,0832	-0.0655	-0.0394	0.0384	0.1139	-0.1164
IIb(35°)	0.0846	-0.0657	-0.0394	0.0395	0.1131	-0.1037
IIc(55°)	0.0861	-0.0667	-0.0410	0.0403	0.1127	-0.0946
IId(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
XVI	0.0542	-0.0442	-0.0442	0.0542	-	-
XVII	0.0950	-0.0680	-0.0442	0.0475	-	-
XIX	0.0709	-0.0202	-0.0571	0.0533	-	-

* In parentheses the values of dihedral angle φ are given.

function of its own charge and those of the neighboring atoms (separately for pyrroles and vinylpyrroles). Verification of the equations obtained after Fisher's criterion shows that the introduction of additional arguments in the correlation are statistically justified:

$$\delta C_i^{NH} = 118.7(\pm 0.6) + 220.5(\pm 15.3)q_i + 66.5(\pm 9.2)q_{i-1} + 84.7(\pm 9.2)q_{i+1}$$

$$R = 0.996, \quad S_0 = 0.71 (n = 10)$$

$$\delta C_i^{NCH=CH_2} = 121.1(\pm 1.2) + 266.7(\pm 30.4)q_i + 132.4(\pm 24.0)q_{i-1} + 151.0(\pm 27.5)q_{i+1}$$

$$R = 0.979, \quad S_0 = 1.44 (n = 12)$$

The large values of the vinylpyrrole equation coefficients show a higher sensitivity of $\delta^{13}C$ to the charge changing (both of its own atoms and of the neighbouring ones) as compared with N-unsubstituted pyrroles.

A comparison of the correlation equations reveals one interesting feature more. The vinylpyrrole correlation line is shifted by about 2 ppm to lower field. The most probable reason for this shift is an influence of the pyrrole ring current. According to numerous data (see Refs. 37 and 38 and references therein) this influence is fairly strong for the carbon ring atoms. For example, in benzene a ^{13}C diamagnetic shielding due to the ring currents amounts to 6 ppm. In 1-vinylpyrroles the conjugation of the double bond with the nitrogen atom decreases the extent of participation of its electron lone pair in the ring current which should be expressed in a diminishing of diamagnetic contribution from the latter to $\delta^{13}C$ of the ring carbon atoms as compared with pyrroles. Certainly, this idea requires a quantitative verification. We should like to note two cases. Aromaticity of the pyrrole ring is substantially lower than that of the benzene (approximately 60%).[39] An application of some criteria of aromaticity (effect of the CH_3-group on the proton chemical shifts, sums of the bond orders)[40] shows that the N-vinyl group makes the pyrrole ring aromaticity somewhat lower in fact. Therefore, the observed displacement of the correlation line, in both sign and magnitude, is fairly well explained by these causes.

EXPERIMENTAL

Details of syntheses of 1-vinylpyrroles studied were published earlier.[41] The purity of compounds was monitored by GLC and ^1H NMR and was not below 98%.

The ^1H NMR spectra of 1-vinylpyrroles were recorded on a Tesla BS 487C (80 MHz) spectrometer, the ^{13}C, spectra on a Varian XL-100/12 (25.2 MHz) spectrometer. The samples were analysed as 0.5 M solutions in CCl_4 (^1H), neat liquid (^{13}C). The ^{13}C NMR spectra of 1-non-substituted pyrroles were registered in FT mode on a Varian CFT-20 spectrometer using 0.5 M solution in CCl_4. In this condition the association effects on the carbon chemical shifts are believed to be approximately constant in all the compounds studied. To all samples 5% vol TMS was added, which served as an internal standard for the δ^1H and $\delta^{13}C$ chemical shift measurements and also for locking when running the ^1H NMR spectra. For the ^{13}C spectra the deuteron signal from D_2O in a 1 mm o.d. capillary was used for the lock.

The accuracy of the ^1H and ^{13}C chemical shifts and ^1H–^1H spin-spin coupling constant measurements was ±0.005 ppm, ±0.02 ppm and ±0.05 Hz, respectively.

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