NMR SPECTRA AND STRUCTURES OF PROTONATED 1-VINYLPYRROLES

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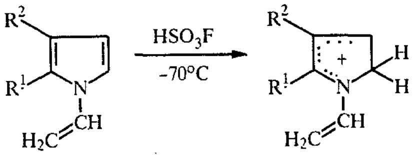
Stable 1-vinylpyrrolium fluorosulfonates were prepared by the reaction of 1-vinylpyrroles with excess HSO_3F at $-50°C$ in CD_2Cl_2 and their ^1H and ^{13}C NMR spectra were obtained. Despite its overall positive charge, the pyrrole ring remains an electron donor relative to the vinyl group. Delocalization of the positive charge onto substituents decreases in the order 2-heteroaryl > 2-aryl > 2-alkyl.

Protonated pyrroles have been known for about 30 years [1, 2]. The ^1H [1-4] and ^{13}C NMR [5] spectra of some of them, principally polysubstituted pyrroles, have been described, mainly as an aid in structure determination, but there has not been a systematic investigation of their structure until now. The problems addressed in most previous publications have been the determination of the predominant position of protonation, the basicity of pyrroles and the effect of substituents on the basicity [2-4, 6]. Changes in conformation and electron distribution in substituted pyrroles on protonation have scarcely been discussed. On the other hand. homoaromatic cations have been very widely studied from this point of view [7].

Thanks to the discovery of a direct synthesis from ketoximes and acetylene [8-11] and the development of new and effective methods of vinylation [9], 1-vinylpyrroles have become in the last decade one of the most accessible and intensely studied groups of pyrrole compounds [8, 9]. Consequently the study of the electronic and spatial structures of their protonated forms, which are the active intermediates in many of their reactions, remains an important task.

The ^1H and ^{13}C NMR spectra of a wide range of 1-vinylpyrrolium cations (IA-XXIIA) have been investigated in this study. They were generated at $-50°C$ by the reaction:



A list of the substituents R^1 and R^2 is given in Tables 1 and 2. The parameters of the NMR spectra of the cations are given in Tables 3-5 and of their neutral predecessors in Tables 1 and 2. The structures of the cations are indicated unambiguously by a broad signal for the CH_2 groups in the 5.5-5.8 ppm region and the retention of the vinyl group signals in the ^1H NMR spectra.

Comparison of the chemical shifts of the terminal carbon atoms of the vinyl groups $C\beta$ in the 1-vinylpyrrolium cations IA-XXIIA and the initial 1-vinylpyrroles I-XXII (110-115 and 95-100 ppm respectively) shows that there is less electron density on this atom in the cations. Nevertheless, the shielding of the β-carbon atom in the cations is greater than the shielding of the carbon nuclei in ethylene (123.3 ppm). This means that the protonated pyrrole ring is a π-donor for the N-vinyl groups (although weaker than the nonprotonated ring), despite its positive charge (i.e., the sharp increase in its negative inductive effect). Thus the extent of bonding between the unshared pair of the nitrogen atom and the vinyl group in the cations (IA-XXIIA) and in the initial pyrroles is quite comparable (taking into account the increased electronegativity of the pyrrole ring on protonation). Hence the relative orientation of the vinyl group and the heterocycle (and consequently the chemical shift of

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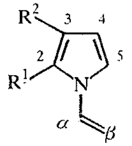
TABLE 1. ^{13}C Chemical Shifts (δ, ppm) for 1-Vinylpyrroles ($CDCl_3$, 25°C)



Compound	R¹	R²	C_2	C_3	C_4	C_5	C_α	C_β	R¹	R²
I	H	H	118,79	110,35	110,35	118,79	133,28	96,94		
II	H	*i*-Pr*	113,97	109,06	136,03	118,88	133,11	95,63		
III	Me	H	127,70	108,26	109,38	116,02	130,59	97,73	12,09	
IV	*t*-Bu	H	140,00	106,39	108,17	118,82	133,64	99,71	40,15 (α); 30,78 (β)	
V	Me	Me	124,50	116,14	111,54	114,68	130,93	96,30	9,32	11,17
VI	Me	Et	123,87	123,38	109,79	114,87	130,85	96,68	9,43	19,29 (α); 15,56 (β)
VII	Me	*i*-Pr	122,93	128,50	107,40	114,98	130,85	96,68	9,47	25,49 (α); 24,11 (β)
VIII	-$(CH_2)_4$-		127,60	119,05	109,53	115,05	130,44	95,67	21,94; 23,21; 23,59;	23,33;
IX	2-Furyl	H	124,70	110,65	111,24	118,68	131,97	99,55	148,23 (C2'); 106,10 (C3'); 109,22 (C4'); 140,58 (C5')	
X	5-Methyl-2-furyl	H	124,97	110,06	110,33	118,26	131,98	99,09	146,48 (C2'); 108,53 (C3'); 111,74 (C4'); 153,20 (C5')	
XI	2-Thienyl	H	127,30	110,35	111,54	118,64	131,41	99,29	135,23 (C2'); 125,68 (C3'); 125,50 (C4'); 124,12 (C5')	
XII	2-Thienyl	Me	122,96	120,83	111,96	117,01	131,57	97,34		

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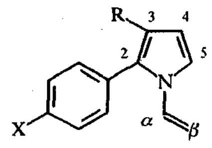
*Isopropyl group at C_4.

TABLE 2. ^{13}C Chemical Shifts (δ, ppm) for 1-Vinyl-2-arylpyrroles XIII-XXII ($CDCl_3$, 25°C)



Compound	X	R	C_2	C_3	C_4	C_5	$C\alpha$	$C\beta$	C_i	C_o	C_m	C_p
XIII	H	H	132,49	110,20	110,20	118,23	131,93	98,62	132,26	128,35	129,38	127,11
XIV	Me	H	132,20	109,77	110,09	117,99	132,17	98,34	129,90	129,14	129,35	137,07
XV	MeO	H	132,05	109,56	110,06	117,67	132,05	98,17	124,77	113,97	130,66	159,16
XVI	Cl	H	130,93	110,31	110,53	118,75	131,67	99,11	130,58	128,54	130,25	133,09
XVII	Cl	*i*-Pr	129,13	129,13	107,73	116,87	131,60	97,43	130,44	128,58	132,37	133,40
XVIII	H	*i*-Pr	130,59	129,10	107,70	116,32	131,86	96,60	132,08	128,24	131,15	127,45
XIX	MeO	*i*-Pr	130,10	129,05	107,52	115,89	131,81	96,51	124,70	128,58	132,37	159,42
XX	H	Me	130,59	118,43	112,20	116,35	132,15	96,78	132,15	128,37	130,97	127,30
XXI	H	Et	129,88	125,36	110,16	116,32	131,93	96,68	131,93	128,24	130,96	127,30
XXII*			129,69	124,17	108,89	120,21	133,54	101,00	129,26 (C1')	136,29 (C2'); 121,95 (C6')	125,31 (C3'); 128,72 (C5')	126,77

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*1-Vinyl-4,5-dihydrobenzo[g]indole (atom numbering is designed to facilitate discussion of the results and is not as required by IUPAC).

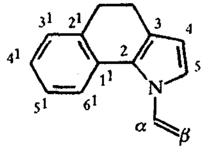

TABLE 3. ^{13}C Chemical Shifts (δ, ppm) of 1-Vinylpyrrolium Fluorosulfonates IA-XIIA (CD_2Cl_2,–20°C)*

Compound	C_2	C_3	C_4	C_5	$C\alpha$	$C\beta$	R^1	R^2	$\Sigma\delta_i^+ - \Sigma\delta_i^0$
IA	169,78	129,15	157,91	63,27	132,00	113,31			117,3
IIA**	169,52	128,00	186,40	62,82	131,65	112,00		30,74 (α); 21,62 (β)	124,9
IIIA	181,96	132,51	155,11	64,01	128,78	113,28	16,40		124,2
IVA	198,85	130,42	156,19	66,78	130,79	114,58	45,17 (α); 28,31 (β)		130,9
VA	182,63	140,73	148,05	61,77	129,22	111,89	14,64	12,32	119,2
VIA	181,81	146,03	146,03	62,00	129,97	112,12	14,49	15,72 (α); 11,28 (β)	116,8
VIIA	182,03	151,26	146,18	62,14	129,37	112,49	14,86	26,59 (α); 21,66 (β)	120,6
VIIIA	182,93	141,32	147,82	61,77	128,33	111,89	26,59; 23,68; 21,21; 20,32		115,9
IXA	157,75	131,54	151,03	63,94	128,10	111,90	143,19 (C_2'); 133,03 (C_3'); 116,57 (C_4'); 155,44 (C_5')		93,7
XA	155,74	131,54	151,14	63,12	127,58	110,18	141,81 (C_2'); 135,57 (C_3'); 113,88 (C_4'); 168,96 (C_5')		92,1
XIA	165,52	131,02	152,38	65,06	129,67	114,43	126,98 (C_2'); 129,99 (C_3'); 142,22 (C_3'); 143,27 (C_5')		99,7
XIIA	169,04	139,61	149,24	62,60	130,64	113,23	126,01 (C_2'); 131,69 (C_3'); 141,03 (C_4'); 141,05 (C_5')	14,94	102,1

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* Atom numbering is the same as for the neutral compounds (Table 1).

** Isopropyl group at C_4.

TABLE 4. ^{13}C Chemical Shifts (δ, ppm) of 1-Vinyl-2-arylpyrrolium Fluorosulfonates XIIIA-XXIIA (CD_2Cl_2, $-20°C$)

Compound	C_2	C_3	C_4	C_5	C_α	C_β	C_i	C_o	C_m	C_p	$\Sigma\delta_i^+ - \Sigma\delta_i^0$
XIIIA	176,58	130,57	155,39	65,51	131,54	113,84	125,49	131,54	130,57	136,47	109,6
XIVA	176,13	132,14	154,77	65,66	131,32	113,39	122,80	131,83	132,14	148,79	110,8
XVA	174,79	131,09	153,72	65,58	131,60	112,94	117,94	134,90	116,15	166,04	107,6
XVIA	175,61	130,42	155,74	66,03	131,47	114,51	124,07	133,03	131,09	142,39	110,0
XVIIA	177,77	151,70	148,72	62,74	129,30	113,83	123,77	131,20	131,20	141,47	
XVIIIA	178,59	151,41	148,27	62,52	129,57	113,31	125,48	130,30	130,30	134,52	110,9
XIXA	177,38	151,41	147,15	62,37	130,49	112,64	117,94	132,36	116,00	163,51	
XXA	178,97	140,95	150,21	62,44	130,50	113,24	124,81	130,50	130,50	135,27	109,0
XXIA	178,52	146,70	148,05	62,82	130,30	113,16	124,82	130,30	130,30	134,90	107,7
XXIIA*	170,27	144,32	147,57	64,85	128,94	113,92	122,64	144,32 (C2′); 131,05 (C6′)	128,44 (C3′); 131,05 (C5′)	138,15 (C4′)	99,4

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*1-Vinyl-4,5-dihydrobenzo[g]-indolium cation

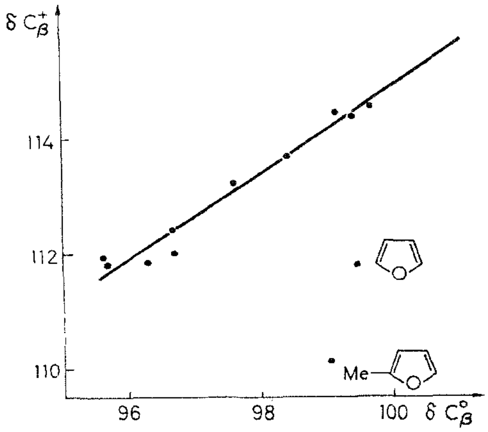

Fig. 1. Relation between the Cβ chemical shifts in the cations IA-XIIA and the neutral molecules I-XII.

Cβ which acts as indicator) should be determined in principle by the same factors as in the neutral predecessor molecules — the extent of p,π-conjugation between the nitrogen atom and the double bond and steric hindrance to coplanarity [12].

In contrast to Cβ, protons H_A and H_B bonded to it are deshielded relative to ethylene (5.28 ppm) (Table 5). The reason for this is evidently the known polarization of the C-H bond in charged systems (in protonated amines in particular [13]), as a result of which the electron deficit on the carbon atom is partially compensated by a shift of charge from the hydrogen atom. The change in the shift for protons H_A and H_B with structure is analogous to the change in shift for Cβ.

There is a satisfactory correlation between the chemical shifts of Cβ in the 1-vinylpyrrolium cations IA-XIIA and their nonprotonated predecessors (Fig. 1). The points corresponding to the 2-(2-furyl) and 2-(5-methyl-2-furyl) substituents show the greatest deviation from this correlation. Excluding these two points the following correlation equation is obtained:

$$\sigma C\beta^{+} = 39{,}4 + 0{,}76(\pm 0{,}14)\sigma C\beta^{0},\ r = 0{,}983,\ s_0 = 0{,}05,\ n = 10$$

This relation emphasizes the commonality of the factors that determine the electronic structures of the protonated and nonprotonated pyrrole molecules. However the chemical shifts of the cations are somewhat less sensitive to these factors than those of the neutral molecules: the change in charge distribution caused by substituents is less in the first series than in the second. For example, introduction of a methyl group at $C_{(2)}$ (cf. cations IA and IIIA) does not affect the Cβ chemical shift, whereas in the 1-vinylpyrroles the change in shift is about 0.8 ppm, while the change from a 2-methyl to a 2-tert-butyl substituent causes descreening of Cβ by 1.3 ppm in the cations and by 2.0 ppm in the neutral molecules.

The shielding of Cβ and $C_{(5)}$ is somewhat greater (by 0.5-2 ppm) in 3-alkyl substituted cations in comparison with compounds without a 3-substituent. The reason for this strong field shift, which was previously noted for 1-vinylpyrroles [12], is the π inductive effect of the alkyl substituent which polarizes the π system. The change in shift for $C_{(5)}$, despite the fact that its hybridization is sp^3, not sp^2, should be noted. This change disrupts the aromatic system. However, the effect of the $C_{(3)}$ substituent in cations is specifically different from that in the nonprotonated molecules. For example, a methyl group at $C_{(3)}$ (ions VA, XIIA, XXA) deshields $C_{(2)}$ and shields $C_{(4)}$. The reverse effect occurs for the 1-vinylpyrroles (Tables 1 and 2). This is the β-effect of the methyl group described earlier [14], i.e., the variation in chemical shift of the β-carbon atom (δ) on substituting H by CH_3:

$$H - C\alpha - C\beta \rightarrow CH_3 - C\alpha - C\beta$$

with the pπ-order of the Cα-Cβ bond calculated by the ChPDP method:

$$\Delta = 12{,}5 - 18{,}6\ p\pi.$$

TABLE 5. Hydrogen Chemical Shifts (δ, ppm) of 1-Vinylpyrrolium Fluorosulfonates (CD_2Cl_2, -20°C)

Compound	H_A	H_B	H_C	H_4	CH_2	R^1	R^2
IA	5,89	5,72	7,29	8,15	5,30	8,81	7,20
IIA	5,76	5,60	7,17	6,90*	5,16	8,66	3,15 (α); 1,39 (β)
IIIA	5,84	5,70	7,15	7,99	5,20	2,80	7,00
IVA	5,81	5,72	7,40	8,00	5,28	1,60	7,17
VA	5,81	5,64	7,15	7,58	5,04	2,69	2,22
VIA	5,82	5,66	7,16	7,56	5,07	2,70	2,45 (α); 1,17 (β)
VIIA	5,83	5,67	7,15	7,56	5,07	2,74	2,80 (α); 1,28 (β)
VIIIA	5,79	5,59	7,08	7,56	5,07	3,04; 2,73; 1,92	
IXA	5,73	5,58	8,00	7,80	5,30	7,96 (H_3); 7,03 (H_4); 8,23 (H_5)	7,25
XA	5,69	5,50	7,92	7,80	5,27	8,06 (H_3); 6,75 (H_4); 2,65 (Me)	7,22
XIA	5,93	5,75	7,49	7,93	5,38	8,43 (H_3); 7,63 (H_4); 8,27 (H_5)	7,39
XIIIA	5,93	5,70	7,28	8,09	5,41	7,8	7,34
XIVA	5,90	5,68	7,28	8,03	5,38	7,5—7,8	7,34
XVA	5,87	5,65	7,26	7,98	5,33	7,3—7,9	7,30
XVIA	5,94	5,74	7,28	8,12	5,40	7,7—8,0	7,33
XVIIA	5,82	5,60	6,96	7,73	5,27	7,5—7,8	2,90 (α); 1,17 (β)
XVIIIA	5,84	5,54	6,96	7,70	5,24	7,5—7,8	2,88 (α); 1,12 (β)
XIXA	5,85	5,57	7,00	7,62	5,22	7,3—7,7	2,88 (α); 1,13 (β)
XXA	5,88	5,58	7,08	7,70	5,25	7,5—7,9	2,22
XXIA	5,90	5,59	7,06	7,63	5,27	7,5—7,9	2,52 (α); 1,25 (β)

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*Chemical shift of H_3

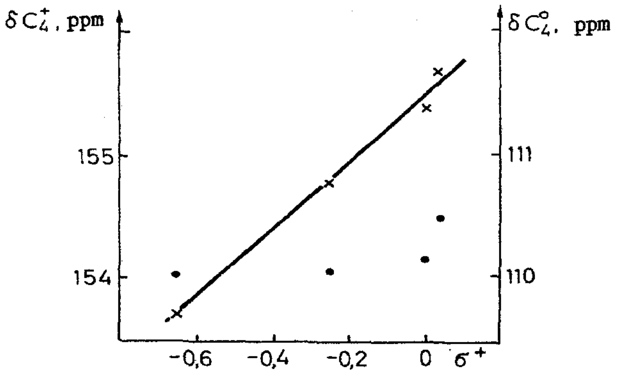
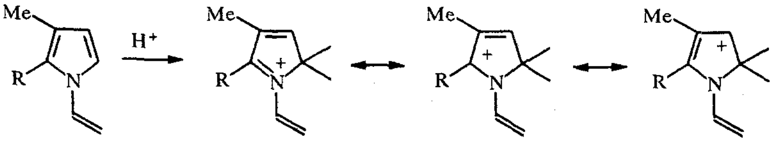


Fig. 2. Relation of C_4 chemical shifts on the σ^+ constant for the substituent X in the cations XIIIA-XVIA (×) and the neutral molecules XIII- XVI (·).

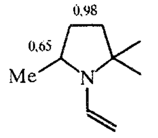
It follows from this equation that Δ changes sign at $p\pi = 0.67$. With a large $p\pi$ order, the β-effect of the CH_3 group causes shielding; with a low order it causes deshielding. In a qualitative sense, the observed behavior corresponds to a redistribution of the bond order on cation formation:

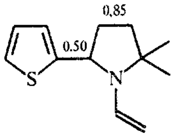


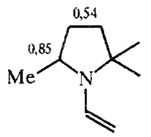
In distinction from the neutral molecules, the values of δ in the cations clearly depend on the type of substituent at $C_{(2)}$:

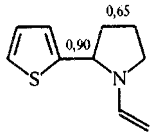
R	Compound		Chemical shift of H_3	
	$\Delta c_{(2)}$	$\Delta c_{(4)}$	$\Delta c_{(2)}$	$\Delta c_{(4)}$
Me	+0,7	-7,1	-3,2	+2,2
Ph	+2,4	-5,2	-1,9	+2,0
2-Thienyl	+3,5	-3,1	-4,3	+0,4

These results allow a comparison of the pπ-order for the $C_{(2)}$-$C_{(3)}$ and $C_{(3)}$-$C_{(4)}$ bonds in the cations and 1-vinylpyrroles:









In order to follow the redistribution of the positive charge on addition of a proton to the 1-vinylpyrrole molecule, we have compared the sum of the chemical shifts $\Sigma\delta_i^+$ in the cations for atoms $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ (i.e., those atoms with no change of hybridization on protonation) with the analogous sum for the neutral molecules, $\Sigma\delta_i^0$. The difference $\Sigma\delta_i^+ - \Sigma\delta_i^0$ is the sum of the deshielding of the carbon nuclei in the ring. This method was used previously in the analysis of the ^{13}C NMR spectra of alkylbenzene derivatives [7]. It was observed that in alkyl derivatives the total deshielding was 120 ± 5 ppm, in 2-aryl substituents it decreased to 109 ± 2 ppm, and it was least for heteroaryl substituents (97 ± 5 ppm). The total descreening in the 1-vinyl-4,5-dihydrobenzo[g]indolium cation XXIIA, the derivative with the greatest coplanarity of the rings, was 10 ppm less in the other phenyl-substituted compounds and about the same as in the heteroaryl-substituted compounds. It is not possible to reach quantitative conclusions on charge redistribution since there is no information on the electron density at nitrogen; nevertheless the results obtained clearly show an increased degree of positive charge delocalization in the series: 2-heteroaryl > 2-aryl > 2-alkyl. This sequence does not correspond to the electrophilic constants δ^+ for the substituents nor with the stability series for the 1-vinylpyrrolium cations in trifluoroacetic acid that we discussed earlier [15], where the substituents were placed in an order of decreasing stability of the ions : 2-furyl ~ 2-thienyl > 2-CH_3 > 2-phenyl. Evidently charge delocalization by a π-π conjugative mechanism is not the only factor which determined the ion stability under uniform conditions: additional stabilization of the alkyl-substituted cations may be explained by hyperconjugative interactions.

The chemical shifts of C_p may be used as an independent of the extent of interring interactions in phenyl derivatives. The maximum delocalization of positive charge is observed in cation XXIIA with the most planar geometry: the change in the C_p shift is 11.4 ppm on protonation. In cation XIIIA this change is substantially less (9.4 ppm), while it is still less for XVIIIA at 7.1 ppm, i.e., an increasing volume of the substituent in the cation, as in the vinylpyrrole series, is accompanied by an increase in noncoplanarity of the benzene and pyrrole fragments.

This conclusion is confirmed by the shift to strong field of the signal for the H_C proton of the vinyl group with increasing volume of the substituent at C_3 (by 0.32 ppm in the series of cations XIIIA, XXA, XXIA, XVIIIA). It was shown previously using 2-aryl-1-vinylpyrroles that the shift of this proton is linked to the torsion angle ψ between the planes of the aromatic units. This occurs because with the vinyl group in an S-trans conformation relative to C_2, proton H_C is under the screening influence of the benzene ring and this increases with increases in ψ.

We shall now discuss the influence of cation formation on the transmissibility of the electronic effects of the substituents. The limited range of substituents prevents a quantitative study using correlation analysis, so we simply compare the ^{13}C chemical shifts for the atoms in the heterocycle and vinyl groups in the cations XIIIA-XVIA and those in their precursors. Evidently there is a shift in the reaction center on protonation: C_4 is the ring position most sensitive to the effect of substituents among the cations (the difference in shifts with p-Cl and p-MeO substituents, which characterizes sensitivity, is 2.0 ppm) whereas the opposite is true in neutral molecules where C_4 is the least sensitive to substituent effects (the corresponding value for the change in shift is 0.5 ppm). The nature of the electronic interaction in the aryl ring changes along with the fourfold increase in sensitivity. Figure 2 shows the relation of the chemical shift for C_4 on the substituent σ^+ constants for both cations and neutral molecules. The relation is linear for the cations, but definitely not for the neutral molecules. This indicates that the mesomeric effect of the substituents is predominant in the cation series [17]. The chemical shift for $C\beta$ of the vinyl group is less sensitive with a 1.5-fold increase only.

EXPERIMENTAL

Cations were generated by mixing in an NMR ampul 0.02 g (^1H) or 0.1 g (^{13}C) of a vinylpyrrole with a 5-10 fold excess of fluorosulfonic acid (0.25 and 1.0 ml respectively) in an equal volume of CD_2Cl_2 at -50°C.

NMR spectra were recorded with a Tesla BS 567A instrument at 100 MHz (^1H) or 25.14 MHz (^{13}C). The ^{13}C signals were assigned using the pulsed decoupling method [18].

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