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PROTONATION OF 1,4-BIS(1-VINYL-2-PYRROLYL)BENZENE

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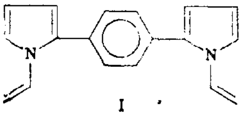
In the reaction of 1,4-bis(1-vinyl-2-pyrrolyl)benzene with hydrogen chloride and hydrogen bromide the hydrogen halide adds at the vinyl groups, and α-protonation takes place in both pyrrole rings. In reaction with the superacidic system $HSO_3F + SbF_5$ (in SO_2ClF) position 5 of one heterocycle and position 4 of the other are protonated with retention of the vinyl groups.

In molecules containing directly linked five-membered aromatic heterocycles their mutual effect is extremely important. For example, the trifluoroacetylation of 1-vinyl-2-(2-furyl)pyrrole by trifluoroacetic anhydride leads to a mixture of products from acylation at positions 5 of either the pyrrole or the furan rings. Double acylation is not observed [1]. The protonation of furylpyrroles by hydrogen halides also takes place either in the pyrrole ring or in the furan ring but not in both rings at the same time [2]. These facts result from the strong deactivating effect of the partial positive charges that arise at the respective carbon atoms of the nonreacting heterocycle as a result of the formation of a common system of conjugation [3].

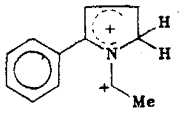
The aim of the present work was to study the mutual effect of N-vinylpyrrole fragments separated by a benzene ring in the case of the protonation of 1,4-bis(1-vinyl-2-pyrrolyl)benzene (I) by the superacidic system $HSO_3F + SbF_5$ in SO_2ClF and hydrogen halides HCl and HBr. The obtained cations were identified by PMR spectroscopy.



I

On the one hand, the formation of the common system of conjugation can favor ready delocalization of the charge that appears during the protonation of this compound to the most distant atoms in the molecule. On the other hand, the appreciable population of the nonplanar conformations (with respect to the phenyl—heterocycle bonds) [4] should lead to some isolation of the two heterocycles from each other.

It is known that 1-vinyl-2-phenylpyrrole undergoes double protonation at the α position of the ring and the β position of the vinyl group in the $HSO_3F + SbF_5$ system with the formation of the dication [5]:



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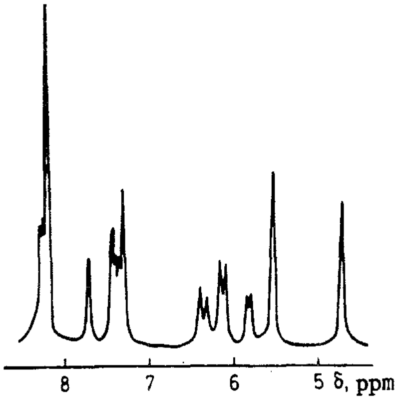


Fig. 1

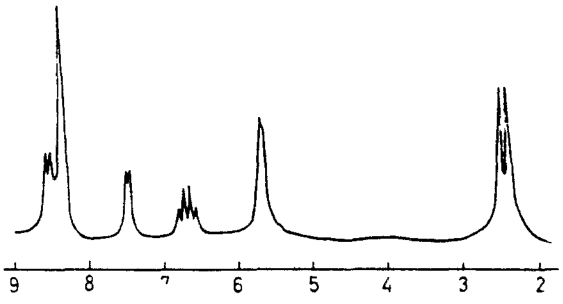


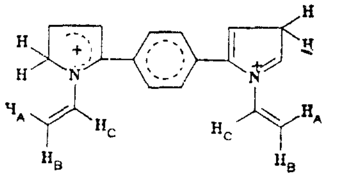
Fig. 2

Fig. 1. PMR spectrum of the cation (Ia) at −70°C. (For the assignment of the signals, see the text.)

Fig. 2. PMR spectrum of the cation (Ic) at −70°C. (X = Br, for the assignment of the signals, see the text.)

Its relative stability is promoted by the delocalization of the positive charge of the protonated heterocycle with the participation of the benzene ring. It could be supposed that the delocalization would not be so effective in the presence of the two identical heterocycles in the molecule, and this hinders protonation of the vinyl group.

The reaction of compound (I) with the superacidic system HSO_3F + SbF_5 (at −70°C) gives the dication (Ia).



In the PMR spectrum of the dication (Ia) the α-protonated pyrrole ring corresponds to signals at 5.54 (5-CH_2), 7.42 (d, 3-H), and 8.25 ppm (d, 4-H); $^3J_{34}$ = 6.0 Hz. The vinyl group attached to this ring gives signals at 7.36 (C-H), 6.35 (A-H), and 5.83 ppm (B-H). The β-protonated ring corresponds to the following signals: 4.75 (4-CH_2); 7.30 (d, 3-H) and 7.71 ppm (d, 5-H); $^4J_{35}$ = 3.0 Hz. The protons of the vinyl group corresponding to this ring resonate at 7.36 (C-H) and 6.13 ppm (A-H, B-H). The signals for the protons of the vinyl groups were assigned by double resonance and published data [6].

It should be noted that the observation of stable σ complexes with a β-protonated pyrrole ring is a fairly rare phenomenon. It has only been observed before for 2,5-disubstituted pyrroles in equilibrium with α-protonation, where the latter as a thermodynamically controlled process predominated [7].

The formation of the cation (Ia) and the unsymmetrical nature of the protonated pyrrole rings can be explained by the fact that in the intermediate formed at the first stage of the reaction (a cation with a protonated α position in one of the pyrrole rings) the second ring is deactivated with respect to attack by the proton:

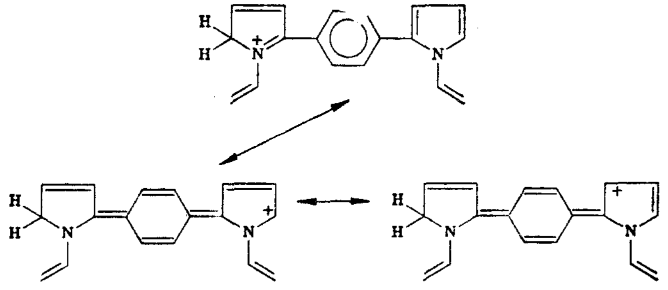
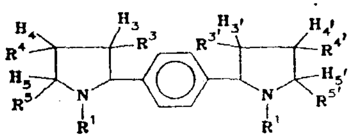


TABLE 1. PMR Spectra of the Cations of Compound (I)



Cation	R^1 ($R^{1'}$)	R^3 ($R^{3'}$)	R^4 ($R^{4'}$)	R^5 ($R^{5'}$)	Chemical shifts, δ, ppm, J, Hz						
					R^1 ($R^{1'}$)	3-H (R^3)	4-H (R^4)	5-H (R^5)	3'-H ($R^{3'}$)	4'-H ($R^{4'}$)	5'-H ($R^{5'}$)
Ia	CH=CH$_2$	—	—	H	6,35 (H$_A$); 5,83 (H$_B$); 7,35 (H$_C$)	7,42 $^3J_{34}$=6,0	8,25	5,54	7,30 $^4J_{35}$=3,0	4,75	7,71
	(CH=CH$_2$)	(−)	(H)	(−)	(6,13 (H$_A$, H$_B$); 7,36 (H$_C$))						
Ib	CHBrCH$_3$	—	—	H	6,61 (CH)	7,44	8,49	5,64	7,44	8,49	5,64
	(CHBrCH$_3$)	(−)	(−)	(H)	2,40 (CH$_3$)						
Ic	CHBrCH$_3$	H	Br	H	6,51 (CH)	4,05 $^2J_{3R^3}$=20,5	5,22	4,96 $^2J_{5R^5}$=14,6	4,05	5,22	4,96
	(CHBrCH$_3$)	(H)	(Br)	(H)	2,28 (CH$_3$)	(5,16)	(−)	(5,30)	(5,16)	(−)	(5,30)

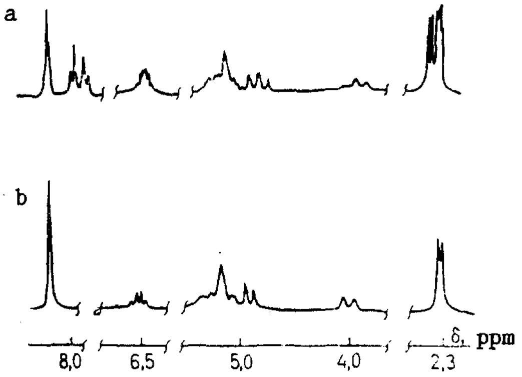
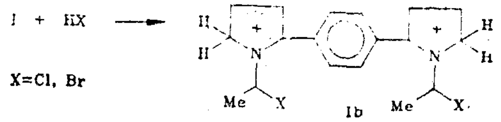


Fig. 3. PMR spectrum of the cation (Ic). (For the assignment of the signals, see Table 1.) a) At −40°C; b) 0°C.

As seen from the presented resonance structures, the most likely protonation center in this particle is still $C_{(4)}$ of the second heterocycle, where the proton adds at the second stage of the reaction.

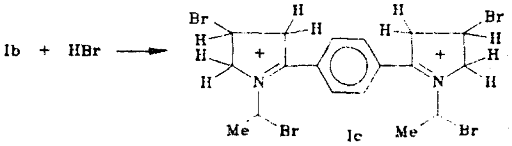
The reaction of compound (I) with HCl and HBr takes place differently. The hydrogen halide adds to the vinyl groups, and both heterocycles are protonated at the α position:



Ib

In the PMR spectrum of the protonation product (Ib) (X = Br) (Fig. 2, Table 1) α-protonation is indicated by the presence of signals at 5.64 (5-CH_2), 7.44 (d, 3-H), and 8.49 ppm (d, $^3J_{34}$ = 5.3 Hz, 4-H). The $CHBrCH_3$ fragment is represented by a quartet at 6.61 and a doublet at 2.40 ppm. Such a direction of protonation demonstrates the relative independence of the pyrrole rings in this case. A possible reason for this is the steric hindrances to coplanarity of the molecule, created by the bulky α-halogenoethyl substituents at the nitrogen atoms.

The formation of the dication (Ib) in the reaction of compound (I) with HBr at −70°C is the first stage of the process. At higher temperature (−40°C) another HBr molecule adds to the protonated pyrrole rings with the formation of the dication (Ic):

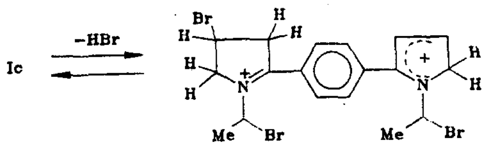


Ic

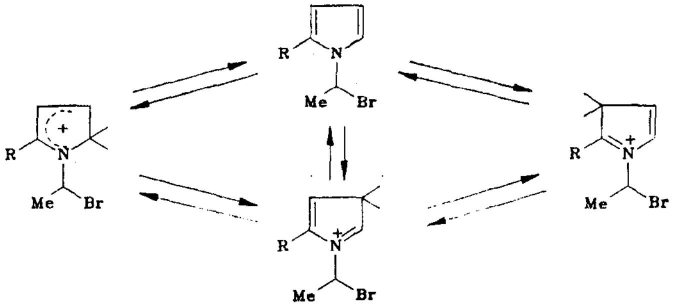
The PMR spectrum of the dication (Ic) (Fig. 3) contains signals for the five-spin system of the protons of the substituted 4-bromo-4,5-dihydropyrrolium ring. (The spectral parameters of this system, similar to those we observed earlier [2], are given in Table 1.) The identity of the two substituents in the benzene ring in the cations (Ib) and (Ic) is confirmed by the singlet resonance of its protons (Figs. 2 and 3a).

The spectrum of the dication (Ic) depends reversibly on temperature. Heating of the sample to −20°C and above (Fig. 3b) leads to the appearance of new signals. In the aromatic region there is a characteristic A_2B_2 system for a para-substituted phenyl with different substituents (chemical shifts 7.97 and 8.10 ppm, $^3J_{AB}$ = 8.4 Hz). Two new doublets with the same spin—spin coupling constants (chemical shifts 4.87 and 3.96 ppm) appear alongside the doublets of the 3-H and 5-H protons. Two doublets (2.30 and 2.40 ppm) appear in the region of the methyl protons. The shift of the last signal corresponds exactly to the shift of the protons of the CH_3 group in the spectrum of the cation (Ib).

Such a change in the spectrum indicates that the following equilibrium exists:



The absence of signals for the protonated pyrrole ring in the spectrum is explained by the fact that fast intermolecular proton transfer on the NMR scale, in which all the hydrogen atoms of this ring participate, occurs at these temperatures:



As a result the signals of all the ring protons merge with the signal of HBr (−2.5 ppm, not shown in the figure). We observed similar exchange of a proton between a cation and the medium earlier [8] during the protonation of 1-vinylpyrroles with hydrogen chloride.

EXPERIMENTAL

The PMR spectra were obtained on Tesla BS-567A (100 MHz) and Bruker WR-200 SY spectrometers. The internal standard was the tetramethylammonium cation [for (Ia)] and TMS [for (Ib, c)].

1,4-Bis(1-vinyl-2-pyrrolyl)benzene was obtained by analogy with [9].

The cations were generated by mixing 0.02 g of the substrate with the $HSO_3F + SbF_5$ (5:1, molar) solution in SO_2ClF in the NMR sample tube at −70°C or by passing dry hydrogen halide into a 0.5 M solution of compounds (I) in CD_2Cl_2 at −70°C.

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