PROTONATED FORMS OF 2-(2-FURYL)PYRROLES AND THEIR INTERCONVERSIONS

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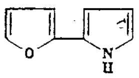
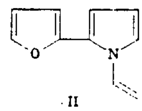
It was shown by ^1H NMR spectroscopy that 2-(5-R^1-2-furyl)-3-R^2-1-R^1-pyrroles (R^1 = H, Me; R^2 = H, Me; R^3 = H, Et, CH=CH$_2$) are protonated by acids (HSO_3F, HCO_2CF_3, HCl, HBr) either at the $C_{(5)}$ atom of the pyrrole ring or at the $C_{(5')}$ atom of the furan ring, depending on the conditions. The energies of formation (ΔH), the charges, and the partial electron densities of the boundary orbitals of 2-(2-furyl)pyrrole (I) and its protonated forms (IA and IB) were calculated by the MNDO method. The calculated ΔH values for the IA and IB forms are in agreement with their experimental ratio. According to the calculated reactivity indexes, the protonation of pyrrole is subject to orbital control and may include the prior formation of less stable protonated forms.

The reactivities of the simplest five-membered aromatic heterocycles – pyrrole, furan, and thiophene – in electrophilic reactions have been studied quite thoroughly [1, 2]. It is known that they decrease in the order pyrrole >> furan > thiophene. For example, the rate of acid-catalyzed isotope exchange of hydrogen for pyrrole is six orders of magnitude higher than for furan [3]. With respect to the stabilities of the protonated forms, pyrrole derivatives also, as a rule, significantly surpass furan compounds. Stable furanium cations have been observed only in superacids [4] (ring cleavage with subsequent resinification occurs in the presence of ordinary acids [2]), while the protonated forms of pyrrole derivatives are also quite stable in a less acidic medium [5-8]. The chemistry of protonated aromatic systems continues to be the subject of intensive development [9].

Directly bonded five-membered aromatic heterocycles are currently attracting more and more attention not only as synthetic intermediates with unexpected possibilities [10], models of porphyrins, and electrically conducting polymers (polypyrroles, polythiophenes) [11-13] but also as convenient subjects for the study of the mutual effect of heteroaromatic systems, particularly in the course of electrophilic reactions in which the effects of interannular stabilizing p–π and π–π conjugation should be most pronounced. In this connection we used ^1H NMR spectroscopy to investigate the protonation of the following 2-(2-furyl)pyrroles and their N-vinyl derivatives:



I



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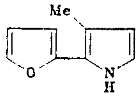
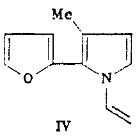
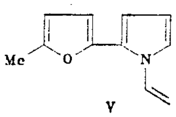


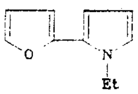
III



IV



V



VI

Experiments showed that at –80°C all of the pyrroles, regardless of the nature of the acid, are protonated at the $C_{(5)}$ atom of the pyrrole ring; the vinyl group is retained when R^3 = C=CH$_2$:

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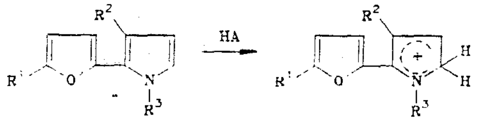
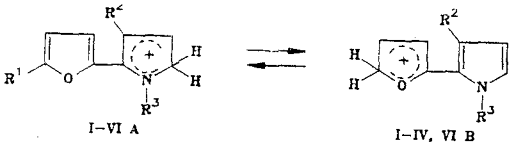


R^1=H, Me; R^2=H, Me; R^3=H, $CH{=}CH_2$, Et; A=SO_3F, CF_3CO_2, Cl, Br

An increase in the temperature of the sample to 0°C (in the case of trifluoroacetic acid) and to ~20°C (in the case of fluorosulfonic acid) does not change the form of the spectra of the protonated forms of all of the investigated compounds.

The reaction of pyrroles I-IV with hydrogen halides (HCl and HBr) at −30°C leads to the formation of a mixture of pyrrolium (A) and furanium (B) cations. The same thing is also observed when the temperature of the sample is raised gradually from −80°C to −30°C; 2-(5-methyl-2-furyl)-1-vinylpyrrole (V) constitutes an exception. Thus, at least formally, proton transfer from the protonated pyrrole ring to the furan ring occurs (in the case of vinyl compounds the addition of the hydrogen halide to the double bond occurs):



I–VI A

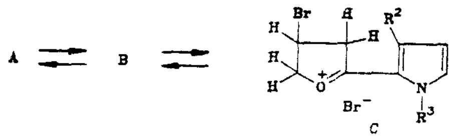
I–IV, VI B

IA $R^1=R^2=R^3$=H; **IIA** $R^1=R^2$=H, R^3=CHAMe; **IIIA** $R^1=R^3$=H, R^2=Me; **IVA** R^1=H, R^2=Me, R^3=CHAMe; **VA** R^1=Me, R^2=H, R^3=CHAMe; **VIA** $R^1=R^2$=H, R^3=Et
IB $R^1=R^2=R^3$=H; **IIB** $R^1=R^2$=H, R^3=CHAMe; **IIIB** $R^1=R^3$=H, R^2=Me; **IVB** R^1=H, R^2=Me, R^3=CHAMe; **VIB** $R^1=R^2$=H, R^3=Et

The rates of establishment of the $A \rightleftarrows B$ equilibrium and addition of HHal to the vinyl group are lower, the greater the excess amount of HHal contained in solution. The ratio of the concentrations of cations A and B, within the limits of the experimental accuracy, does not depend on the structure of the radical attached to the nitrogen atom (R^3) and is ~1:1 (in the case of protonation with HCl) and ~2:1 (in the reaction with HBr) for the I, II, and VI molecules. The pyrrolium cation predominates (~2:1 in the case of HCl) for the 3-methyl derivatives III and IV.

Cation VA, in the molecule of which both α positions of the furan ring are occupied, adds hydrogen halide only to the double bond on heating from −80°C to −30°C.

The reaction of furylpyrroles I-IV and VI with HBr is not confined to this. Further heating of the samples (to 0°C) leads to a gradual decrease in the spectra of the signals of the cations of the A and B groups (their intensities decrease synchronously, which confirms the existence of the $A \rightleftarrows B$ equilibrium) and to the appearance of signals of new cations − 2-(2-pyrrolyl)-4-bromo-4,5-dihydrofuranium ions (C) − which are formed as a result of the addition of a molecule of HBr to the protonated furan ring of cations B:



C

IC $R^2=R^3$=H; **IIC** R^2=H, R^3=CHBrMe; **IIIC** R^2=Me, R^3=H; **IVC** R^2=Me, R^3=CHBrMe;
VIC R^2=H, R^3=Et

If one continues to raise the temperature, at ~20°C furanium cations C are converted completely to 4,5-dihydropyrrolium cations D − 2-(2-furyl)-4-bromo-4,5-dihydropyrrolium bromides − with retroaromatization of the furan part of the molecule. It is apparent that this occurs through a step involving dehydrobromination of cation C to cation B and its subsequent deprotonation to a neutral molecule, i.e., ultimately through cation A.* (Scheme, top, following page.)

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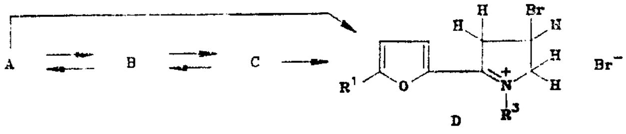
*It must be noted that the temperature ranges over which the above-described transformations occur are not characteristic and overlap in most experiments; the sequence of these processes remains unchanged. The greater the amount of HBr contained in the solution, the slower the transformations (and the higher the temperature of their complete accomplishment).



IID R^1=H, R^3=CHBrMe; **VD** R^1=Me, R^3=CHBrMe

Cations D are formed only from II and V. In the case of 1-vinyl-2-(5-methyl-2-furyl)-pyrrole (V) the steps involved in the formation of cations B and C are not detected, and pyrrolium cation VA is the direct precursor of cation VD. Dihydrofuranium cations IC, IIIC, IVC, and VIC, respectively, remain the final products of the reaction with HBr in the case of unsubstituted 2-(2-furyl)pyrrole (I), 3-methyl-substituted III and IV, and 1-ethyl-2-(2-furyl)-pyrrole (VI).

When the reaction with hydrogen halides is carried out in the presence of $AlCl_3$ or $AlBr_3$, the rates of all of the examined processes decrease sharply, and cations A are the principal reaction products in these case. The addition of a certain amount of Me_4NBr to a sample of 2-(2-furyl)-1-vinylpyrrole (II), on the other hand, facilitates the reaction with HBr, which is manifested by a decrease of ~15-20°C in the temperature of the formation of cations C and D.

All of the indicated transformations are detected reliably by ^1H NMR spectroscopy. The spectra of the cations with a protonated pyrrole ring generated by the reaction of the furylpyrroles with HSO_3F, CF_3COOH, and hydrogen halides at −80°C (Fig. 1, Table 1) contain a signal of a 5-CH_2 group with a chemical shift of 4.97-5.38 ppm and either two doublets at 7.20-7.36 ppm and 7.74-8.04 ppm with spin-spin coupling constant (SSCC) $^3J \approx 6$ Hz [$H_{(3)}$ and $H_{(4)}$ − cations from I, II, and V) or a singlet at 7.60-7.62 ppm [$H_{(4)}$ − cations from III and IV]. The protons of the vinyl group (in the cations from II, IV, and V) experience greater weak-field shifts (to 1.5 ppm) as compared with the unprotonated molecules [10]. The $^3J_{AC}$ and $^3J_{BC}$ vicinal SSCC do not change relative to the corresponding values for N-vinylpyrroles (~15 and ~9 Hz, respectively), but the geminal SSCC increase significantly (from 0.8 to 3.0 Hz). All of this indicates marked weakening of the p—π conjugation in the N-vinyl group [15].

The spectra of pyrrolium cations that have added a molecule of hydrogen halide to the vinyl group have an important peculiarity: the protons of the 5-CH_2 group in them are nonequivalent because of the presence of an asymmetric carbon atom in the α-haloalkyl radical (Fig. 2) and have an unusually large (for geminal coupling) constant ^2J = 27 Hz.

Evidence for the structures of cations IB-IVB is provided by the presence in the spectra (Fig. 2, Table 2) of signals of a protonated furan ring (δ, ppm): 5.9-6.16 br s (5'-CH_2), 7.35-7.52 dt [$H_{(3')}$, ^3J = 6 Hz, ^4J = 1.5 Hz], 8.28-8.32 dt [$H_{(4')}$, ^3J = 1.0 Hz] [3].

The spectra of cations of the C and D groups (Figs. 3-5, Tables 3 and 4) at 3.5-6.0 ppm contain signals of a five-spin system of protons corresponding to protonated 4-bromo-4,5-dihydropyrrole and -furan rings. In the spectra of cations IIC and IVC, the precursors of which are 1-vinylpyrroles, all of the signals are doubled (Fig. 3); this may be due to both the existence of diastereomerism due to two asymmetric centers and to the retarded character of rotation of the heterorings about the $C_{(2)}$(furyl)—$C_{(2)}$(pyrrolyl) bond:

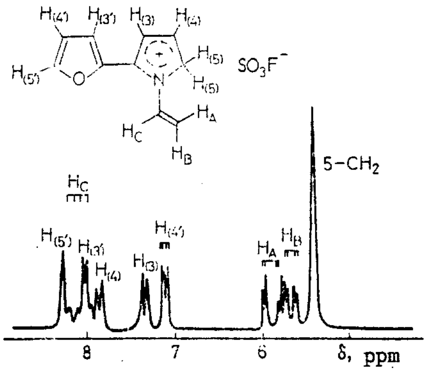
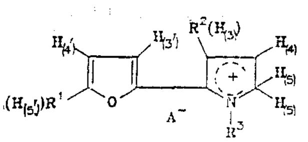
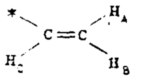


Fig. 1. ^1H NMR spectrum (100 MHz, CD_2Cl_2, −30°C) of 1-vinyl-2-(2-furyl)pyrrolium fluorosulfonate.

TABLE 1. ^1H Chemical Shifts (δ, ppm) of Cations

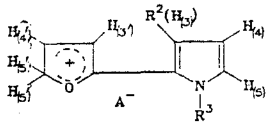


R^1	R^2	R^3	A^-	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	$H_{(3')}$	$H_{(4')}$	$H_{(5')}$	R^i
H	H	H	SO_3F	7,29	8,02	5,15	7,87	6,97	8,15	—
H	H	$CH=CH_2$*	SO_3F	7,30	7,83	5,34	7,98	7,04	8,24	5,77 (H_B), 5,99 (H_A), 8,03 (H_C)
H	Me	H	SO_3F	—	7,62	4,97	7,85	6,92	8,12	2,44 (Me)
H	Me	$CH=CH_2$*	SO_3F	—	7,60	5,18	8,00	7,08	8,10	5,60 (H_B), 5,78 (H_A), 7,98 (H_C), 2,45 (Me)
Me	H	$CH=CH_2$*	Cl	7,20	7,74	5,26	7,94	6,74	—	5,48 (H_B), 5,67 (H_A), 8,09 (H_C), 2,67 (Me)
H	H	CHClMe	Cl	7,35	8,02	5,23** 5,15	8,14	7,10	8,32	7,16 (CH), 2,24 (Me)
H	H	CHBrMe	Br	7,36	8,04	5,38 5,03**	8,19	7,12	8,38	7,27 (CH), 2,36 (Me)
H	Me	CHClMe	Cl	—	7,73	5,16	8,08	7,08	8,26	7,12 (CH), 2,14 (Me)
Me	H	CHClMe	Cl	7,26	7,86	5,20	8,05	6,76	—	7,07 (CH), 2,68 (Me), 2,17 (CHMe)
Me	H	CHBrMe	Br	7,31	7,94	5,32	8,15	6,80	—	7,26 (CH), 2,69 (Me), 2,37 (CHMe)
H	H	Et	Br	7,35	7,87	5,18	7,98	7,01	8,20	4,50 (CH_2), 1,59 (Me)

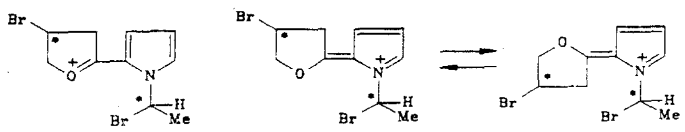


**An AB system of two nonequivalent protons ($^2J_{AB}$ = 27 Hz). It can be observed only at 200 MHz.

TABLE 2. Chemical Shifts (δ, ppm of Cations



Cation	R^2	R^3	$H_{(3')}$	$H_{(4')}$	$H_{(5')}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	R^i
IB	H	H	7,35	8,28	6,01	7,94	6,87	8,01	—
IIB	H	CHClMe	7,52	8,32	6,16	8,05	6,83	8,27	6,83 (CH), 2,18 (Me)
IIB	H	CHBrMe	7,58	8,38	6,21	8,04	6,95	8,30	7,08 (CH), 2,43 (Me)
IIIB	Me	H	7,60	8,15	5,90	—	6,63	7,90	2,57 (Me)
IVB	Me	CHClMe	7,49	8,32	6,00	—	6,70	8,10	6,94 (CH), 2,67 (Me), 2,19 (CHMe)



Doubling of the signals vanishes when the 1-bromoethyl radical is replaced by an ethyl radical (cation VIC) (Fig. 4).

A substantial difference in the spectra of cations IID and VD from the spectra of the cations of the C group is the absence of doubling of the signals, despite the fact that, as before, two asymmetrical centers remain in the molecules (Fig. 5).* The $^2J_{AB}$ constants differ appreciably (11 Hz for cations of the C group and 14 Hz for cations of the D group). The

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*When the temperature is decreased to −50°C, the form of the spectrum does not change after accomplishment of the C → D transition.

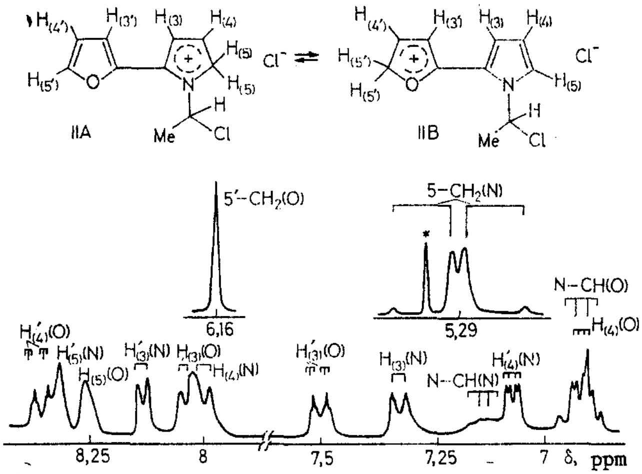


Fig. 2. ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, −30°C) of an equilibrium mixture of cations IIA $\rightleftarrows$ IIB: 1-(1-chloroethyl)-2-(2-furyl)pyrrolium and 2-[1-(1-chloroethyl)-2-pyrrolyl]furanium chlorides. The O and N indexes pertain, respectively, to the protonated furan and pyrrole rings. Here and subsequently, the signals of the residual protons of the solvent are designated by an asterisk.

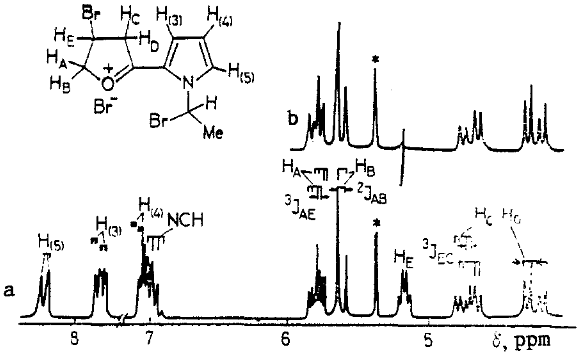


Fig. 3. ^{1}H NMR spectrum (200 MHz, CD_2Cl_2, 0°C) of 2-[1-(1-bromoethyl)-2-pyrrolyl]-4-bromo-4,5-dihydrofuranium bromide (IIC): a) monoresonance; b) double resonance with irradiation of the H_E proton.

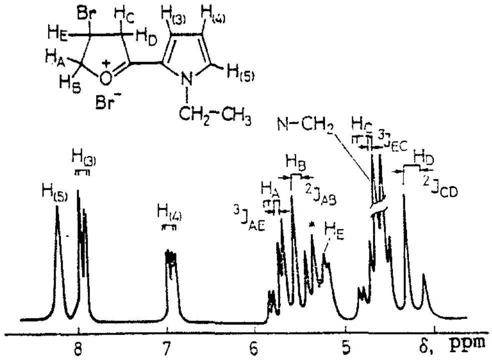
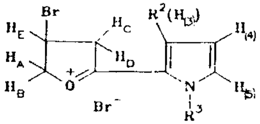


Fig. 4. ^{1}H NMR spectrum (100 MHz, CD_2Cl_2, 0°C) of 2-(1-ethyl-2-pyrrolyl)-4-bromo-4,5-dihydrofuranium bromide (VIC).

TABLE 3. Parameters of the ^{1}H NMR Spectra of Cations



Cation	R^2	R^3	Chemical shifts, δ, ppm								SSCC, Hz			
			H_A	H_B	H_C	H_D	H_E	R^2 $(H_{(3)})$	$H_{(4)}$	$H_{(5)}$	H_A, H_B	H_A, H_E	H_C, H_D	H_C, H_E
IC	H	H	5,58	5,48	4,52	4,12	5,11	7,88	6,92	8,25	11,7	4,5	21,0	—
IIC*	H	CHBrMe	5,72	5,57	4,65	4,21	5,12	8,04	6,97	8,43	12,0	4,2	21,0	6,5
			5,77	5,58	4,69	4,25	5,14	8,08	7,00	8,49				
IVC*	Me	CHBrMe	5,67	5,49	4,62	4,10	5,21	2,57	6,81	8,33	—	—	—	—
			5,69	5,50	4,66	4,14	5,23	2,57	6,83	8,39				
VIC	H	Et	5,68	5,43	4,72	4,10	5,13	7,85	6,84	8,14	11,7	4,2	20,2	5,6

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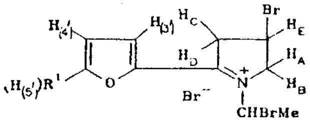
*Doubling of all signals is observed.

TABLE 4. Parameters of the ^{1}H NMR Spectra of Cations



Cation	R^1	Chemical shifts, δ, ppm									
		H_A	H_B	H_C	H_D	H_E	R^1 $(H_{(5')})$	$H_{(3')}$	$H_{(4')}$	CH	Me
IID	H	5,17*	4,70	3,97**	4,78	5,12	8,35	8,09	7,09	7,29	2,27
VD	Me	5,12	4,60	3,86	4,77	5,07	2,73	8,05	6,82	7,24	2,28

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*J_{AB} = 14.5 Hz; J_{AE} = 5.0 Hz.
**J_{CD} = 20.5 Hz; J_{CE} = 6.5 Hz.

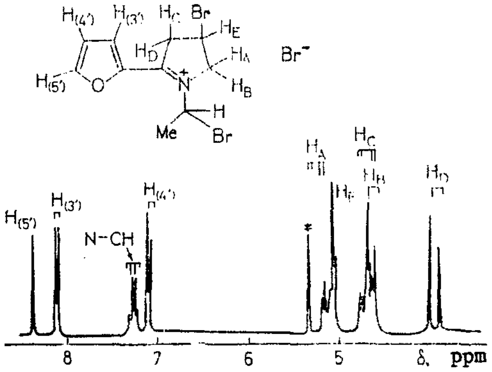


Fig. 5. ^1H NMR spectrum (200 MHz, CD_2Cl_2, 20°C) of 1-(1-bromoethyl)-2-furyl-4-bromo-4,5-dihydropyrrolium bromide (IID).

spectra of such cations have not been described in the literature, but one should expect precisely this difference for the protons of the CH_2 group adjacent to oxygen and nitrogen [16].

It is apparent from the information set forth above that the 2-(2-furyl)pyrrolium cations that are formed initially as a result of α protonation of the pyrrole ring undergo extremely different subsequent transformations with an increase in the temperature, depending on the nature of the protonating acid. The chief reason for this is undoubtedly the increased stabilities of these cations in HSO_3F and CF_3COOH and the substantially lower stabilities in HCl and HBr.

It is known [9, 17] that the stabilities of carbonium ions are determined not only by their structure (the nature of the substituents) but also by the acidity and nucleophilicity of the medium. In the case of HSO_3F, because of the superacid character of the medium, the equilibrium is shifted to favor the cation, and the nature of the substituents in the pyrrole ring therefore does not play a substantial role in reversible processes that occur through a deprotonation step. The manifestation of the effect of substituents on such processes should evidently be expected in a less acidic medium.

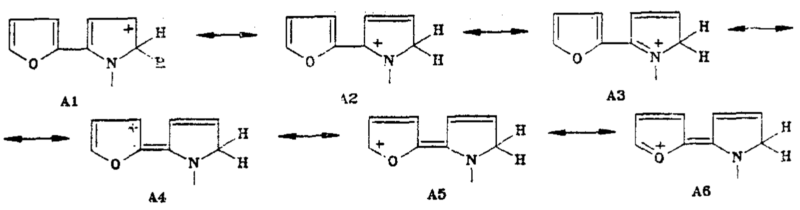
Approximately identical acidities of CF_3COOH, HCl, and HBr in chloroform were established in [18]. The quite high stability of 1-vinyl-2-(2-furyl)pyrrolium cations in trifluoroacetic acid (in contrast to the 2-alkyl- and 2-phenylvinylpyrrolium analogs, which undergo dimerization in this medium, the latter at a substantially higher rate [7]) is due to the effect of the furyl substituent. The dependence of the rates of dimerization of the 1-vinylpyrrolium cations on the substituents attached to the $C_{(2)}$ atom (Ph > Me >> 2-furyl) correlates qualitatively with the values of their σ_p^+ electrophilic constants (0.08, −0.26, and −0.86, respectively).

As a result of the presence in solution of nucleophilic Cl^- and Br^- anions, as well as HCl_2^- and HBr_2^- anions [19], which are capable of detaching a proton from the pyrrolium σ complex, the protonation reaction becomes virtually reversible. Under these conditions the direction of attack by the proton on the furylpyrrole molecule should be determined by the activation barriers (kinetic control) and the relative stabilities of the resulting cations (thermodynamic control). In conformity with the σ_p^+ values (−0.86 for the 2-furyl substituent and −1.7 for the 2-pyrrolyl substituent [20]) it might be assumed that stabilization of the furanium cation by the 2-pyrrolyl radical is realized more effectively than stabilization of the pyrrolium cation by the 2-furyl radical.

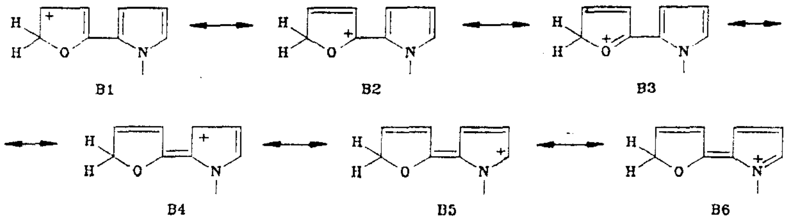
Thus, selective protonation of the pyrrole ring at a low temperature (−80°C) can be regarded as a kinetic result that leads to a thermodynamic nonequilibrium state with preponderance of the pyrrolium cations (A), the energies of which are comparable to the energies of their furanium isomers (B). With an increase in the temperature (−30°C) the system rapidly reaches equilibrium, and the concentrations of the isomeric cations (A and B) are equalized in conformity with their energies (Fig. 6).

An examination of the mesomeric canonical structures of cations A and B (Schemes 1 and 2) makes it possible, on a qualitative level, to understand why they have close (if not equal) energies, although the furanium ions (structures B1-B3) in themselves are less stable than the pyrrolium ions (structures A1-A3).

Scheme 1



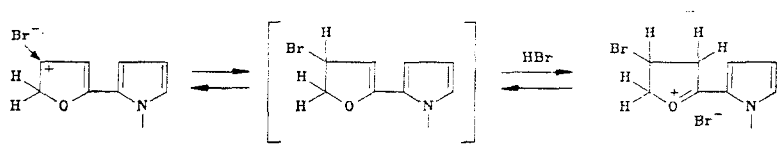
Scheme 2



As a consequence of the greater (than in the case of oxygen) ability of the nitrogen atom to stabilize an adjacent positive charge, the inclusion of a pyrrolyl radical in stabilization actually leads to charge transfer to the pyrrole ring (structures B4-B6). On the other hand, protonation of the pyrrole ring includes in the stabilization of the cation a 2-furyl radical with transfer of a significant part of the charge to the furan ring (structures A4-A6). In other words, as much as pyrrolium cation A is less stabilized by an adjacent furan ring, furanium cation B is more stabilized by an adjacent pyrrole ring. Within the framework of this interpretation the effect of a 3-methyl group in the pyrrole ring (an increase in the fraction of ion A) is also explainable: this group additionally stabilizes the pyrrolium ion via hyperconjugation and inductive mechanisms and also decreases the effectiveness of π—π conjugation between the rings due to a decrease in their coplanarity. One might predict that the introduction of a bulky substituent into the 3 position of the furan ring (with retention of the substituent in the 3 position of the pyrrole ring) would lead to further turning of the planes of the rings relative to one another and to restoration of the customary hierarchy pyrrole >> furan in reactivity with respect to the proton.*

The addition of $AlCl_3$ or $AlBr_3$ markedly increases the acidity of the medium and decreases its nucleophilicity due to the formation of Hal_2X_7 (X = Cl, Br) complex acids. As a consequence of this, not only is proton transfer hindered but so is the addition of hydrogen halide to the vinyl group. This fact makes it possible to also exclude a diprotonated form (protonation simultaneously in the pyrrole and furan rings) from consideration as an intermediate particle between the pyrrolium and furanium σ complexes, since in a more acidic medium its percentage (if it is formed) should increase.

The formation of 2-(2-pyrrolyl)-4-bromo-4,5-dihydrofuranium bromide occurs as a result of attack by Br^- on the ($C_{4'}$) atom and subsequent protonation of the intermediate dihydrofuran:



This sort of occurrence of the process is confirmed by the fact that in the presence of $AlBr_3$, which ties up the bromide ion in the Al_2Br^{7-} complex anion, this reaction is hindered markedly and also by the fact that the introduction of an additional amount of bromide ions in the form of Me_4NBr, on the other hand, accelerates the reaction. In the case of the reaction with HCl, attack by the less nucleophilic chloride ion does not occur at all.

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*This is confirmed by quantum-chemical calculations, to which a special communication will be devoted.

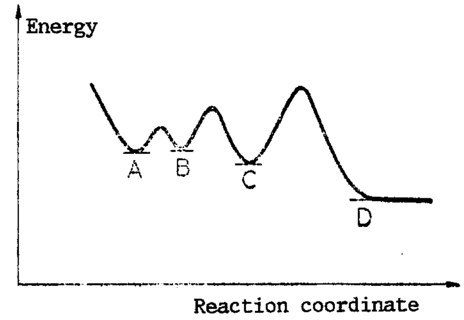
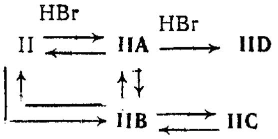


Fig. 6. Potential curve of the following reaction sequence:



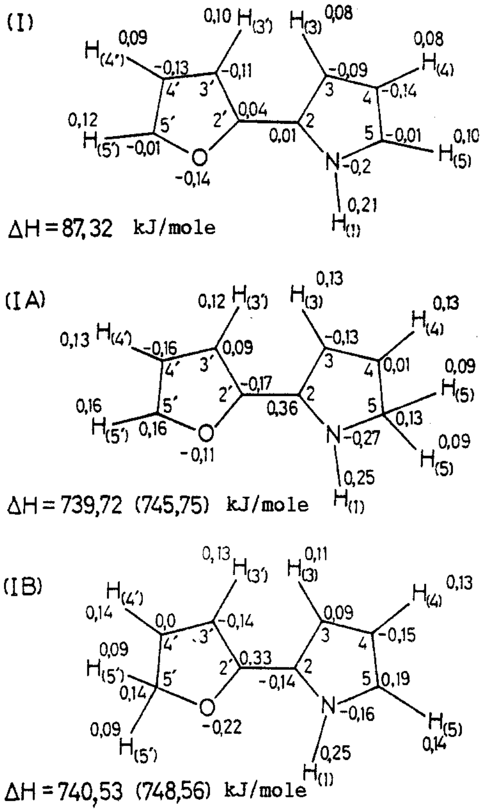
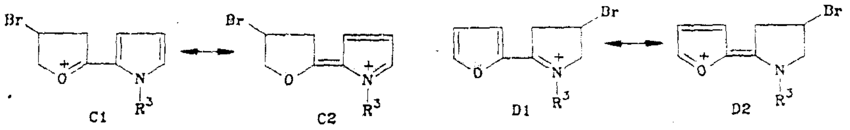


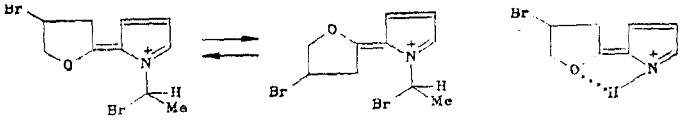
Fig. 7. Total charges and energies of formation (ΔH) of 2-(2-furyl)pyrrole (I) and its protonated forms: IA) addition of the proton to the pyrrole ring; IB) addition of the proton to the furan ring. The ΔH values for the anti conformations (the dihedral angles of the syn conformations were taken for them) are presented in parentheses under the diagrams of IA and IB.

As we have already noted, one of the reasons for doubling of the signals of 4,5-dihydrofuranium cations may be the retarded character of the rotation of the heterorings relative to one another. In cations C this rotation should be more hindered than in cations D because of the stronger conjugation of the pyrrole ring with the adjacent cationic center:


C1 C2 D1 D2

In other words, cations C are closer to doubly bonded canonical structure C2, while cations D are closer to singly bonded structure D1.

Thus the syn and anti isomers (relative to the mutual orientation of the heteroatoms) for cations C should be more stable; if the anti isomer may be quite populated when R^3 = CHBrMe as a consequence of repulsion of the unshared electron pairs of the oxygen and bromine atoms, the probability of the existence of primarily the syn isomer due to the formation of an O•••H hydrogen bond is high when R^3 = H.



On the other hand, the fact that in the reaction of HBr and 1-ethyl-2-(2-furyl)pyrrole (VI) the parameters (chemical shifts and SSCC) of the spectrum of the resulting cation VIC are extremely close to those for ions IIC and IVC (Table 3) but doubling of the signals is absent (Fig. 4) may speak in favor of the diastereomeric nonequivalence of the protons. However, the absence of doubling of the signals in the spectra of the cations of the D group remains difficult to explain in this case.

Particular attention should be directed to the conversion of cations C to D, which leads to rearomatization of the furan ring and to migration of the covalently bonded bromine atom from the furan ring to the pyrrole ring. This fact can be interpreted in the following way: for kinetic reasons (the lower barrier) the 4 position of the furanium cations (B) becomes the site of initial attack by the Br^- anion. However, cations D should be thermodynamically more stable as a consequence of the greater stabilization of the positive charge by the nitrogen atom as compared with the oxygen atom and the somewhat greater stability of the furan aromatic system. Consequently, cations C can be regarded as kinetic products that, upon further heating, are converted to the less energy-rich cations D:

$$A \rightleftharpoons B \rightleftharpoons C \rightarrow D.$$

The energy profile of the reaction of 1-vinyl-2-(2-furyl)pyrroles with HBr is depicted qualitatively in Fig. 6.

The absence of the C → D transition for unsubstituted 2-(2-furyl)pyrrole (I) and for 1-ethyl-2-(2-furyl)pyrrole (VI) is explained qualitatively well by the decreased electrophilicity of the pyrrole ring in cations IA and VIA as a consequence of the higher electron-acceptor character of the CHBrMe radical as compared with hydrogen and the ethyl group.

In order to make a theoretical analysis of the observed transformations we carried out quantum-chemical calculations by the MNDO method of 2-(2-furyl)pyrrole (I) and its protonated forms (IA in the case of protonation in the pyrrole ring and IB in the case of protonation in the furan ring) with complete optimization of the geometry (bond lengths and bond and dihedral angles). The calculated values of the total charges and energies of formation (ΔH) are presented in the molecular diagrams in Fig. 7. The reactivity indexes (boundary electron densities) are given in Tables 5-7.

In comparing the charges and boundary electron densities of the highest occupied molecular orbital (HOMO) on the atoms of the unprotonated I molecule (Fig. 7, Table 5) with the observed result of primary protonation (addition of a proton to the $C_{(5)}$ atom of the pyrrole ring) it might be concluded that the regiospecificity of the first step of the reaction is determined not by the charge distribution (the charges on the $C_{(3)}$, $C_{(4)}$, $C_{(3')}$, and $C_{(4')}$ atoms are significantly higher than the charge on the $C_{(5)}$ atom) but by the partial electron densities of the HOMO. In fact, as seen from Table 5, the contributions of the atomic orbitals (with respect to their character these are the p_z orbitals) to the HOMO are greater for the $C_{(2)}$ and $C_{(5)}$ positions of the pyrrole ring (0.21) and substantially exceed the partial

TABLE 5. Breakdown of the Boundary MO of 2-(2-Furyl)-pyrrole (I) with respect to the Atomic Orbitals*

MO	Energy of the MO, eV	Squares of the contributions of the p_z AO to the MO									
		$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	N	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	O
HOMO	−8,12	0,21	0,12	0,06	0,21	—	0,10	0,12	0,03	0,12	—
LVMO	0,08	0,08	0,12	—	0,09	0,07	0,20	0,15	0,02	0,15	0,08

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*The contributions less than 0.01 were disregarded.

TABLE 6. Breakdown of the Boundary MO of Protonated (in the pyrrole ring) 2-(2-Furyl)pyrrole (I) with respect to the Atomic Orbitals*

MO	Energy of the MO, eV	Squares of the contributions of the AO to the MO									
		p_z $C_{(2)}$	p_z $C_{(3)}$	p_z $C_{(4)}$	1s $H_{(5)}$	1s $H_{(5)}$	p_z N	p_z $C_{(2')}$	p_z $C_{(3')}$	p_z $C_{(5')}$	p_z O
HOMO	−13,51	0,01	0,03	0,03	0,01	0,01	0,14	0,37	0,16	0,11	0,03
LVMO	−5,92	0,37	0,01	0,15	0,02	0,02	—	—	0,11	0,14	0,06

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*The contributions less than 0.01 were disregarded.

TABLE 7. Breakdown of the Boundary MO of Protonated (in the furan ring) 2-(2-Furyl)pyrrole (I) with respect to the Atomic Orbitals*

MO	Energy of the MO, eV	Squares of the contributions of the AO to the MO									
		p_z $C_{(2)}$	p_z $C_{(3)}$	p_z $C_{(4)}$	p_z $C_{(5)}$	p_z N	p_z $C_{(2')}$	p_z $C_{(3')}$	p_z $C_{(4')}$	1s $H_{(5')}$	1s $H_{(5')}$	p_z O
HOMO	−13,48	0,36	—	0,16	0,19	—	0,05	0,08	0,08	0,01	0,01	0,05
LVMO	−6,02	0,01	0,16	0,02	0,17	0,05	0,36	—	0,14	0,01	0,01	0,07

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*The contributions less than 0.01 were disregarded.

electron densities of the analogous $C_{(2')}$ and $C_{(5')}$ positions of the furan ring (0.10 and 0.12 respectively). Since the $C_{(2)}$ atom is sterically hindered, the proton should attack primarily the $C_{(5)}$ position of the pyrrole ring to form ion IA. This is the actual experimental result of primary (kinetic) protonation of the I molecule. Its correspondence to orbital control is suggested by the participation in protonation of milder electrophiles than the proton: undissociated acid molecules, thermodynamically unstable products of primary (kinetic) protonation of the I molecule in accordance with the charge distribution.

What is the reason for the subsequent protonation of the furan ring with partial deprotonation of the pyrrole ring (the formation of an almost equimolar mixture of ions IA and IB with an increase in the temperature)? This phenomenon can evidently occur only if the energies of protonated forms IA and IB are close, which a priori seems unlikely (although, as demonstrated above, a qualitative explanation for this can be obtained on examining the resonance structures and σ^+_p constants of the 2-pyrrolyl and 2-furyl groups). However, the calculated ΔH values (Fig. 7) unexpectedly completely confirm this prediction and thus unambiguously explain the unprecendented instance of the manifestation of approximately equal reactivities of the pyrrole and furan rings in the thermodynamically controlled electrophilic process.

One can attempt to use the charges (Fig. 7) and partial electron densities of the lowest vacant molecular orbital (LVMO) of protonated forms IA and IB (Tables 6 and 7) for the interpretation of the regiospecificity of the addition of a bromine anion to them (bromination of cation IB → IC but not IA → ID). However, agreement with the experiment is not observed in this case. If one compares the reactivity indexes (the charges and contributions of the LVMO) of the $C_{(4)}$ and $C_{(4')}$ positions that actually participate in the reaction, it may be stated that both with respect to the positive charge and with respect to the partial electron density of the LVMO the $C_{(4)}$ atom in cation IA surpasses, although only slightly, the analogous $C_{(4')}$ atom in cation IB (0.15 and 0.01 for $C_{(4)}$ and 0.14 and 0 for $C_{(4')}$). However, the bromine anion is bonded covalently only to the latter, and reaction at the $C_{(4)}$ atom (A → D) is also observed only for II and IV at a higher temperature. Moreover, in cations IA and IB there are atoms that, according to the reactivity indexes under consideration, should be more likely bromide ion acceptors ($C_{(2)}$, $C_{(5')}$, and $C_{(3')}$ for IA and $C_{(2')}$, $C_{(5)}$, and $C_{(3)}$ for IB), since the positive charges and the contributions of the LVMO for them are considerably greater than for the $C_{(4)}$ and $C_{(4')}$ atoms (Fig. 7, Tables 6 and 7). If one takes into account the fact that ions IA and IB are, of course, significantly more solvated than the neutral I molecule and the fact that the transition state of this reaction is most likely "late" when a molecule of the substrate is perturbed substantially by the reagent (the Br^- gegenion), one should not be surprised at the unsuitability of such simple reactivity indexes for the interpretation of the experimental results.

EXPERIMENTAL

The ^1H NMR spectra were obtained with Tesla BS-567A (100 MHz) and Bruker WP-200SY (200 MHz) spectrometers.

The reaction of 2-(2-furyl)pyrroles I-VI with HSO_3F and CF_3COOH was carried out at −80°C by stirring 0.02 g of the pyrrole with a fivefold to tenfold excess of the acid in equal volumes (0.2 ml) of CD_2Cl_2 in the ampul of the spectrometer. The reactions with hydrogen halides were also accomplished in the ampul of the spectrometer by passing a stream of dry HCl or HBr through a solution of the pyrrole in CD_3Cl_3 at −80°C (or at −30°C).

The methods used for the synthesis and purification of I-IV were described in [10] and in the literature cited therein. The CD_2Cl_2 was purified by shaking with calcined aluminum oxide.

The quantum-chemical calculations of 2-(2-furyl)pyrrole and its protonated forms were made by the MNDO method with an EC-1061 computer in the OS MVS system.

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