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PROTONATION OF 2-(2-THIENYL)PYRROLE AND 2-(2-THIENYL)-1-VINYLPYRROLES

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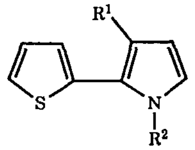
2-(2-Thienyl)pyrrole and its 3-alkyl-1-vinyl derivatives have been shown (^{1}H NMR) to be protonated by HSO_3F, CF_3COOH, HCl and HBr at the pyrrole C-5 atom. Reaction with the superacid system $HSO_3F–SbF_5–SO_2$ results in the equilibrium between pyrrolium and thiophenium ions. The heats of formation (ΔH), charges and HOMO partial electron densities for 2-(2-thienyl)pyrrole and its protonated forms have been calculated by the MNDO method. The calculated ΔH values of thienylpyrrolium and pyrrolylthiophenium ions are in agreement with the experimentally observed ratio.

INTRODUCTION

Protonated pyrroles have been studied for more than 30 years,[1,2] and their $^1H^{1-4}$ and $^{13}C^5$ NMR spectra have been reported. Studies have dealt with the preferred sites of protonation, substituent effects on the process[2–4,6] and the kinetic proton affinities of various positions of the pyrrole ring.[7]

Protonated pyrroles with adjacent heteroaromatic moieties are now available owing to the recent development of general methods for their synthesis,[8,9] and are attractive models for the investigation of the charge redistribution in their extended heteroaromatic systems and of their conformational behaviour.[10] These goals are relevant to the synthesis and properties of 'organic metals' of the polypyrrole and polythiophene families, which are of rapidly increasing interest.[11–13]

The reactivity of the simplest five-membered aromatic heterocycles in electrophilic reactions is known to decrease in the sequence pyrrole ≫ furan > thiophene.[14,15] Recently we found[10] that protonation of 2-(2-furyl)pyrrole and its derivatives with hydrogen halides results in the formation of both pyrrolium and furanium ions. Quantum chemical (MNDO) calculations suggest[10] similar enthalpies for the most stable planar forms of these cations. In this work, we have extended the reactivity range of the two interacting moieties and have studied by ^{1}H NMR the protonation of the 2-(2-thienyl)pyrroles 1–4, using HCl, HBr, HSO_3F, CF_3COOH and the superacid system $HSO_3F–SbF_5–SO_2$.

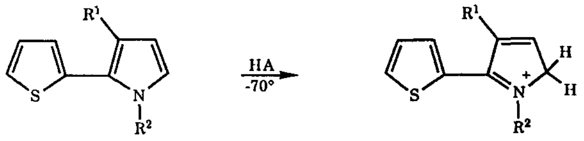


	R^2	R^1
1	H	H
2	$CH=CH_2$	H
3	$CH=CH_2$	Me
4	$CH=CH_2$	*i*-Pr

Heats of formation were calculated and electron distributions were also studied by MNDO for 2-(2-thienyl)pyrrole (1) and its α-protonated forms, and for 2-phenylpyrrole and its pyrrole or phenol ring-protonated forms as model systems.

RESULTS

At −70 °C the only reaction products observed from 1–4 in acid are the 2-(2-thienyl)pyrrolium ions 5–8 (Figure 1), independent of the nature of the acid (except for the superacid system).



1–4 5–8

In contrast to the 2-(2-furyl)pyrroles,[10] increasing the sample temperature to 0 °C (in CF_3COOH medium) and to 20 °C (in the HSO_3F medium) does not result in the formation of isometric cations by protonation of the other heterocyclic ring. Hence the only reaction pro-

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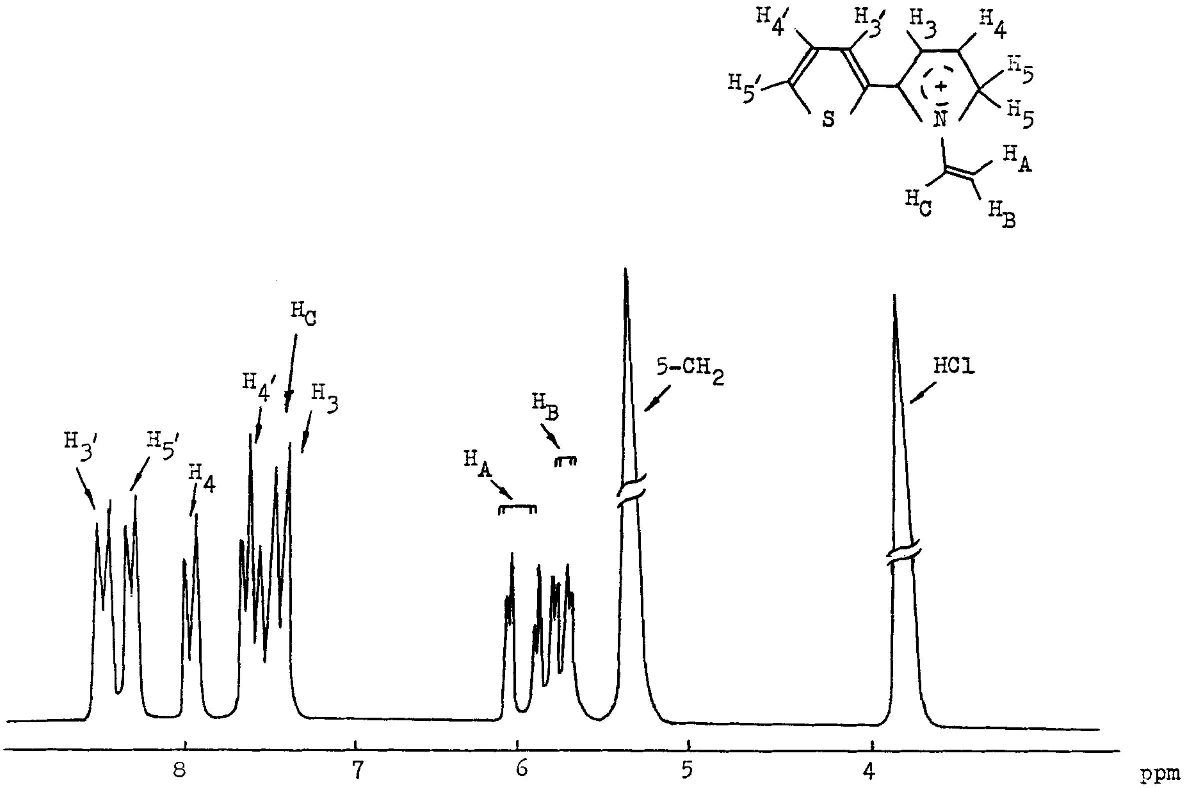
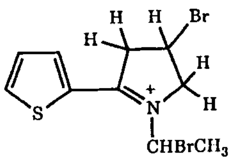


Figure 1. ^{1}H NMR spectrum of 1-vinyl-2-(2-thienyl)pyrrolium chloride (CD_2Cl_2, −70 °C, 100 mHz)

ducts are pyrrolium ions, although modified by addition of HCl or HBr to the vinyl group.

The reaction of pyrrole **2** with HBr at 0 °C (or increasing the sample temperature from −70 to 0 °C) leads to addition of a second HBr molecule to the protonated pyrrole ring to yield the 1-(1-bromoethyl)-2-(2-thienyl)-4-bromo-4,5-dihydropyrrolium ion (**9**). Unlike 2-(2-furyl)pyrroles, no addition to the thienyl ring occurs.



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The interaction of 1-vinyl-2-(2-thienyl)pyrrole (**2**) with the super acid system $HSO_3F–SbF_5–SO_2$ differs sharply from those with the other acids. The spectrum of the mixture obtained at −70 °C contains the signals of three compounds, two being identified reliably as dilations **10** and **11** in a 2 : 1 ratio.

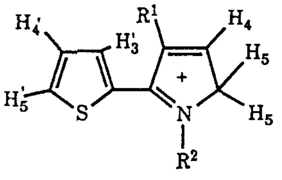
10 **11**

Heating the sample to −10 °C results in the disappearance of the signals of the unidentified compound (which is probably a kinetically unstable product of β-protonation of the pyrrole ring[7]) and also in the reversal of the **10**/**11** dication ratio to 1 : 2. The structure of these ions follow from their ^{1}H NMR spectra (Table 1).

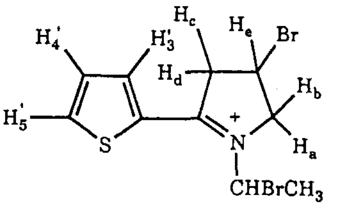
DISCUSSION

In contrast to the 2-(2-furyl)pyrrolium ions, the 2-(2-thienyl)-pyrrolium ions do not isomerize in excess HCl. Two plausible reasons for this may be considered. The first is the greater stability of the thienylpyrrolium ions (**12**, X = S) compared by the corresponding furylpyrrolium ions (**12**, X = O) due to the greater ability of the sulphur atom to form the onium state.[16] In such a case

Table 1. ^{1}H NMR chemical shifts of cations 5–11



5–8, 10



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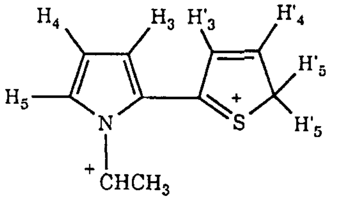

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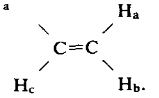
Cation	R^2	H_4	H_5	H'_3	H'_4	H'_5	R^1	R^2
5	H	8·03	5·12	8·27	7·50	8·27	7·35 (H)	
6	$CH{=}CH_2$	7·93	5·38	8·27	7·63	8·43	7·22 (H)	5·93 (H_a)[a], 5·75 (H_b), 7·49 (H_c)
6	$CHClCH_3$	8·06	5·36	8·42	7·62	8·53	7·40 (H)	6·65 (CH), 2·24 (CH_3)
6	$CHBrCH_3$	8·13	5·46	8·49	7·66	8·58	7·64 (H)	6·80 (CH), 2·46 (CH_3)
7	$CH{=}CH_2$	7·70	5·23	8·30	7·67	8·30	2·50 (Me)	5·72 (H_a)[a], 5·49 (H_b), 7·43 (H_c)
8	$CHClCH_3$	7·78	5·24	8·19	7·60	8·34	3·05 (CH), 1·37, 1·06 $(CH_3)_2$	6·49 (CH), 2·18 (CH_3)
9		5·10 (H_e)	4·68 (H_a) 5·20 (H_b)	8·35	7·63	8·63	5·10 (H_c), 4·05 (H_d)	6·80 (CH), 2·28 (CH_3)
10	$^+CHCH_3$	8·57	5·77	9·21	8·18	8·81	7·91 (H)	9·82 (CH^+), 3·46 (CH_3)
11		7·68	8·71	8·23	9·02	5·63	8·45 (H_3)	10·06 (CH^+), 3·58 (CH_3)

[a]



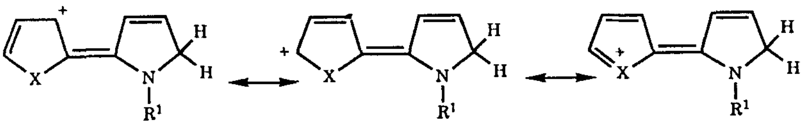
it follows from the mesomeric structures that for X = S the positive charge is more delocalized than for X = O. This is confirmed by the change in the calculated net charges on the O and S atoms on pyrrolium ion formation: the charge on sulfur increases by 0·9 whereas the charge on oxygen increases by only 0·03 (Figures 2 and 3).

Recently we also found[17] that the width of the 5-CH_2 signal in the ^{1}H NMR spectra can serve as a criterion of pyrrolium cation stability. In the intermolecular exchange of these protons with the medium this signal broadens with increase in temperature. Such broadening takes place, for example, in the spectra of 2-alkyl- and 2-arylpyrrolium ions.[17] With cations **5–8** an increase in sample temperature of 10 °C does not alter the width of the 5-CH_2 signal in HCl medium, showing the stability of these ions.

A second reason for the lack of isomerism of the thienylpyrrolium ions is the known lower reactivity of the thiophene ring towards protonation in comparison with the furan ring.[14,15] Both factors evidently contribute to the observed result.

The preferred pyrrole ring protonation with the usual acids at low temperature is determined, as for the 2-(2-furyl)pyrroles, by the HOMO electron densities rather than by the atomic charges (it is seen from Figures 2–4 that the charge on C-5 is minimal). As follows from Figure 4, the p_z atomic orbital contributions to the HOMO from the pyrrole C-5 and C-2 atoms are largest (0·52 and 0·5, respectively), the latter not being protonated owing to steric hindrance.

Dication formation is observed for the interaction of 2-(2-thienyl)-1-vinylpyrrole (**2**) with HSO_3–SbF_5–SO_2, in which three reaction products are observed at



12 X = O,S

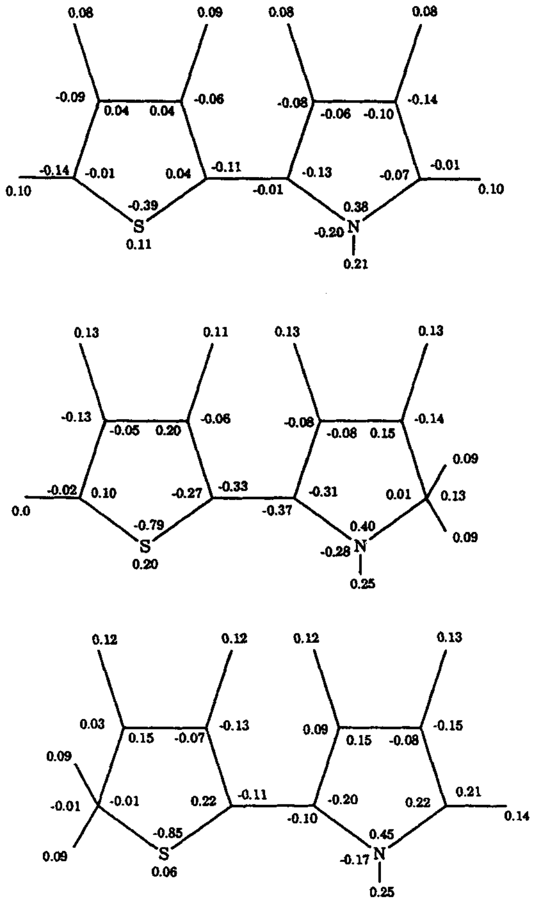


Figure 2. Full charge distribution (MNDO) in the 2-(2-thienyl)pyrrole molecule and its protonated forms. The π-atomic charges are given inside the rings

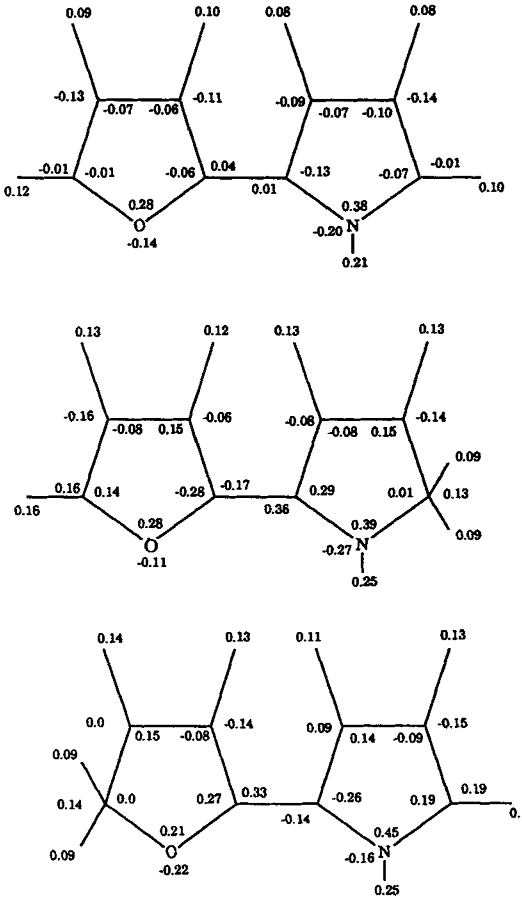


Figure 3. Full charge distribution (MNDO) in the 2-(2-furyl)pyrrole molecule and its protonated forms. The π-atomic charges are given inside the rings

−70 °C, suggesting that charge (kinetic) control acts together with the orbital control. The thiophene C-5 and pyrrole C-4 atoms of **1** have the greatest net charges, and are the most likely sites for attack of the hard acid. At −10 °C the unidentified compound disappears and the dication **11** with a protonated thiophene unit increases. This is in good agreement with the calculated heats of formation (Table 2), which show that the thienylpyrrolium and pyrrolylthiophenium ions have almost the same thermodynamic stability. At the same time, computation of the model cations formed by 2-phenylpyrrole protonation reveals a very large difference between the heats of formation of phenylpyrrolium and pyrrolylbenzenium ions (*ca* 55 kJ mol^{-1}).

Recently we found that 2-phenylpyrroles are protonated by all acids studied, including $HSO_3F–SbF_5–SO_2$, only at the pyrrole ring.[18] Hence the results obtained reflect the adequacy of the method and provide a satisfactory rationalization of the observed experimental facts.

In this work the detailed MNDO calculations with full geometry optimization and construction of the internal rotation potential curves were carried out for 2-(2-thienyl)pyrrole and its protonated forms and for the model 2-phenylpyrrole and its cations. The most important calculated results are listed in the Tables 2 and 3 and shown in Figures 2–4. The similar parameters of 2-(2-furyl)pyrrole and its cations are given for comparison.

The question of the relation of internal rotation barriers in the cations studied may be considered in more detail, since their heights can serve as a measure of inter-ring conjugation. These heights decrease substantially in the sequence furyl > thienyl > phenyl (Table 3). We have proposed[19] previously that this

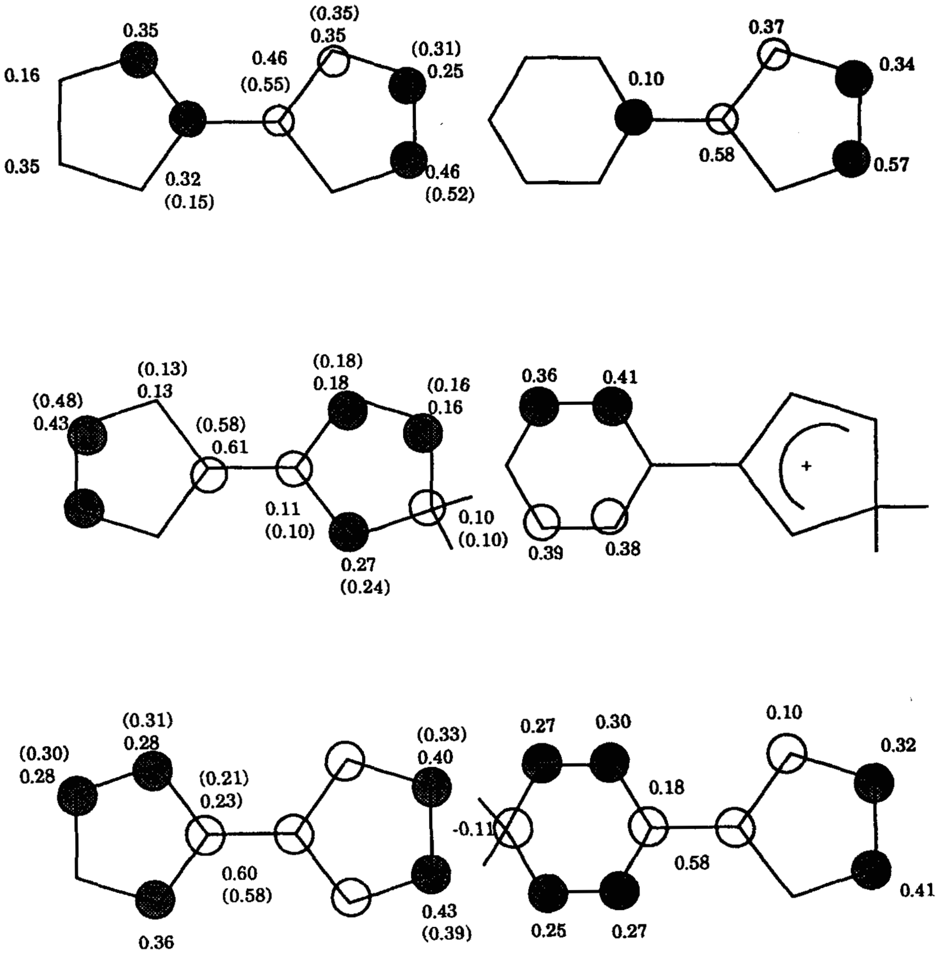


Figure 4. HOMO structures of 2-(2-furyl)-, 2-(2-thienyl)- and 2-phenylpyrrole and their protonated forms. For 2-(2-thienyl)pyrrole, the values of p_z atomic orbital contributions are given in parentheses

Table 2. Heats of formation (kJ mol^{-1}) by MNDO of the most stable conformers of 2-furyl-, 2-thienyl- and 2-phenylpyrroles[a]

Compound	Conformer	Neutral molecule	N (+)[b]	2-Substituent (+)[c]
2-(2-Furyl)pyrrole	*cis*[d]	87·32	738·43	740·57
	trans[d]	94·22	745·80	748·60
2-(2-Thienyl)pyrrole	*cis*[d]	249·55	908·21	903·39
	trans[d]	249·55	910·84	907·24
2-Phenylpyrrole		224·52	880·70	935·88

[a] With full geometry optimization.
[b] Protonated pyrrole ring.
[c] Protonated 2-substituent ring.
[d] Relative to the ring heteroatoms.

Table 3. Main parameters characterizing inter-ring conjugation

Compound	Change	C_2—C'_2 bond order[a]	C_2—C'_2 bond length (Å)	Barrier height (kJ mol^{-1})	V_2 (kJ mol^{-1})	Inter-ring angle (°)
2-(2-Furyl)pyrrole	Neutral	1·02	1·45	—	2·51	12·7
	N(+)	1·17	1·43	31·05	34·39	0
	O(+)	1·38	1·40	80·84	85·48	0
2-(2-Thienyl)pyrrole	Neutral	1·01	1·45	—	−2·93	54·8
	N(+)	1·14	1·43	15·28	17·12	0
	S(+)	1·49	1·38	88·07	86·94	0
2-Phenylpyrrole	Neutral	0·98	1·47	—	−8·16	70·8
	N(+)	1·07	1·46	2·47	2·93	38·6
	Ph(+)	1·42	1·40	63·17	41·61	4·5

[a] Bond order is defined as the sum of squares of density matrix elements bonding two atoms.

indicates a decrease in the stabilizing influence of these heterocycles toward the pyrrolium ion. In the alternative protonated forms the increase in the pyrrole ring-stabilizing effect is clearly seen. Hence the internal rotation barrier height in the pyrrolyfuranium ion is about 2·5 times larger than that in the furylpyrrolium ion. The similar ratio for the pair of thienylpyrrole cations is about 6, and for phenylpyrrole it is about 25. Previously, the internal rotation barrier height in protonated 2,2′-bithienyl was estimated to be 48 kJ mol^{-1} dynamic NMR,[20] i.e. the electron density delocalization in this cation is higher than that in the thienylpyrrolium ion, but lower than in the pyrrolythiophenium ion.

CONCLUSION

2-(2-Thienyl)pyrroles **1–4** are protonated by acids at C-5 of the pyrrole rings and, in contrast to 2-(2-furanyl)pyrroles, no monocations due to protonation on the other ring are observed. 1-Vinyl-2-(2-thienyl)pyrrole (**2**) in HSO_3F–SbF_5–SO_2 gives dications involving protonation of the vinyl group and either of the heterocyclic rings. The experimental results agree with MNDO calculations of the position of protonation and the rotational barriers in the cation.

EXPERIMENTAL

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

The reaction of 2-(2-thienyl)pyrroles **1–4** with HSO_3F and CF_3COOH was carried out −70 °C by adding 0·02 g of the pyrrole in an equal (0·2 ml) volume of CD_2Cl_2 in the NMR tube to a 5–10-fold excess of acid. A similar procedure was used in the reaction of the pyrrole **2** with the superacid system, with liquid SO_2 (80 vol.%) as solvent. The pyrrole (0·02 g in liquid SO_2) was introduced into the acid solution.

The reactions with hydrogen halides were also performed in the NMR tube, by passing of dry HCl (or HBr) through the pyrrole solution in CD_2Cl_2 at −70 or −30 °C.

Since the resolution of the spectra was not sufficient for the measurement of coupling constants owing to the low temperatures and intermolecular proton exchange, the signal assignments were confirmed, where necessary, from double resonance runs.

The methods of synthesis of the compounds studied have been described previously.[8,9,21]

Quantum chemical (MNDO) calculations were performed on an EC-1061 computer.

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