

9. S. K. Klimenko, T. V. Stolbova, M. N. Berezhnaya, N. S. Smirnova, I. Ya. Evtushenko, and V. G. Kharchenko, *Zh. Org. Khim.*, 10, 1942 (1974).
10. T. V. Stolbova, S. K. Klimenko, and V. G. Kharchenko, *Zh. Org. Khim.*, 16, 178 (1980).

QUANTUM-CHEMICAL INTERPRETATION OF THE MASS SPECTRA OF PYRROLE, FURAN,  
AND THIOPHENE

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A simple quantum-chemical interpretation of the mass-spectrometric fragmentation of organic molecules in which the probability of the cleavage of the bonds under the influence of electron impact is related to their self-consistent  $\pi$ -electron orders and the possible rearrangement processes are described on the basis of the long-range bond orders is proposed. This approach was tested in the case of pyrrole, furan, and thiophene.

In the modern literature there are several approaches to the theoretical description of mass spectra: a statistical approach [1] in which the intensity of an ion peak is assumed to be higher, the greater the number of fragments of a given mass that can be obtained as a result of cleavage of the various bonds of the starting molecule; the charge-localization approximation [2-6] in which bond cleavage depends on the site of the primary location of the positive charge in the molecular ion; taking into account the bond orders [4] and energies [7, 8] (calculated, as a rule, by the Nüchel method); application of the Dewar theory of perturbed MO [9] and the method of potential surfaces [10, 11]. In some of these models, which are based on quasi-equilibrium theory, identity of the structures of the molecular ion and the neutral molecule is assumed without substantiation [12]; this clearly does not correspond to the physical pattern of the phenomenon. Other methods, for example, the method of potential surfaces, while being physically correct, are extremely laborious from a computational point of view, and this substantially limits their range of application. Virtually all of the theoretical schemes (except for the method of potential surfaces) do not take into account the role of rearrangement processes, which are intimately associated with the stabilities of the resulting fragments and, consequently [13], with the intensities of their peaks in the mass spectra. Let us note that some isomerization processes of this sort have been observed [with the use of the MIKES (DADI) [14] and CID/MIKE [15] methods with devices with "inverse" geometry] experimentally (see [16]).

We assume that the pathways of the fragmentation of a molecular ion are due to its electronic structure and that the pattern of the mass spectrum is determined to a significant degree by rearrangements of the corresponding cation radicals or cations. As in [17, 18], we describe cyclizations by means of the long-range bond orders, which, moreover, are a measure of the aromatic character [19], i.e., the thermodynamic stabilities of the resulting rearrangement ions. We determine the probability of bond cleavage in the fragmentation of conjugated systems from the corresponding self-consistent  $\pi$ -electron bond orders; we assume that the ion undergoing fragmentation exists in the ground state. In contrast to [17, 18], in which the mass-spectrometric recyclizations of cations with a closed electron shell were examined, the rearrangements and fragmentation of pyrrole, furan, and thiophene cation radicals were studied here. The parameters of the  $\pi$ -electron Hamiltonian are the same as in [20-22].

The bond orders of pyrrole (Ia), furan (Ib), and thiophene (Ic) cation radicals, as well as their  $\pi$ -open forms II-IV, calculated by the unrestricted Hartree-Fock method are presented in Table 1.

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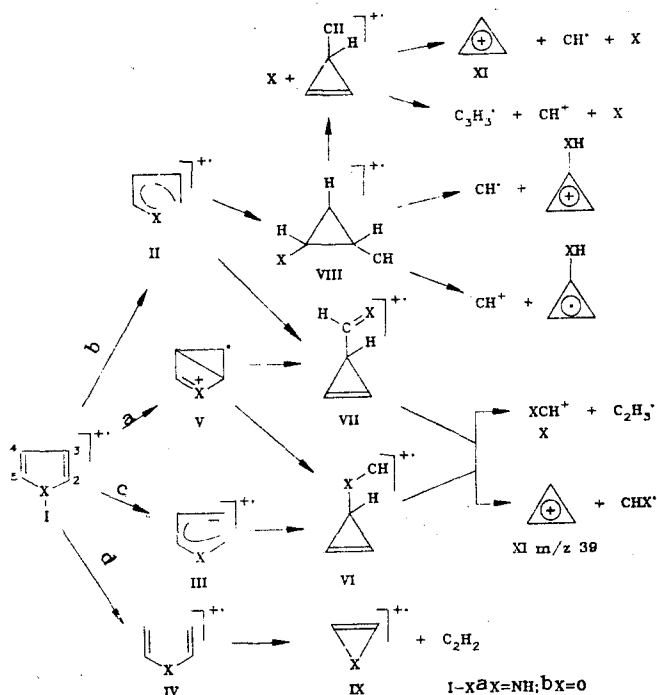
TABLE 1.  $\pi$ -Bond Orders of Pyrrole, Furan, and Thiophene Cation Radicals and Their  $\pi$ -Open Forms

$P_{ik}$	Ia*	IIa	IIIa	IVa	ib	IIb	IIIb	IVb	ic	IIc	IVc
$P_{12}$	0.490 (0.501)	0.004	0.622	0.519	0.420 (0.442)	0.013	0.523	0.453	0.723 (0.527)	-0.032	0.630
$P_{23}$	0.514 (0.740)	0.703	0.137	0.724	0.541 (0.763)	0.690	0.173	0.719	0.647 (0.715)	0.707	0.730
$P_{34}$	0.753 (0.609)	0.619	0.777	-0.079	0.735 (0.596)	0.617	0.778	-0.099	0.297 (0.635)	0.598	-0.011
$P_{45}$	0.514 (0.740)	0.546	0.579	0.724	0.541 (0.763)	0.570	0.587	0.719	0.647 (0.715)	0.601	0.730
$P_{31}$	0.490 (0.501)	0.609	0.520	0.519	0.420 (0.442)	0.486	0.464	0.453	0.723 (0.527)	0.742	0.690
$P_{13}$	-0.226 (-0.227)	-0.163	-0.183	-0.040	-0.200 (-0.204)	-0.122	-0.162	-0.055	0.147 (-0.315)	-0.245	0.014
$P_{14}$	-0.226 (-0.227)	-0.121	-0.067	-0.040	-0.200 (-0.204)	-0.130	-0.079	-0.055	0.147 (-0.315)	-0.141	0.014
$P_{24}$	0.109 (-0.128)	0.145	-0.186	-0.263	0.136 (-0.105)	0.167	-0.165	-0.271	-0.108 (-0.028)	0.201	-0.188
$P_{25}$	-0.076 (-0.424)	-0.111	-0.258	-0.202	-0.111 (-0.459)	-0.107	-0.316	-0.253	-0.390 (-0.400)	-0.129	-0.202
$P_{35}$	0.109 (-0.128)	0.184	0.150	-0.263	0.136 (-0.105)	0.213	0.196	-0.271	-0.108 (-0.028)	0.171	-0.188

\*The bond orders of the neutral heterocycles are presented in parentheses for comparison.

1. It is apparent from Table 1 that the detachment of an electron in Ia, b leads to marked weakening of the 2-3 and 4-5 bonds and to strengthening of the 3-4 bonds vis-à-vis virtually unchanged heteroatom-carbon bond orders; in contrast to neutral molecules, in which all of the long-range orders  $P_{ik}$  are negative (which constitutes evidence for resistance of the neutral forms to rearrangements), there are positive  $P_{24}$  values in cation radicals Ia, b. This indicates the possibility of ring contraction in the examined cation radicals with the formation of bicyclic intermediate V (only one of the boundary structures is presented in the scheme) and the subsequent development through cation radicals VI and VII of  $[C_3H_3]^+$  fragment XI (see Scheme 1, pathway a).

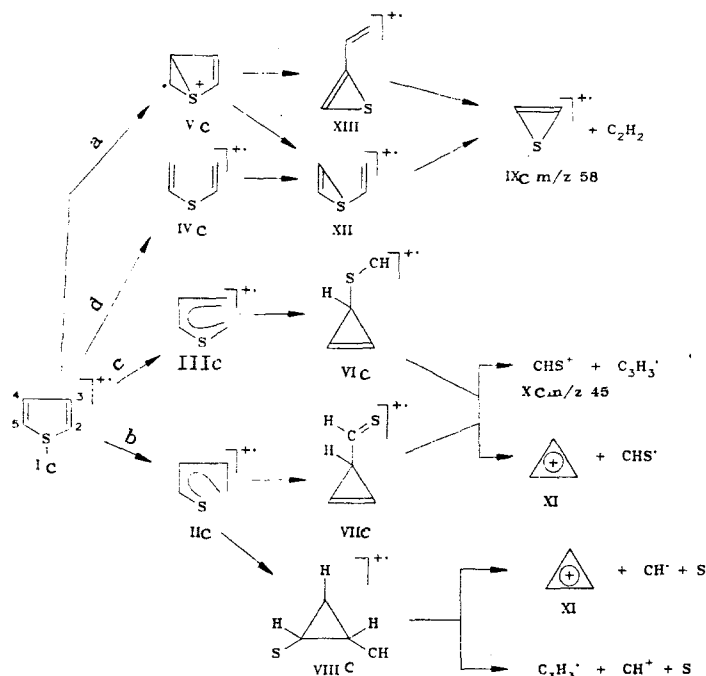
Scheme 1



The behavior of thiophene (Ic) in ionization should differ from the behavior of furan and pyrrole, since the inclusion of hybrid  $pd^2$  orbitals in conjugation (see [21]) leads to qualitative differences in their cation-radical electron states. Thus, as compared with the neutral molecule, the 2-3 and 3-4 bonds are weakened and the 1-2 bond is strengthened in cation radical Ic, and positive 1-3 and 1-4, but not 2-4 and 3-5, long-range orders develop. According to this, Ic can be converted to bicyclic intermediate Vc, which should undergo fragmentation through structures XII and XIII to particles that include cyclic cation radical IXc (Scheme 2, pathway a).

Let us note that the dissimilarity in the electron structures of Ia-c is also manifested in their charge distributions. In cation radicals Ia, b the positive charge is localized on the 1 and 2 (5) atoms (0.355 and 0.282 for pyrrole and 0.249 and 0.318 for furan, respectively), while in the thiophene cation radical it is concentrated primarily in the 1 and 3 (4) positions (0.410, 0.281).

2. Let us now examine possible ring opening in the investigated cation radicals. It follows from the data presented in Table 1 that the 1-2 and 2-3 bond orders in structure Ia are approximately equal, while the 3-4 bond is substantially stronger. This result also occurs for structure Ib, although the difference in the strengths of the 1-2 and 2-3 bonds is more perceptible in this case. Thus opening of the ring of Ia and Ib at the 1-2 bond (pathway b, Scheme 1) and then at the 2-3 bond (pathway c, Scheme 1) is most likely during fragmentation, and cleavage of the 3-4 bond (pathway d, Scheme 1) is considerably less likely. Let us also note that since  $P_{12}(Ib) < P_{12}(Ia)$  and  $P_{24}(Ib) > P_{24}(Ia)$ , the intensity of the peak of cation XI ( $m/z$  39) in the mass spectra of furan should be greater than in the case of pyrrole. Getting somewhat ahead of ourselves, let us note that this corresponds to the experimental data [22].



The situation is just the opposite for thiophene cation radical I c. The weakest bond in this case is the 3-4 bond, the  $\pi$ -electron order of which is so low that it almost completely determines the fragmentation (pathway d, Scheme 2), thereby virtually excluding ring opening at the other bonds (pathways b and c, Scheme 2).

3. The results of calculation of the  $P_{ik}$  values of the  $\pi$ -open forms of the pyrrole, furan, and thiophene cation radicals (see Table 1) make it possible to form a judgement regarding subsequent rearrangement of these intermediates during fragmentation. Thus the long-range positive 2-4 and 3-5 bond orders increase in the cleavage of the 1-2 bond in Ia, b (structures IIa, b). This should lead to cyclization of these cation radicals to structures VII and VIII and ultimately, after their fragmentation, to cation XI (pathway b, Scheme 1). Let us emphasize that the orders of the valence bonds of  $\pi$ -acyclic structures IIa, b were equalized as compared with Ia, b, i.e., their subsequent cleavage (without cyclization) is unlikely. However, let us note that the weakest bond in IIa is the 4-5 bond, cleavage of which leads to cation XI. In cation radical IIb the smallest  $P_{ik}$  value corresponds to the 1-5 bond, cleavage of which should lead to the  $[C_4H_4]^+$  cation radical with  $m/z$  52.

It is apparent from Table 1 (see the  $P_{ik}$  values for IIIa, b) that cleavage of the 2-3 bonds in structures Ia, b leads, in contrast to the remaining  $\pi$ -open forms (this is also valid for thiophene), to a tendency of the system to close up the cleaved bond, which naturally decreases the probability of this reaction pathway (pathway c, Schemes 1 and 2). In addition, long-range bond orders  $P_{35} > P_{23} > 0$  indicate the possibility of cyclization at the 3-5 positions in structures VIa, b, which are subsequently transformed to cations X and XI. The weakest valence bonds in cation radicals IIIa, b are the 1-5 bonds, and their cleavage (with the subsequent formation of a  $C_3H_3$  ring) gives the same fragment ions X and XI.

Finally, cleavage of the 3-4 bond in the pyrrole and furan cation radicals (which is least likely; see section 2) leads to structures IVa, b. All of the long-range bond orders in these structures are negative, i.e., the cyclization-fragmentation process should not occur in this case, and a fragmentation-cyclization process is more likely realized. It is apparent from Table 1 that the 1-2 (1-5) bonds will be the least strong in these cation radicals; this should lead to the elimination of a molecule of acetylene and to the appearance in the mass spectra of a peak of the IX cation (pathway d in Scheme 1). Let us emphasize that the possible migration of an NH proton in structures IIa and IIIa, and particularly IVa (which leads to the formation of cyclic fragment ion  $C_2H_2N^+$  and radical  $C_2H_3^{\cdot}$ ), remains

outside the scope of the present study by virtue of the limited character of the  $\pi$ -electron approximation used.

As noted in section 2, opening of the thiophene cation radical via pathway d through structure IVc is most likely; an analysis of the bond orders of IVc (see Table 1) shows that, despite the smallness of the  $P_{13}$  value, cyclization of this  $\pi$ -open form to structure XII with the subsequent formation of cation radical IXc is possible. However, the closeness of the  $P_{13}$  value to zero together with the strengths of valence bonds  $P_{12} \sim P_{23} \sim 0.7$  in IVc nevertheless constitute evidence for the preferableness of pathway a with the formation of bicyclic Vc or even a tricyclic (of the "Ladenburg thiophene" type) intermediate [23] as compared with fragmentation via pathway d.

Cleavage of the 1-2 and 2-3 bonds in cation radical Ic (structures IIc and IIIc) should lead (see Table 1) to the same cyclizations of the  $\pi$ -acyclic forms as in the case of pyrrole and furan (pathways b and c in Scheme 2, respectively). In addition, the fragmentation-cyclization process for these intermediates differs. Thus the weakest bond in cation radical IIIc is not the 1-5 bond but rather the 4-5 bond, and its cleavage should lead to cation radical IXc rather than to cation XI. Similarly, the 3-4 bond, cleavage at which also gives IXc, will be the least strong bond in structure IIc.

In summing up, let us note that, according to the results of the calculation, the peak corresponding to the  $C_3H_3^+$  ion ( $m/z$  39) in the mass spectra of pyrrole and furan should have the maximum intensity as compared with the other fragment ions, while the intensity of the peak of the  $C_2H_2S^+$  ion ( $m/z$  58) in the mass spectra of thiophene should be higher than for the peak of the  $C_3H_3^+$  ion. This conclusion is in agreement with the experimental data [24], and this constitutes evidence for the possibility of the description of mass spectrometric transformations on the basis of the approach developed here.

#### LITERATURE CITED

1. H. M. Rosenstok, M. B. Wallenstein, and T. L. Warhoftig, Proc. Natl. Acad. Sci., **38B**, 667 (1952).
2. J. C. Lorquent, Mol. Phys., **9**, 29 (1965).
3. J. C. Lorquent, Mol. Phys., **9**, 101 (1965).
4. R. C. Dougherty, R. L. Foltz, and L. B. Kier, Tetrahedron, **26**, 1989 (1970).
5. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972).
6. G. R. Lester, in: Advances in Mass Spectrometry [Russian translation], edited by G. D. Waldron, Inostr. Lit., Moscow (1963).
7. M. Ogata and H. Ichikawa, Bull. Chem. Soc. Jpn, **45**, 3231 (1972).
8. S. Tajima, N. Wasada, and T. Tsuchia, Bull. Chem. Soc. Jpn, **44**, 884 (1971).
9. R. C. Dougherty, J. Am. Chem. Soc., **90**, 5780 (1968).
10. M. J. S. Dewar and D. Landman, J. Am. Chem. Soc., **99**, 4633 (1977).
11. M. J. S. Dewar, Faraday Disc. Chem. Soc., **62**, 197 (1977).
12. T. Bently and R. Johnston, Methods and Advances in Physical Organic Chemistry [in Russian], Mir, Moscow (1973), p. 9.
13. P. B. Terent'ev, Mass Spectrometry in Organic Chemistry [in Russian], Vyssh. Shkola, Moscow (1979).
14. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, Metastable Ions, Elsevier, Amsterdam (1973).
15. K. Levsen and H. Schwarz, Angew. Chem. Inst. Ed., **15**, 509 (1976).
16. A. A. Polyakova, Molecular Mass-Spectral Analysis of Organic Compounds [in Russian], Khimiya, Moscow (1983), p. 381.
17. Yu. B. Vysotskii and B. P. Zemskii, Khim. Geterotsikl. Soedin., No. 12, 1673 (1982).
18. Yu. B. Vysotskii and B. P. Zemskii, Khim. Geterotsikl. Soedin., No. 3, 341 (1983).
19. Yu. B. Vysotskii, N. A. Kovach, and O. P. Shvaika, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, 3 (1980).
20. Yu. B. Vysotskii, Zh. Struk. Khim., **19**, 605 (1978).
21. Yu. B. Vysotskii, B. P. Zemskii, E. A. Zemskaya, and N. N. Alekseev, Zh. Strukt. Khim., **22**, 13 (1981).
22. Yu. B. Vysotskii and L. N. Sivyakova, Teor. Éksp. Khim., **21**, 293 (1985).
23. O. Meth-Cohn, in: General Organic Chemistry [Russian translation], Vol. 9, edited by N. K. Kochetkov, Khimiya (1985), p. 229.

FIVE-MEMBERED 2,3-DIOXO HETEROCYCLES.

2.\* SYNTHESIS AND [1,5]-SIGMATROPIC REARRANGEMENT

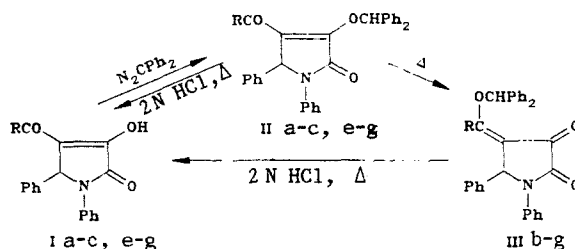
OF 4-ACYL-3-DIPHENYLMETHOXY-1,5-DIPHENYL-2,5-DIHYDROPYRROL-2-ONES

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4-Acyl-1,5-diphenyltetrahydropyrrole-2,3-diones react with diphenyldiazomethane to give O-alkylation products, which upon heating undergo [1,5]-sigmatropic suprasurface rearrangement to form 4-[methyl- and 4-[aryl(diphenylmethoxy)-methylene]-1,5-diphenyltetrahydropyrrole-2,3-diones.

We have previously established that 4-arylsulfonyl-3-diphenylmethoxy-2,5-dihydrofuran-5-ones at 170-175°C undergo [1,3]-sigmatropic rearrangement to 4-arylsulfonyl-4-diphenylmethyltetrahydrofuran-2,3-diones [2]. It seemed of interest to investigate the possibilities and pathways of similar rearrangements among diphenylmethoxy derivatives of other heterocyclic compounds. With this end in mind, in the reaction of diphenyldiazomethane with 4-acyl-1,5-diphenyltetrahydropyrrole-2,3-diones Ia-c, e-g we obtained products of O-alkylation of the enol form of the latter at the keto carbonyl group in the 3 position of the heteroring, viz., 4-acyl-3-diphenylmethoxy-1,5-diphenyl-2,5-dihydropyrrol-2-ones IIa-c, e-g (Table 1). The reaction proceeds in dioxane at 20°C in 4-48 h.



Judging from the time required for disappearance of the characteristic color of diphenyldiazomethane, electron-acceptor substituents in the para position of the aryl fragment increase the reaction rate; this is evidently associated with an increase in the acidic properties of the enol hydroxy group in starting pyrrolediones Ia-g. The effect of electron-donor substituents in the same position is just the opposite.

The IR spectra of pyrrole-2-ones IIa-c, e-g (Table 2) contain intense absorption bands at 1699-1712 (lactam carbonyl) and 1630-1636 cm<sup>-1</sup> (ketone carbonyl group conjugated with a double bond). In addition to signals of aromatic substituents and the groups bonded to them, the PMR spectra of the compounds in d<sub>6</sub>-DMSO contain a singlet of a methylidyne proton in the 5 position of the heteroring at 5.65-6.35 ppm.

When IIa-c, e are heated at 170-195°C for 20-90 min, they undergo quantitative conversion to 4-[aryl(diphenylmethoxy)methylidene]-1,5-diphenyltetrahydropyrrole-2,3-diones IIIb-e.

In the IR spectra of rearrangement products IIIb-g the band of the lactam carbonyl group is shifted to the high-frequency region as compared with starting pyrrolediones Ia-g and is observed at 1760-1764 cm<sup>-1</sup>; this is evidently a consequence of an increase in the strain

\*See [1] for Communication 1.

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