agitatable reactor of the long necked hydrogenation flask type that is thermostated at 40°C and saturated with hydrogen sulfide for two hours. Then, 3 mmoles of the appropriate furan is added to the reaction mixture. The course of the reaction is followed with the help of TLC, and when it has ended, the mixture is neutralized with a saturated NaOH solution to a weakly alkaline reaction and extracted with ether. The ethereal extract is washed with water and dried with calcined $MgSO_4$. After removal of the ether, the residue is sublimed in vacuum.

LITERATURE CITED

1. V. G. Kharchenko, I. A. Markushina, and T. I. Gubina, Dokl. Akad. Nauk SSSR, 255, No. 5, 1144 (1980).
2. V. G. Kharchenko, T. I. Gubina, and I. A. Markushina, Zh. Org. Khim., 18, 394 (1982).
3. V. G. Karchenko, I. A. Markushina, and S. P. Voronin, Khim. Geterotsikl. Soedin., No. 2, 219 (1983).
4. V. G. Kharchenko, S. P. Voronin, T. I. Gubina, I. A. Markushina, and A. F. Oleinik, Khim. Geterotsikl. Soedin., No. 12, 1606 (1984).
5. V. G. Kharchenko, T. I. Gubina, S. P. Voronin, and I. A. Markushina, Khim. Geterotsikl. Soedin., No. 11, 1453 (1986).
6. V. G. Glukhovtsev and S. V. Zakharova, Khim. Geterotsikl. Soedin., No. 1, 151 (1966).
7. S. V. Zhuravlev and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 5, 597 (1983).

KINETICS OF IONIZATION OF CH BONDS OF FIVE-MEMBERED HETEROCYCLES AND THEIR BENZO DERIVATIVES AND MECHANISM OF THE ELEMENTARY ACT OF PROTON TRANSFER.

1. QUANTUM-CHEMICAL CALCULATION OF GEOMETRICAL AND ELECTRON STRUCTURES OF THE MOLECULES AND CARBANIONS

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and I. O. Shapiro

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The heats of formation and the parameters of the geometrical and electron structures of the molecules and carbanions of furan, thiophene, N-methylpyrrole, N-methylimidazole, benzofuran, benzothiophene, N-methylindole, benzene, and naphthalene were calculated by the self-consistent-field (SCF) MO LCAO method within the MNDO and CNDO/2 approximations. According to the calculations, the deprotonation of the indicated CH acids leads to relatively small changes in the geometrical structures of the anionic fragments. The charge on the deprotonated carbon atom changes most markedly in the formation of the carbanions.

The proposed series of studies continues systematic investigations to ascertain the interrelationship between the mechanism of the elementary act of proton transfer in reactions involving the ionization of CH acids and the structures of the reagents [1, p. 128; 2-4].

Data on the geometrical and electron structures of the molecules and carbanions are necessary to obtain information regarding the peculiarities of the structural reorganization of the anionic fragments of five-membered heterocycles in ionization reactions. In the proposed research the geometrical and electron structures of furan (I), thiophene (II),

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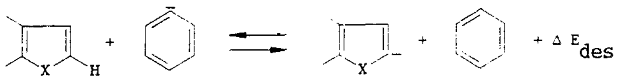
TABLE 1. Heats of Formation of the Molecules and Anions of I-IX, Heats of Isodesmic Reactions (1), and pK_a Values of the Compounds

Compound	ΔH_f, kJ/mole*	ΔE_{des}, kJ/mole	pK_a [6]	Compound	ΔH_f, kJ/mole*	ΔE_{des}, kJ/mole	pK_a [6]
I	−36,4	−61,5	35,6	Va	72,4		
	(−34,7)			VI	165,4	−80,0	32,4
Ia	68,1			VIa	251,4		
II	125,7	−47,0	33,0	VII	187,0	−77,9	38,1
	(115,5)			VIIa	275,2		
IIa	224,8			VIII	88,7	0	~43 [7]
III	134,8	−23,4	39,5		(82,9)		
IIIa	277,5			VIIIa	254,8		
IV	135,9	−90,0	33,7	IX	159,5		
IVa	211,9				(151,1)		
V	16,7	−110,4	33,0	IXa	294,7		

*The experimentally measured values are indicated in parentheses [5].

N-methylpyrrole (III), N-methylimidazole (IV), benzofuran (V), benzothiophene (VI), and N-methylindole (VII) molecules, as well as their carbanions Ia-VIIa, were calculated by quantum-chemical semiempirical methods; similar data were obtained for benzene (VIII) and naphthalene (IX) molecules and their carbanions VIIIa and IXa.* The calculations of the energy and structural parameters were made by the semiempirical self-consistent-field (SCF) MO LCAO method within the MNDO approximation with complete optimization of the geometry of the molecules. In the calculation of carbanions Ia-IXa the lengths of the CH bonds of the heteroaromatic and benzene rings were assumed to be equal to the lengths of the analogous bonds in the molecules (1.08 and 1.09 Å, respectively). The charge densities on the atoms for the optimized structures of the molecules of I-IX and anions Ia-IXa were calculated by the MNDO and CNDO/2 methods. Both of the methods used give satisfactory results in calculations of the electron-density distributions (the MNDO method was calibrated with respect to the dipole moments). The d orbitals were not taken into account in the calculations for the compounds with a sulfur atom.



I–VII VIIIa Ia–VIIa VIII (1)

I–VII X=O, S, NCH_3

The heats of formation (ΔH_f) of the molecules of I-IX and anions Ia-IXa obtained were close to the analogous experimental data (Table 1). The heats of isodesmic (ΔE_{des}) reactions of heterocycles I-VII with phenyl anion VIIIa, which characterize the gas phase thermodynamic acidities of these compounds (see Table 1), were calculated from the ΔH_f values.

The literature does not contain ΔE_{des} values. In series of related CH acids that have identical character of the stabilization of the negative charge in the conjugated carbanions the gas-phase acidities usually correlate with the pK_a values determined in aprotic slightly polar solvents [8]. In this connection a comparison of the calculated ΔE_{des} values with the liquid-phase acidities of I-VII determined in slightly polar solvents seems of interest. A similar comparison for systems with charge delocalization was made in [9]. In this case good correlation between the ΔE_{des} and pK_a values was observed.

It follows from a comparison of the ΔE_{des} values found with the pK_a values of the heterocycles measured in solution in tetrahydrofuran [6] (Table 1) that the pK_a values vary symbatically with respect to the ΔE_{des} values in narrow series when CH acids with the same heteroatom are compared. Thus, this dependence is satisfied for heterocycles III, IV, and VII; I, V and II, VI. A correlation between the pK_a and ΔE_{des} values is absent when one examines

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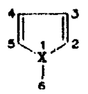
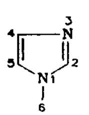
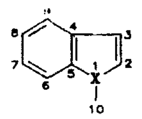
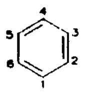
*The calculations were made for the deprotonated (in the α position) hetarenes and naphthalene (in the 2 position for N-methylimidazole).

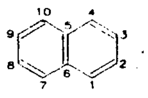
TABLE 2. Bond Lengths and Bond Angles in the Molecules and Anions of I-IX


I-III, Ia-IIIa


IV, IVa


V-VII, Va-VIIa


VIII, VIIIa


IX, IXa

Compound	Bond lengths, Å											Bond angles, deg		
	R_{12}*	R_{23}	R_{34}	R_{45}	R_{15} (R_{61})	R_{49} (R_{510})	R_{56}	R_{89}	R_{67}	R_{78}	R_{110} (R_{910})	∠512 (∠612)	∠123	∠234
I	1,367	1,390	1,444	1,390	1,367	—	—	—	—	—	—	107,6	110,3	105,9
Ia	1,345	1,419	1,433	1,390	1,379	—	—	—	—	—	—	109,6	108,1	107,2
II	1,692	1,368	1,456	1,368	1,692	—	—	—	—	—	—	93,2	111,9	111,5
IIa	1,705	1,379	1,450	1,369	1,696	—	—	—	—	—	—	95,6	108,4	113,8
III	1,408	1,391	1,437	1,391	1,408	—	—	—	—	—	1,457	108,2	108,2	107,7
IIIa	1,403	1,412	1,434	1,389	1,423	—	—	—	—	—	1,437	111,2	104,9	109,6
IV	1,406	1,338	1,394	1,390	1,409	—	—	—	—	—	1,459	106,6	110,7	106,6
IVa	1,422	1,346	1,395	1,384	1,421	—	—	—	—	—	1,436	108,9	107,6	108,2
V	1,375	1,381	1,456	1,431	1,368	1,414	1,416	1,400	1,402	1,417	—	106,8	111,8	106,9
Va	1,349	1,420	1,428	1,461	1,375	1,412	1,398	1,401	1,409	1,411	—	109,5	109,7	107,5
VI	1,697	1,362	1,464	1,430	1,695	1,410	1,404	1,403	1,404	1,413	—	93,5	113,1	111,9
VIa	1,704	1,377	1,448	1,445	1,694	1,413	1,395	1,403	1,408	1,408	—	95,9	109,8	114,4
VII	1,415	1,382	1,449	1,442	1,408	1,414	1,417	1,395	1,396	1,421	1,458	107,9	109,9	107,7
VIIa	1,409	1,410	1,430	1,463	1,415	1,412	1,401	1,402	1,408	1,410	1,443	111,0	106,6	109,8
VIII	1,407	1,407	1,407	1,407	(1,407)	—	1,407	—	—	—	—	(120,0)	120,0	120,0
VIIIa	1,396	1,408	1,408	1,408	1,396	—	1,408	—	—	—	—	119,2	120,9	119,7
IX	1,382	1,429	1,382	1,439	(1,439)	(1,439)	1,436	1,429	1,439	1,382	(1,382)	(120,9)	120,3	120,3
IXa	1,383	1,417	1,396	1,427	1,420	1,441	1,444	1,426	1,435	1,385	1,382	120,3	120,4	120,8

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*The lengths of the CH bonds of the methyl groups in the molecules and anions of I-IX are 1.11 and 1.12 Å, respectively.

TABLE 3. Charge Densities (q_i, au of charge) on the Carbon Atoms and Heteroatoms in the Molecules and Anions of I-IX*

Compound	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}
Calculated by the MNDO method										
I	−0,128	+0,107	−0,043	−0,043	+0,107	—	—	—	—	—
Ia	−0,145	−0,254	−0,342	−0,092	−0,167	—	—	—	—	—
II	+0,102	−0,047	−0,004	−0,004	−0,047	—	—	—	—	—
IIa	−0,111	−0,296	−0,369	−0,041	−0,243	—	—	—	—	—
III	−0,261	+0,073	−0,051	−0,051	+0,073	—	—	—	—	+0,217
IIIa	−0,268	−0,255	−0,326	−0,093	−0,166	—	—	—	—	+0,108
IV	−0,283	+0,191	−0,230	+0,042	+0,051	—	—	—	—	+0,229
IVa	−0,328	−0,172	−0,212	−0,029	−0,369	—	—	—	—	+0,110
V	−0,139	+0,140	−0,027	−0,101	+0,034	+0,034	+0,016	−0,023	+0,066	—
Va	−0,147	−0,176	−0,326	−0,004	−0,068	−0,001	−0,139	−0,059	−0,081	—
VI	+0,108	−0,035	+0,019	−0,069	−0,126	+0,045	+0,013	−0,092	+0,047	—
VIa	−0,069	−0,258	−0,288	+0,039	−0,179	+0,010	−0,129	−0,049	−0,074	—
VII	−0,282	+0,119	−0,038	−0,095	+0,057	−0,018	+0,016	−0,038	−0,006	+0,222
VIIa	−0,287	−0,180	−0,313	+0,004	−0,029	−0,046	−0,134	−0,073	−0,082	+0,140
VIII	0	0	0	0	0	0	—	—	—	—
VIIIa	−0,469	−0,078	−0,102	−0,171	−0,102	−0,078	—	—	—	—
IX	+0,017	+0,002	+0,002	+0,017	−0,038	−0,038	+0,017	+0,002	+0,002	+0,017
IXa	−0,417	−0,116	−0,036	−0,166	−0,036	−0,032	+0,066	−0,142	−0,065	−0,056
Calculated by the CNDO/2 method										
I	−0,144	+0,103	−0,031	−0,031	+0,103	—	—	—	—	—
Ia	−0,183	−0,312	−0,261	−0,121	−0,123	—	—	—	—	—
II	−0,066	−0,005	+0,038	+0,038	−0,005	—	—	—	—	—
IIa	−0,307	−0,336	−0,125	−0,073	−0,159	—	—	—	—	—
III	−0,047	+0,030	−0,044	−0,044	+0,030	—	—	—	—	+0,075
IIIa	−0,042	−0,365	−0,233	−0,119	−0,155	—	—	—	—	−0,087
IV	−0,054	+0,135	−0,188	+0,020	+0,008	—	—	—	—	+0,079
IVa	−0,079	−0,280	−0,311	−0,076	−0,158	—	—	—	—	−0,095
V	−0,181	+0,128	−0,052	−0,003	+0,148	−0,026	+0,004	−0,020	+0,002	—
Va	−0,198	−0,249	−0,263	+0,034	+0,088	−0,094	−0,119	−0,073	−0,128	—
VI	−0,101	+0,001	+0,027	+0,052	+0,007	+0,026	−0,009	+0,012	−0,015	—
VIa	−0,276	−0,303	−0,126	+0,061	−0,029	−0,070	−0,101	−0,051	−0,105	—
VII	−0,092	+0,067	−0,063	+0,001	+0,086	−0,036	−0,003	−0,025	+0,057	+0,071
VIIa	−0,076	−0,307	−0,240	+0,038	+0,031	−0,086	−0,112	−0,077	−0,116	−0,055
VIII	0	0	0	0	0	0	—	—	—	—
VIIIa	−0,132	−0,104	−0,113	−0,434	−0,113	−0,104	—	—	—	—
IX	−0,011	−0,001	−0,001	−0,011	+0,024	+0,024	−0,011	−0,001	−0,001	−0,011
IXa	−0,408	−0,121	−0,069	−0,143	+0,006	+0,034	−0,048	−0,101	−0,068	−0,082

*The numbering of the atoms in the molecules and anions of I-IX is given in Table 2.

the entire series of heterocyclic compounds I-VII. This may be associated with the fact that the effect of the cation, which is manifested markedly for systems with a localized charge, was not taken into account in the calculations.

The geometrical parameters of the molecules of I, II, VIII, and IX that we obtained (Table 2) are close to the analogous experimental and calculated values in [5]. In the CH acids under consideration detachment of a proton from the α-carbon atom leads to relatively small changes in the structure of the anionic fragment. Thus in anions Ia-IXa as compared with the starting molecules of I-IX the greatest changes are associated with an increase (by 0.02-0.04 Å) in the length of the bond of the deprotonated carbon atom with the adjacent atom (see Table 2).

A comparison of the charges on the CH_3 and CH groups, as well as on the carbon, nitrogen, and sulfur atoms, in the molecules of II-IV and VI-IX and anions IIa-IVa and VIa-IXa calculated within the CNDO/2 and MNDO approximations showed that the data obtained by the MNDO method are, as a rule, greater than the values calculated by the CNDO/2 method (Table 3). The charges on the nitrogen atoms differ particularly markedly (by a factor of ~5-6). On the sulfur atom in the II and VI molecules and on the CH_3 groups in the IIIa, IVa, and VIIa anions, as well as on the carbon atoms in the molecules and anions of V-VII, the charges differ not only in value but also in sign. In carbanions Ia-IIIa and Va-VIIa the negative charges on the deprotonated carbon atom calculated by the MNDO method turn out to be lower than on the adjacent carbon atoms. According to the calculations by the CNDO/2 method the deprotonated carbon atom in anions Ia-IIIa, VIa, and VIIa has the greatest negative charge. This character of the electron-density distribution seems most reasonable. For the analysis of the character of the distributions of the charge densities in the molecules and anions of heterocycles I-IX we used the data obtained within the CNDO/2 approximation.

According to these results, in the I and III-VII molecules the CH group in the α position with respect to the heteroatom is positively charged, while the β-CH group bears a negative charge. This character of the charge distribution in five-membered heterocycles makes it possible to explain the higher proton lability of the hydrogen atom in the α position. In carbanions Ia-VIIa, as compared with the starting molecules, the negative charge on the deprotonated carbon atom increases markedly. The negative charge on the carbon atoms (the nitrogen atom in the case of IV) in the α and β positions with respect to the heteroatom also changes substantially. On passing from the molecules of I, III-V, and VII to the conjugated carbanions the negative charge on the oxygen or nitrogen atoms remains virtually unchanged. In carbanions Va-VIIa the negative charge on the annelated benzene ring changes only slightly.

The density of the charges on the deprotonated carbon atom changes most markedly in the formation of carbanions VIIIa and IXa. In carbanion IXa the change in the negative charge in the annelated benzene ring is relatively small. Consequently, the character of the electron-density distribution in the carbanions of five-membered heterocycles and aromatic hydrocarbons is similar.

LITERATURE CITED

1. I. O. Shapiro, Physical Chemistry. Contemporary Problems [in Russian], edited by Ya. M. Kolotyrkin, Khimiya, Moscow (1987).
2. I. O. Shapiro, N. G. Zharova, Yu. I. Ranneva, M. I. Terekhova, and A. I. Shatenshtein, Teor. Éksp. Khim., No. 4, 443 (1986).
3. N. G. Zharova, É. D. German, A. I. Kuznetsov, and I. O. Shapiro, Izv. Akad. Nauk SSSR, Ser. Khim. (1989).
4. I. O. Shapiro, Yu. I. Ranneva, and A. I. Shatenshtein, Zh. Obshch. Khim., 49, 2030 (1979).
5. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4907 (1977).
6. R. R. Fraser and T. S. Nansour, Can. J. Chem., 63, 3505 (1985).
7. A. Streitwieser, P. J. Scannon, and H. M. Niemeyer, J. Am. Chem. Soc., 94, 7936 (1972).
8. N. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, G. J. McCollum, and N. R. Vanier, J. Am. Chem. Soc., 97, 7006 (1975).
9. J. E. Bartmess, J. A. Scott, and R. T. McIver, J. Am. Chem. Soc., 101, 6046 (1979).