RESEARCH ON AROMATIC HETEROCYCLES

XXI.* STUDY OF THE π-ELECTRONIC STRUCTURE OF THE ANION AND CATION RADICALS OF 1,2,5-OXA-, 1,2,5-THIA-, AND 1,2,5-SELENADIAZOLES AND THEIR BENZO DERIVATIVES

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The π-electronic structures of the anion and cation radicals of 1,2,5-oxa-, 1,2,5-thia-, and 1,2,5-selenadiazoles and their benzologs were investigated within the framework of the MO LCAO method within the approximation of zero differential overlap by the Pariser–Parr–Pople method for open shells and by the Longuet-Higgins–Pople method (the "half-electron" method). The two methods give close results.

The electronic structures of the anion and cation radicals of 1,2,5-oxadiazole (I), 1,2,5-thiadiazole (II), 1,2,5-selenadiazole (III), 2,1,3-benzoxadiazole (IV), 2,1,3,-benzothiadiazole (V), and 2,1,3-benzoselenodiazole (VI) were investigated in the present research within the framework of the MO LCAO method and the π-electron approximation. The calculations were made by the Pariser–Parr–Pople (PPP) method for open shells [2] and by the Longuet-Higgins–Pople (LHP) method [3].†

The PPP method for open shells is a semiempirical variant of the Roothaan method [4]. The other semiempirical approach – the LHP method – is also based on the Roothaan method but differs from the PPP method with respect to its disregard of certain terms in the expression for the total energy [5]. This method makes it possible, for example, in the calculation of the total energy of doublet states to use equations obtained for systems with closed electron shells. The application of the LHP method to open electron shells is therefore attractive because programs composed for systems with closed electron shells can be used for calculations with a computer. However, one should bear in mind that the LHP method is not completely equivalent to the PPP method. A comparison of the results obtained by these methods therefore seems of definite interest. It has been found that the results of the two methods are close for a large number of hydrocarbon systems [5, 6]. In the present research we set out to accomplish two things: 1) make a thorough analysis of the results of the calculations of the electronic structures of heterocyclic anion radicals of I-VI molecules by the PPP and LHP methods; 2) estimate the ionization potentials and electron affinities of the I-VI molecules, considering these values to be the differences in the total energies of the molecules and the total energies of the corresponding cation or anion radicals.

The same I_μ (ionization potential of atom μ), $\gamma_{\mu\nu}$ (the coulombic integral), and $\beta_{\mu\nu}$ (resonance integral) parameters as in [7] were used in the solution of these problems. The calculations were made in the computer center of the Academy of Sciences of the USSR with a BÉSM-3 computer with programs composed by the authors. The total energies of the anion and cation radicals, $(M^{-\cdot})$ and $(M^{+\cdot})$, respectively, for molecules (M) I-VI, calculated by the PPP (E^{PPP}) and LHP (E^{LHP}) methods are presented in Table 1. It follows from Table 1 that the E^{PPP} $(M^{\pm\cdot})$ and E^{LHP} $(M^{\pm\cdot})$ values corresponding to the $(M^{\pm\cdot})$ ion radicals differ little

*See [1] for communication XX.

†This method is called the "half-electron method" in the literature [3].

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TABLE 1. Total π-Electron Energies of the I-VI Molecules and of the Corresponding Anion and Cation Radicals (in eV) by the PPP (E^{PPP}) and LHP (E^{LHP}) Method*

M	$E(M)$	$-E^{PPP}(M^-)$	$-E^{LHP}(M^-)$	$-E^{PPP}(M^+)$	$-E^{LHP}(M^+)$	$I(M)$	$I^{PPP}(M)$	$I^{LHP}(M)$	$A(M)$	$A^{PPP}(M)$	$A^{LHP}(M)$
I	181,31	182,80	182,79	169,61	169,60	11,76	11,70	11,71	1,45	1,49	1,48
II	157,90	160,06	160,05	146,59	146,57	11,41	11,31	11,33	2,08	2,16	2,15
III	152,72	154,82	154,81	142,71	142,33	10,20	10,01	10,39	2,05	2,10	2,09
IV	341,87	344,38	344,35	332,06	332,05	9,85	9,81	9,82	2,46	2,51	2,48
V	316,26	319,22	319,18	306,40	306,50	9,81	9,86	9,76	2,88	2,96	2,92
VI	312,34	315,55	315,53	302,72	302,74	9,88	9,62	9,60	2,99	3,21	3,19

*The I(M) and A(M) values are the ionization potentials and electron affinities of the M molecules determined by the Koopman theorem: $I^{PPP/LHP}(M) = E^{PPP/LHP}(M^+) - E(M)$, and $A^{PPP/LHP}(M) = E(M) - E^{PPP/LHP}(M^-)$.

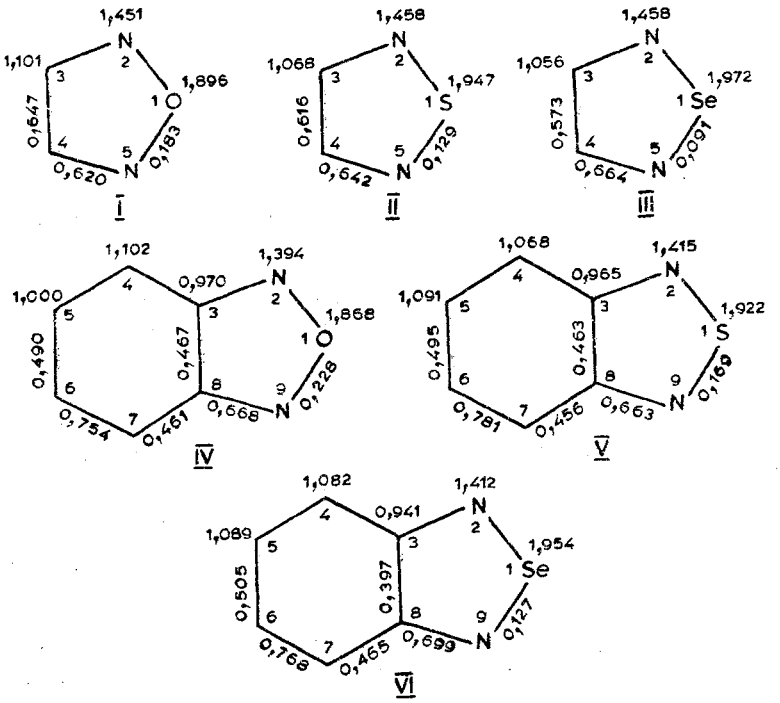

Fig. 1. Distribution of the π-electron density and bond orders in the anion radicals of the I-VI molecules found by the PPP method.

($\approx$0.01-0.04 eV) from one another. An exception to this is the cation radical of the III molecule, for which $E^{PPP}(III^+) - E^{LHP}(III^+) = -0.38$ eV. The total π-electron energies of the cation radicals of benzo-condensed molecules IV-VI decrease from oxygen to sulfur to selenium (Table 1). This result is in agreement with the results of a mass-spectrometric experiment: the fraction of molecular ions with respect to the sum of all of the ions (W) that arise from the IV-VI molecules increases in the same order and proves to be higher, the lower the store of π-electron energy of the corresponding cation. It was found that $W^{IV} = 0.26$, $W^{V} = 0.35$, and $W^{VI} = 0.49$.*

The first ionization potential [I(M)] and the electron affinity [A(M)] of the neutral molecule (M) were evaluated as the absolute value of the difference in the total π-electron energy E(M) of molecule (M) and the energy of the cation or anion radical [$E(M^{\pm})$] corresponding to this molecule. The results obtained are presented in Table 1. It is seen that the $I^{PPP}(M)$ and $I^{LHP}(M)$ values and the $A^{PPP}(M)$ and $A^{LHP}(M)$

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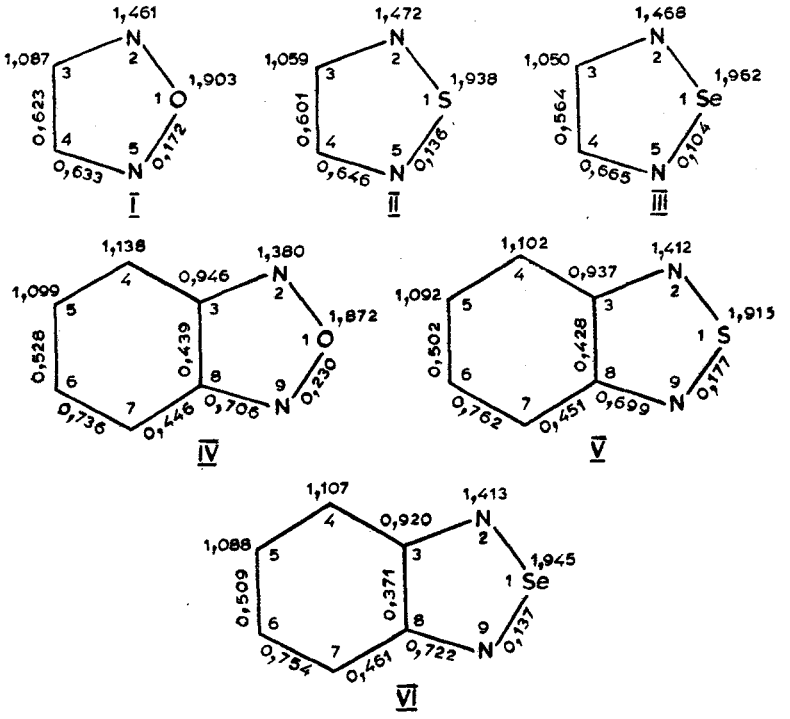

Fig. 2. Distribution of the π-electron density and bond orders in the anion radicals of the I-VI molecules found by the LHP method.

TABLE 2. Spin Densities on the Atoms in the Anion Radicals of the I-VI Molecules

Molecule	ρ^*	Atom 1	2	3	4	5
I	ρ	0,091	0,295	0,159	0,159	0,295
	ρ_{PPP}	0,104	0,322	0,127	0,127	0,322
	ρ_{LHP}	0,096	0,307	0,145	0,145	0,307
II	ρ	0,072	0,286	0,178	0,178	0,286
	ρ_{PPP}	0,053	0,316	0,158	0,158	0,316
	ρ_{LHP}	0,062	0,299	0,170	0,170	0,299
III	ρ	0,062	0,272	0,196	0,196	0,272
	ρ_{PPP}	0,029	0,301	0,186	0,186	0,301
	ρ_{LHP}	0,038	0,288	0,192	0,192	0,288
IV	ρ	0,074	0,204	0,039	0,128	0,090
	ρ_{PPP}	0,097	0,248	0,031	0,109	0,063
	ρ_{LHP}	0,074	0,197	0,028	0,146	0,091
	ρ_{exp}	—	0,220	—	0,145	0,087
V	ρ	0,071	0,225	0,067	0,092	0,079
	ρ_{PPP}	0,067	0,277	0,055	0,080	0,055
	ρ_{LHP}	0,063	0,223	0,051	0,112	0,082
	ρ_{exp}	—	0,210	—	0,107	0,066
VI	ρ	0,055	0,216	0,075	0,096	0,084
	ρ_{PPP}	0,039	0,251	0,066	0,094	0,068
	ρ_{LHP}	0,044	0,211	0,062	0,116	0,089
	ρ_{exp}	—	0,240	—	0,087	0,087

*The ρ value is the spin density determined with respect to the lower vacant orbital of the neutral molecule, the $\rho_{PPP/LHP}$ value is the spin density found by the PPP or LHP method, and ρ^{exp} values are the experimental data from [8, 9].

values are close to one another. An exception to this is the ($III^{\dagger}$) ion radical mentioned above. For comparison, the ionization potentials and electron affinities determined by the Koopman theorem are presented in Table 1. These values differ from the values found by the methods mentioned above by up to 0.3 eV.

Moreover, the electron affinity found by the PPP and LHP methods proved to be greater than the value determined from the Koopman theorem.

We note that the electron affinities [A(M)] for IV-VI determined both from the Koopman theorem and by the PPP and LHP methods increase in the order X = O, S, and Se. The difference between the energies of the ground states of the IV-VI molecules and the energies of the corresponding anion radicals determined by the PPP method also increase from oxygen to sulfur to selenium. In addition, according to the experimental data [7], reversible one-electron transfer under polarography conditions proceeds most readily for benzoselenadiazole and with greatest difficulty for benzothiadiazole; benzoxadiazole occupies an intermediate position. It is possible that the σ electrons should be taken into account explicitly in order to obtain better agreement between the results of the calculation and these experimental data. The fact is that an unpaired electron impinging on the molecule may be delocalized in the σ rather than in the π orbitals. The calculations carried out within the π approximation therefore may not always insure the desired correlation. The calculations that we carried out by the CNDO/2 method for benzoxadiazole (IV) and benzothiadiazole (V) molecules lead to an inequality in the electron affinities of the form A(V) < A(IV). This inequality is in complete agreement with the experimental data.

The π-electron densities on the atoms and the bond orders in the anion radicals of the I-VI molecules calculated by the PPP and LHP methods are presented in Figs. 1 and 2. The two methods lead to pictures of the electron density distribution that are in qualitative agreement. The spin densities (ρ_μ) on atoms μ in the anion radicals of the I-VI molecules found by the PPP method (ρ_μ^{PPP}) and the LHP method (ρ_μ^{LHP}) are presented in Table 2. The ρ_μ values determined from calculations of the neutral molecule with respect to the lower vacant orbitals are also presented in Table 2 for comparison. It follows from Table 2 that in anion radicals from five-membered heterocycles and from their benzo derivatives the spin density on the key heteroatom found by the PPP and LHP methods and determined with respect to the lower vacant orbital of the neutral molecule decreases from oxygen to sulfur to selenium. In all three of the variants it turns out that the highest spin density in the anion radicals of the I-VI molecules is found on the nitrogen atoms. The highest spin density in the six-membered ring of the anion radicals from the IV-VI molecules is found on the 4 atom, and the lowest spin density is found on the 3 atom. These results are in complete agreement with the experimental data (compare the results with the ρ_μ^{exp} values, which are also presented in Table 2).

It follows from the results of our calculations that the three methods used to calculate the fundamental characteristics of the electronic structures of the anion and cation radicals of the I-VI molecules are practically completely equivalent. However, substantial deviations are observed for the ionization potentials and the electron affinities.

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