AN INVESTIGATION IN THE FIELD OF AROMATIC HETEROCYCLES

XIX.* CALCULATION OF THE π-ELECTRONIC STRUCTURE OF BENZO AND NAPHTHO DERIVATIVES OF 1,2,5-OXADIAZOLE, 1,2,5-THIADIAZOLE, AND 1,2,5-SELENADIZOLE

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UDC 547.794:541.67

The electronic structures of benzo[c][1,2,5]oxadiazole, benzo[c][1,2,5]thiadiazole, benzo[c][1,2,5]selenadiazole, naphtho[1,2-c][1,2,5]oxadiazole, naphtho[1,2-c][1,2,5]thiadizole, naphtho[1,2-c][1,2,5]selenadiazole, naphtho[2,3-c][1,2,5]oxadiazole, naphtho[2,3-c][1,2,5]thiadiazole, and naphtho[2,3-c][1,2,5]selenadiazole have been investigated in the π-electronic approximation by the Pariser–Parr–Pople method. Molecular diagrams have been calculated and the energies of the first singlet transitions have been calculated. A correspondence has been found between the calculated results and those obtained by experiment (UV spectra, reactivities, etc.).

The electronic structure of heterocyclic molecules containing elements of group VI in the chain of conjugation is widely discussed in the literature. The O, S, and Se atoms can each supply two electrons to the general π-electron system of the molecule. It appeared of interest to investigate how the degree of participation of this pair in conjugation changes as a function of the nature of the heteroatom.

In the present paper, using the Pariser–Parr–Pople (PPP) method [2] in the multiconfigurational approximation† this problem has been solved for the case of benzo and naphtho derivatives of 1,2,5-oxadiazole, 1,2,5-thiadiazole, and 1,2,5-selenadiazole. The following compounds have been considered: benzo[c][1,2,5]oxadiazole (I); benzo[c][1,2,5]thiadiazole (II); benzo[c][1,2,5]selenadiazole (III) (group A); naphtho[1,2-c][1,2,5]oxadiazole (IV); naphtho[1,2-c][1,2,5]thiadiazole (V); naphtho[1,2-c][1,2,5]selenadiazole (VI) (group B; naphtho[2,3-c][1,2,5]oxadiazole (VII); naphtho[2,3-c][1,2,5]thiadiazole (VIII); naphtho[2,3-c][1,2,5]-selenadiazole (IX) (group C).

The electronic structure of compounds (I-III) and also of the anion radicals corresponding to them, have been studied repeatedly by the Hückel method (see, for example [3, 4]). The electronic structure of compound (I) has been studied by the PPP method [5]. However, the authors concerned [5] assumed that the six- and five-membered rings in the molecule are regular polygons with sides 1.395 Å long, which does not correspond to the actual geometry [6].

The existence of voluminous experimental material on the physical and chemical properties of the molecules (I-IX) makes an investigation of their electronic structures by the methods of quantum chemistry particularly attractive.

Choice of Parameters. The values of the first and second ionization potentials $I_X^{(j)}(\nu)$ (j = 1, 2) and of the electron affinity $A_X(\nu)$ of the valence state ν of the atom X (X = O, S, Se) used in the construction of the effective Hamiltonian in the PPP method were taken from the literature [7]. The values of the first

*For Communication XVIII, see [1].

†Configurations corresponding to all the one-electron transitions from MOs occupied in the ground state of the molecule to vacant MOs were taken into account.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1473-1478, November, 1973. Original article submitted July 28, 1972.

$[I_X^{(1)}(\nu)]$ and second $[I_X^{(2)}(\nu)]$ ionization potentials of the Se atom in the valence state $\nu = tr^2trtr\pi^2$, which are not given in this source [7], were evaluated in the following way. According to [7], we have

$$I_{Se^{(1)}}(v) = I_{Se^{(1)}}(v_0) + P_{Se^+}(tr^2trtr\pi) - P^0_{Se}(tr^2trtr\pi^2),$$

$$I_{Se^{(2)}}(v) = I_{Se^{(2)}}(v_0) + P_{Se^{2+}}(tr^2trtr) - P_{Se^+}(tr^2trtr\pi),$$

where $I_{Se}^{(k)}(\nu_0)$ is the k-th ionization potential of the ground state of the Se atom, and $P_{Se}^{k+}(\nu)$ is the energy of the promotion of the Se atom from the ground state of the cation (k+) into its valence state ν. The values of $P_{Se^+}(tr^2trtr\pi)$ and $P_{Se}^0(tr^2trtr\pi^2)$ were taken from [7]. In the determination of $P_{Se^{2+}}(tr^2trtr)$, we assumed that

$$P_{Se^{2+}}(tr^2trtr) = \frac{P_{As^+}(tr^2trtr)}{P_{As^+}(trtrtr\pi)} P_{Se^{2+}}(trtrtr\pi).$$

The values of $I_{Se}^{(1)}(\nu_0)$ and $I_{Se}^{(2)}(\nu_0)$ were determined from tables [8]. Finally, it was found that $I_{Se}^{(1)}(\nu) =$ 12.0 eV and $I_{Se}^{(2)}(\nu) = 22.14$ eV.

To estimate the one-center Coulomb integrals γ_{XX} we used the approximate formulas $\gamma_{XX} = I_X^{(1)}(\nu) - A_X(\nu)$ (for X atoms supplying the π-electronic system with one electron each) and $\gamma_{XX} = I_X^{(2)}(\nu) - I_X^{(1)}(\nu)$ (for X atoms supplying the π-electronic system with two electrons each). The two-center Coulomb integrals were determined by the Mataga–Nishimoto formulas [9]. The values of the resonance integrals β_{rs} for the r–s bond were calculated from the formula $\beta_{rs} = \beta_{rs}^0 S_{rs}(S_{rs}^0)^{-1}$, where β_{rs}^0 is the standard value of the resonance integral, and S_{rs}^0 is the overlap integral corresponding to this resonance integral. The following values were used for β_{rs}^0: $\beta_{CC}^0 = -2.39$ eV at R = 1.397 Å [10], $\beta_{CN}^0 = -2.576$ eV at R = 1.36 Å, and $\beta_{CS}^0 = -1.36$ eV at R = 1.74 Å [11]. For nitrobenzene a value of $\beta_{NO}^0 = -2.73$ eV is recommended [12]. We used a somewhat smaller value, namely −2.5 eV, for β_{NO}^0.* The values of β_{NS} and β_{NSe} were evaluated from the following formulas:

$$\frac{\beta_{NSe}}{S_{NSe}} = \frac{\beta_{NS}}{S_{NS}} = \frac{\beta^0_{CS}}{S^0_{CS}}.$$

The overlap integrals were determined from published tables [13].

For the molecules of group A, the interatomic distances and valence angles were taken as equal to their experimental values [6, 14]. For the molecules of groups B and C we assumed that in the naphthalene moieties of the molecules (IV-IX) the bond lengths and the angles between the bonds are the same as in naphthalene [15], and that in the five-membered moieties of the molecules (IV-IX) the lengths of the C–N and N–X (X = O, S, Se) bonds are equal to the corresponding magnitudes in the benzo[c][1,2,5]oxadiazoles and the corresponding thia and selena compounds; for the XNC and NCC valence angles the following values were chosen: 104°30', 110°18' (IV); 105°10', 115°03' (V); 101°37', 120°53' (VI); 105°42', 109°42' (VII); 106°23', 113°50' (VIII) 102°54', 119°34' (IX).

The results of the calculations of the electronic structures of the molecules (I-IX) are given in Tables 1 and 2 and in Fig. 1.

The calculation was performed by a published program [16] on a BÉSM-3 computer in the Computing Center of the Academy of Sciences of the USSR.

Discussion of the Results of the Calculations

UV Spectra. The experimental results for the electronic absorption spectra of the molecules of groups A and B indicate that within each group on passing from O to S and to Se a bathochromic displacement of the long-wave absorption maximum takes place [17-19]. The results of our calculation (Table 1)

*If the value of β_{NO} is determined from the relation $(\beta_{NO}/\beta_{CO}) = (S_{NO}/S_{CO})$ where β_{CO} and S_{CO} correspond to the C–O bond in furan, β_{NO} must be given a value of −1.887 eV. The value of β_{NO} that we selected is close to the arithmetic mean between this value and that proposed by Peacock [12].

TABLE 1. Wavelengths of the First Singlet Transitions for the Molecules (I-XII)

Molecule	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
λ_{max}, nm, calc.	279	308	327	320	343	353	403	455	480	180	228	291
λ_{max}, nm, exptl.	270	305	330	325	340	350	—	460	—	220	253	285

TABLE 2. Half-Wave Potentials of the Reversible One-Electron Reduction, $\varphi_{1/2}$, (experimental results) and Electron Affinities ε (calculated by the PPP method) for the Molecules (I-IX)

Molecule	I	II	III	IV	V	VI	VII	VIII	IX
$-\varepsilon$, eV	−2,46	−2,88	−2,99	−2,55	−2,91	−3,05	−3,34	−3,65	−3,79
$\varphi_{1/2}$, eV	−1,41	−1,45	−1,32	−1,43	−1,64	−1,48	—	—	—

are in full agreement with these conclusions. Furthermore, the calculated wavelengths λ_{max} of the first singlet transition are close to the corresponding experimental values. For the molecule of (VIII), which belongs to group C, the wavelength of the first singlet transition that we found is also close to the value obtained experimentally [20]. There is no information in the literature on the UV spectra of the molecules of (VII) and (IX). Consequently, on the basis of the good agreement between the results of the calculation of the molecules of groups A and B and the experimental figures it may be assumed that for the molecules of (VII) and (IX) the values of λ_{max} should be close to 403 nm and to 480 nm, respectively.

For comparison, Table 1 gives the calculated and experimental [21] wavelengths of the lowest singlet transitions for the monocyclic systems of 1,2,5-oxadiazole (X), 1,2,5-thiadiazole (XI), and 1,2,5-selenadiazole (XII).* The bond lengths and valence angles for these systems were taken from the literature [23, 24]. It can be seen from Table 1 that in the 1,2,5-X-diazole series on passing from X=O to X=S and to X=Se (from X to XII) a bathochromic shift is again observed. The agreement of the calculated and experimental values of λ_{max} in this case proved to be worse than for groups A and B, which is apparently connected with the considerably smaller number of configurations taken into account than was done for the molecules (I-IX).

By comparing the results of the calculations of the π-electronic spectra of the molecules (I-IX), it may be concluded that the long-wave shift of λ_{max} on passing from O to S and to Se is due mainly to the nature of the key heteroatom of the five-membered ring of the molecule.

Charges on the Atoms and Bond Orders. Figure 1 gives molecular diagrams for the molecules (I-IX). The value of the π-electronic charge q_X on the heteroatom X may serve as a quantitative characteristic of the degree of participation of this atom in conjugation. Within each group, the π-electronic charges q_X on the atom X decrease in the sequence X=O, S, Se, i.e., the degree of participation in conjugation falls from O to S and Se.

The influence of the six-membered ring (or the naphthalene moiety) in the molecules (I-IX) on the degree of participation of the key heteroatom in conjugation can be evaluated from the changes in the charge of this atom as compared with the corresponding five-membered heterocycle (X-XII). It follows from a comparison of the charges (Fig. 1) that in the compounds of group A the influence of the six-membered ring on the charge on the key heteroatom is not very substantial, although it also increases in the sequence X=O, S, Se. Similarly, the naphthalene moieties affect the charges on the heteroatoms of the compounds of groups B and C. It must be noted that the degree of participation of the key heteroatom in conjugation is less in the case of angular ring-fusion (group B) than in the case of linear ring-fusion (group C).

The benzene moieties (in the compounds of group A) and the naphthalene moieties (groups B and C) are π-electron donors. In all the molecules considered, the bulk of the negative charge is localized on the nitrogen atoms. The N−X bonds have the lowest order; the orders of these bonds decrease in the sequence X=O, S, Se. In the molecules of group A, the orders of the 2-3, 4-5, 6-7, and 8-9† bonds (Fig. 1) are close to the orders of double bonds, and this indicates that the structure of these molecules approximates to the quinoid type. However, some authors – for example [4, 20] – assume that in the molecules (II) and (III) the S and Se atoms are tetravalent and the N−S and N−Se bonds are multiple. It follows from our calculation that such a hypothesis is incorrect: the N−S and N−Se bonds have the lowest orders and, moreover, the orders of the C−N bonds are close to the orders of double bonds.

Electron Affinity and Ionization Potential. A quantitative characteristic of the ease of electrochemical reduction is the half-wave potential $\varphi_{1/2}$. In MO theory, the values of the electron affinity of the mol-

*The electronic structures of the molecules of (X) and (XI) have been investigated by the PPP method by Phan-Tan-Luu [22], for example, but using a different method for evaluating the parameters.
†In Fig. 1, the numbers of the atoms, beginning with the key heteroatom and including the C atoms of the adjacent bonds, run counterclockwise.

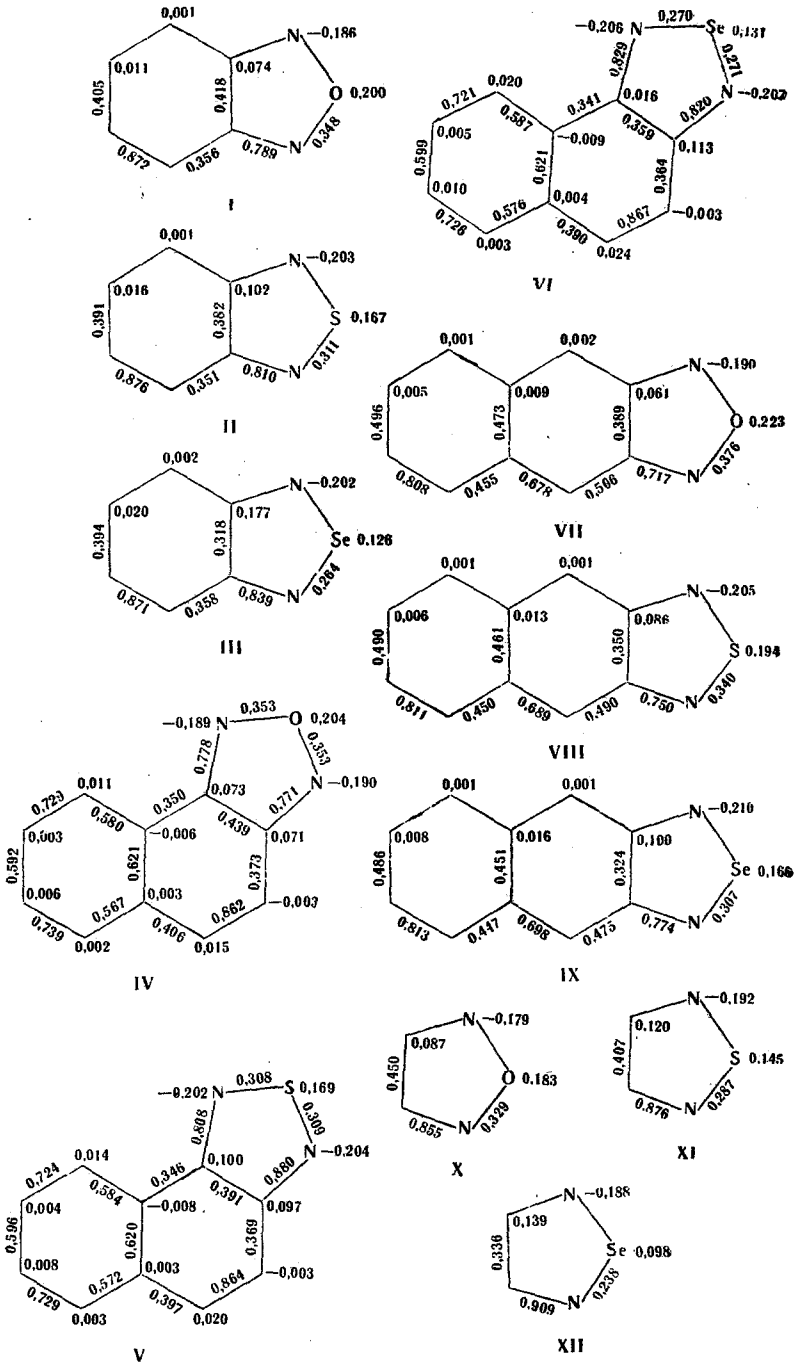

Fig. 1. Molecular diagrams of the molecules (I)-(XII).

ecule calculated by means of Kupman's [sic; Kooyman's?] theorem are generally compared with $\varphi_{1/2}$ of reversible one-electron transitions. Table 2 gives the values $\varphi_{1/2}$ found for the molecules of group A experimentally [25] and confirmed by the work of other authors [26]. In group A, the molecule (III) has the highest electron affinity (2.99 eV), and for (II) this value is 2.88 eV, which is in harmony with the experimental results. At the same time, according to calculation, (I) is characterized by a smaller electron affinity (2.46 eV) than (III). This does not correspond to the relationship between the experimental values of the half-wave potentials. It is possible that for the systems considered with the figures for the parameters that we selected, the values of $\varphi_{1/2}$ should be compared quantitatively not with the energy of the lowest vacant orbital (which gives a fairly rough estimate of the electron affinity of the molecule) but with the magnitude obtained as the difference in the energies of the gound state of the molecule and the energy of the ground state of the anion radical corresponding to it calculated by the PPP method for systems with open shells. However, we did not perform such a calculation in the present work, and we propose to do it in the future.

As can be seen from Table 2, the available experimental values of $\varphi_{1/2}$ for the molecules of groups B and C [26-28] do not fully correlate with the calculated values.

The calculation of the limiting electron densitities $q_{m,r}=2c_{m,r}^2$, where $c_{m,r}$ is the coefficient for the highest occupied MO at the AO of the r-th atom, showed that, for the molecules of group A, atoms 4 and 7 have the highest values of $q_{m,r}$. According to the literature [29], positions 4 and 7 should prove the most favorable for electrophilic attack. This conclusion is in full agreement with the experimental results [17]. For the molecules of group B, positions 11 and 6, and for the molecules of group C, positions 4 and 11 are also the most favorable for electrophilic attack from the point of view of limiting electron densities. It is possible to explain certain experimental facts [20, 30-32] in this way. In the sulfonation and chlorination of (IV), substitution takes place mainly in position 11 [30, 31]. The bromination and sulfonation of (V) are also directed to position 11 [32]. The nitration of (IV) gives, mainly, the 6- and 8-nitro derivatives [13] and that of (V) gives the 5- and 8-nitro derivatives [32]. Experiment shows that in the processes of electrophilic substitution the most active positions are 11 and 6. The entry of a nitro group into the α position of the molecule (IV) and of (V) is apparently explained by the specific nature of nitration. As a rule, in the nitration of naphthalene derivatives the nitro group binds just to a carbon atom in the α position. This rule is apparently also valid for the naphthalene moiety of the naphthodiazoles.

Known facts on the reactivity of (VIII) are also in harmony with our predictions. On its reaction with N-phenylmaleimide and on its rapid oxidation with sodium dichromate in acetic acid, the C_4 and C_{11} atoms are involved [20].

In the present work no use was made of the vacant d orbitals for the S and Se atoms, and therefore their influence on the results of the calculations is not discussed. At the same time, it can be seen that for the molecules (I-IX) it is possible to manage without broadening the basis and with involving the d orbitals of the S and Se atoms and to obtain results agreeing with those of experiment.

In conclusion, we express our gratitude to D. A. Bochvar and A A. Bagatur'yants for a discussion of the results obtained.

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