ARYLENEAZACHALCOGENENES.

2.* PHOTOELECTRON SPECTRA AND ELECTRON STRUCTURES OF BENZO-2,1,3-THIA- AND -SELENADIAZOLES AND THEIR PERFLUORO DERIVATIVES

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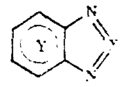
The He(I) photoelectron spectra of benzo-2,1,3-thia- and -selenadiazoles and their perfluoro derivatives were measured and interpreted on the basis of calculations by the MNDO method, the π-fluoro effect, and an analysis of the vibrational structures and relative intensities of the bands. It was observed that replacement of the sulfur atom by a selenium atom leads to only slight changes in the ionization energies of the π MO. This confirms the previous conclusion that replacement of one chalcogen by another has a small effect on the π-electron structures of the molecules of these heteroaromatic compounds.

Previously, on the basis of indirect vibrational-spectroscopic data, it was concluded that the transition from benzo-2,1,3-thiadiazole (I) and 4,5,6,7-tetrafluorobenzo-2,1,3-thiadiazole (II) to benzo-2,1,3-selenadiazole (III) and 4,5,6,7-tetrafluorobenzo-2,1,3-selenadiazole (IV) is accompanied by only slight changes in the π-electron structures of the molecules [1].



I- IV

I, II X=S, III, IV X=Se; I, III Y=H, II, IV Y=F

The aim of the present research was to make a further study of the effect of replacement of the S atom by an Se atom on the electron structures of I-IV molecules. The vertical ionization energies (IE)[†] of these substances were measured by He(I) photoelectron (PE) spectroscopy, and their assignment within the Koopmans approximation [2] was based on calculations by the MNDO method, the π-fluoro effect [2], and an analysis of the vibrational structures and relative intensities of the spectral bands (see Table 1 and Fig. 1). The spectra of I and III were previously published [3, 4].

It follows from Fig. 1 that the spectra of I-IV have similar structures; groups of 1-2, 3-5, and 6-8 bands at 8-15 eV can be isolated in them; bands 6-8 in the spectra of I and III overlap markedly. Bands 1 and 2 in the spectra of all of the investigated compounds correspond to ionization from one MO each, while the group of 3-5 bands undoubtedly corresponds to ionization from three MO. The ratios of the overall intensity of bands 6-8 to the overall intensity of bands 3-5 are 1.61, 1.54, 1.55, and 1.25 for the spectra of I-IV, respectively. If one takes into account the errors in the determination of the intensities and the difference in the ionization cross sections of the hydrocarbon and fluorocarbon analogs, it may be concluded that the number of MO corresponding to bands 6-8 for I-IV is the same and is equal to at least four. Thus the examination encompasses 9-10 upper MO of each investigated compound.

The MO calculations of I and II by the MNDO method performed in [1] and in the present research for various molecular geometries (experimental and partially optimized in [1], model in the present research) and sets of parameters (standard for C, H, N, and F and improved for S in [1], standard in the present research) lead to somewhat different sequences of the MO and the absolute values of their energies; this indicates the special importance in this case of an analysis of the forms of the bands and of taking into account the empirical regularities in a series of related compounds.

It follows from the data in [4], the MNDO calculations performed in [1] and in the present study, and a comparison with the spectrum of a perfluorinated analog that bands 1 and 2 in the spectrum of I are associated with the removal of an electron from the $2a_2$ and $3b_1$ π MO, respectively. The vibrational structure of band 1 with frequency $\nu 1360 \pm 80\ \mathrm{cm}^{-1}$ confirms this interpretation. In the ground state of the neutral I molecule, $M(\tilde{X})$, ν_{CC}

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[*] See [1] for Communication 1.

[†] They correspond to the maxima of the intensities of the spectral bands.

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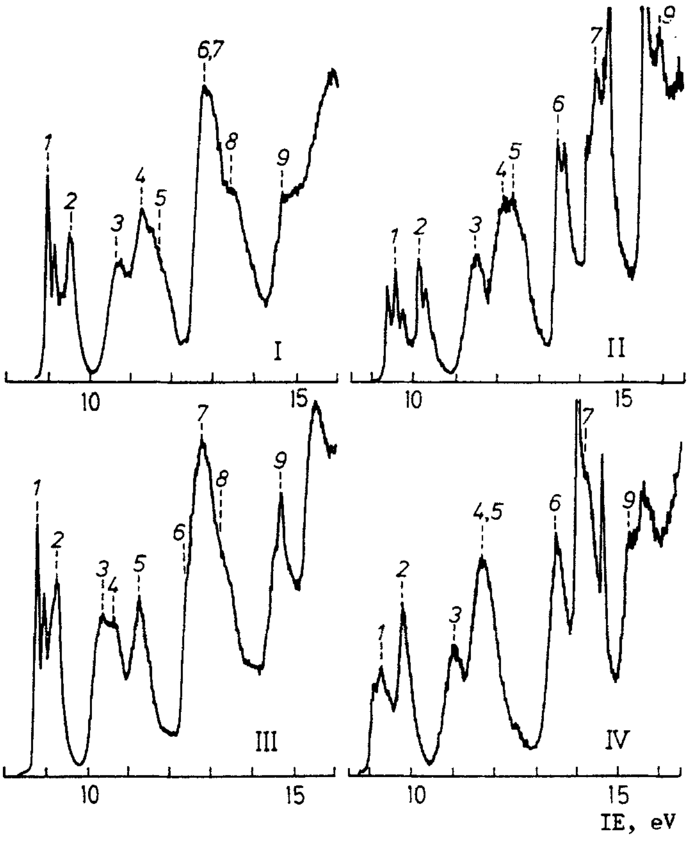

Fig. 1. He(I) photoelectron spectra of I-IV.

TABLE 1. Ionization Energies of I-IV

Compound	Ionization energy (eV) in the assignment of*								
	1, $a_2(\pi)$	2, $b_1(\pi)$	3, $b_2(\sigma N)$	4, $a_2(\pi)$	5, $a_1(\sigma N)$	6, $b_1(\pi)$	7, $a_1(\sigma X)$**; b_2	8, a_1	9, $b_1(\pi)$
I	9,00	9,56	10,69	11,28	11,70	12,78	—	13,45	14,67
II	9,51	10,08	11,45	12,10	12,35	13,41	14,35	—	15,80
III	8,76	9,24	10,36	10,62	11,25	12,41	12,76	13,30	14,65
IV	9,28	9,79	11,01	11,68	—	13,50	14,26	—	15,30

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*Note that 1-9 are the band numbers.

**I, II X = S; III, IV X = Se.

stretching vibrations of the carbocycle, which interact strongly with the ν_{CN} stretching vibrations, appear in this region [1]. The symmetry and localization of this vibration are similar to those for the wave function of the $2a_2$ highest occupied molecular orbital (HOMO) according to the results of MNDO calculations. Bands 3-5 are associated with ionization from three orbitals: one π MO and two σ MO, which are the antibonding (b_2) and bonding (a_1) combinations of the orbitals of the unshared electron pairs (UEP) of the N atoms. According to [4] and the MNDO calculations performed in [1], the sequence of these MO is $b_2(\sigma N)$, $1a_2(\pi)$, $a_1(\sigma N)$, as compared with $1a_2(\pi)$, $b_2(\sigma N)$, $a_1(\sigma N)$ according to the results of the calculations performed in the present study. According to the calculated data in [4], the splitting between the b_2 and a_1 orbitals is 0.74 eV, while the calculations performed in the present study give 0.65 eV. For a simpler related compound — 1,2,5-thiadiazole — the splitting according to the results of nonempirical calculations should be 1.11 eV (the experimental value is 0.56 eV) [5]. Proceeding from this value of the splitting of the orbitals of the UEP of the N atoms one should adopt the sequence $b_2(\sigma N)$, $1a_2(\pi)$, $a_1(\sigma N)$. Bands 6-8 probably correspond to the $2b_1$ π MO and three σ MO, including the $a_1(\sigma S)$ orbital of the UEP of the S atom. It follows from a comparison with the spectrum of perfluoro analog II that band 9 is related to the $1b_1(\pi)$ MO, which, according to the MNDO data, is virtually completely localized in the five-membered ring.

In the spectrum of II bands 1 and 2, which are shifted ≈0.5 eV to the higher-IE region as compared with the spectrum of I, are related to the $4a_2$ and $5b_1$ π MO, respectively. Bands 3-5, with retention of the intensity ratio and mutual orientation, are also shifted ≈0.75 eV to the higher-IE side. They are related to the $b_2(\sigma N)$, $3a_2(\pi)$, and $a_1(\sigma N)$ MO, which are extremely similar with respect to the form of the wave functions to the corresponding MO of I. According to the calculated data, the splitting between the b_2 and a_1 orbitals of the UEP of the N atoms in II should be greater than in I. Proceeding from this, band 3 should be assigned to the $b_2(\sigma N)$ MO, while bands 4 and 5 should be assigned to the $3a_2(\pi)$ and $a_1(\sigma N)$ MO. Band 6 in the spectrum of II is located at the site of a large area of overlapped bands in the spectrum of I; within the framework of the model of the π-fluoro effect this indicates π symmetry of the corresponding MO. Its vibrational structure with ν 1370 ± 80 cm^{-1}, which is equal to the frequency of the vibrations observed in band 2, makes it possible to assign band 6 to the $4b_1(\pi)$ MO. The $a_1(\sigma S)$ σ MO of the UEP of the S atom and two σ MO with b_2 and a_1 symmetry, delocalized primarily over the benzene fragment, can be placed in conformity with band 7. Band 9 is related to the $3b_1(\pi)$ MO, which is analogous to the $1b_1(\pi)$ MO of I. The stabilization of this MO on passing from I to II is considerably greater than the stabilization of the HOMO, which, considering their localization in the five- and six-membered rings of the molecule, respectively, is in agreement with the compensation model of the π-fluoro effect [2].

It follows from the results of a comparison with the spectrum of perfluorinated derivative IV that bands 1 and 2 in the spectrum of III are related to ionization from the $2a_2$ and $3b_1$ π MO, respectively. The vibrational structure of band 1 with ν 1360 ± 80 cm^{-1} confirms this assignment. In the $M(\tilde{X})$ state of III ν_{CC} stretching vibrations of the carbocycle appear in this region [1]. Bands 3-5 are related to ionization from two σ MO (UEP of the N atoms) and the $1a_2$ π MO, bands 6-8 are related to ionization from the $2b_1$ π MO and three σ MO, and band 9 is related to ionization from the $1b_1$ π MO.

In the spectrum of IV bands 1-3 are related to the $4a_2(\pi)$, $5b_1(\pi)$, and $b_2(\sigma N)$ MO, respectively. The vibrational structure of band 1 with ν 1450 ± 80 cm^{-1} confirms its identification. In the $M(\tilde{X})$ state of IV ν_{CC} stretching vibrations of the carbocycle, which interact strongly with the ν_{CN} stretching vibrations, appear at 1460-1480 cm^{-1} [1]. As a result of a comparison with the spectrum of III, bands 4-6 can be assigned to the $3a_2(\pi)$, $a_1(\sigma N)$, and $4b_1(\pi)$ MO, respectively. The assignment of band 6 to the $4b_1(\pi)$ MO is completely unequivocal in view of the clear manifestation of a π-fluoro effect.

Thus the transition from I to III and from II to IV is accompanied by only slight changes in the forms and positions of the maxima of bands 1-9 in the photoelectron (PE) spectra at 8-16 eV; this was previously noted for I and III [4]. In [6] it was established that the same such slight changes in the IE accompany the transition from I to quinoxaline V, on the basis of which it was concluded that the S atom of I behaves like a C=C fragment, i.e., it provides two electrons for the formation of a heteroaromatic π system.* According to [4] and the present study, this conclusion is also extended to the Se atom of III. On the whole these results mean that: 1) replacement of the S atom of I and II by an Se atom does not give rise to substantial changes in the π-electron structures of the molecules; 2) I and III are heteroaromatic systems, like V; 3) in examining the electron structures of compounds such as III and IV one can use data (for example, MNDO calculations, PE spectra) obtained for their thia analogs.

According to the assumption made by Palmer and Kennedy [4], the similarity in the electron structures of the I and III molecules is a consequence of the great closeness of the energies of the valence AO and electronegativities of the S and Se atoms. If this were the only reason, the same sort of situation would also be observed in series of acyclic analogs of I-IV. However, replacement of the S atom of 1,3-disubstituted 1,3-diaza-2-thiaallenes by an Se atom leads to pronounced thermodynamic destabilization of the substances [8-12]. In addition, structural differences, particularly the considerably greater length of the NX bond in heterocycles containing the —N=X=N— fragment when X = Se as compared with X = S (see [13] and the literature cited therein), were not taken into account in [4]. Hence it may be concluded that a factor more important than those noted in [4], namely a factor that equalizes their electron structures — heteroaromatic character — is active in the I-IV molecules.

Thus the results of the present research confirm the conclusions in [1] regarding the heteroaromatic character of I-IV and that replacement of one chalcogen by another has a small effect on the π-electron structure of the molecules of these compounds.

EXPERIMENTAL

Compounds I-IV were synthesized by the method in [1]. The He(I) photoelectron spectra were measured with an ÉS 3201 spectrometer at 20-100°C. The calculations by the MNDO method were made with the standard

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*Let us also note the closeness of the spin-density distributions and the D and E parameters for the triplet states of I and V [7] and the great similarity in their UV spectra [λ_{max}, nm (log ε)]: 313 (3.37), 306 (3.76), and 232 (4.25) for V; 311 (4.14), 305 (4.14), and 224 (4.25) for I.

parametrization [14] for the model geometry. The bond lengths and bond angles were as follows: C–C 1.44, C–H 1.14, C–F 1.33, C–N 1.44, and N–S 1.56 Å; C–C–N 120° and C–N–S 130°.

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