The PE Spectra of the Seleno Analogues of Thieno[3,4-*b*]thiophene

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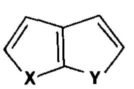
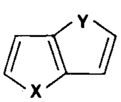
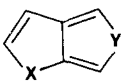
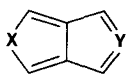
The He(I$_\alpha$) photoelectron (PE) spectra of the three isomeric seleno analogues 7, 8, and 11 of thieno [3,4-*b*]thiophene have been recorded. The first four bands can be assigned to ionizations from π-MO's by comparing their energies with the calculated orbital energies derived from HMO and PPP calculations. The small changes of ionization energies of the three compounds can be rationalized in terms of first-order perturbation theory.

Among the four isomeric thienothiophenes (**1** to **4**), thieno[2,3-*b*]thiophene (**1**)[1)] and thieno[3,2-*b*]thiophene (**2**)[2)] have been known as stable compounds for many years. The most unstable one in this series is thieno[3,4-*c*]thiophene (**4**), which has so far escaped all efforts to isolation[3)], but is known in the form of its tetraaryl-[4)], its tetraester-[4)], and its tetrakis(alkylthio) derivatives[5)].









	X	Y		X	Y		X	Y	
1	S	S	**2**	S	S	**3**	S	S	**4**: X = S, Y = S
5	S	Se	**6**	S	Se	**7**	S	Se	
9	Se	Se	**10**	Se	Se	**8**	Se	S	
						11	Se	Se	

Thieno[3,4-*b*]thiophene (**3**) stands on the stability scale between the extremes, having been isolated recently by Wynberg and Zwanenburg as an unstable oil[6)]. Also its seleno analogue **7**[7)], which has been available only lately, resembles **3** in its stability, while **8**[8)] and **11**[9)] appear to be rather stable compounds.

In connection with our investigations of the spectroscopic properties of fused thiophenes[10,11)] and their seleno analogues[12)], we were interested in the spectroscopic properties of **7**, **8**, and **11**. In this paper we report our results of investigations of their photoelectron (PE) spectra.

The PE spectra of **7**, **8**, and **11** are shown in Figure 2. The vertical ionization energies ($I_{v,j}$'s) of the first bands are collected in Table 1, together with the energies of the highest occupied molecular orbitals (MO's) calculated using the HMO[13)] and PPP[15)] methods.

As seen from Figure 2, the PE spectra of all three compounds look very similar, and only small changes of the band positions are found. This was anticipated owing to the very similar electronegativity of sulfur and selenium and has been encountered previously in the case of **1**, **2**, **5**, **6**, **9**, and **10**[12)]. To interpret the PE spectra, we make use of Koopmans' theorem[16)] by assuming that the calculated negative values of the orbital energies ($-\varepsilon_j$) derived for the

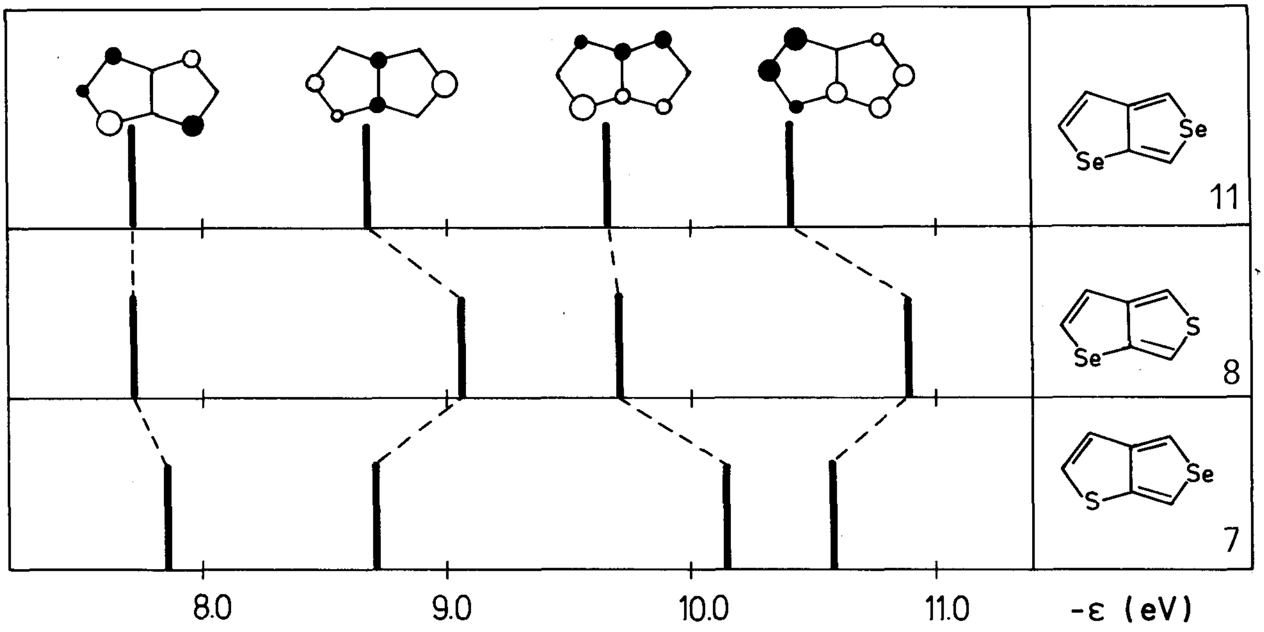


Fig. 1. Correlation between the highest occupied π-MO's of **7**, **8**, and **11** according to the HMO procedure. The corresponding wave functions for **11** are shown schematically

ground state can be set equal to the recorded vertical ionization energies ($I_{v,j}$).

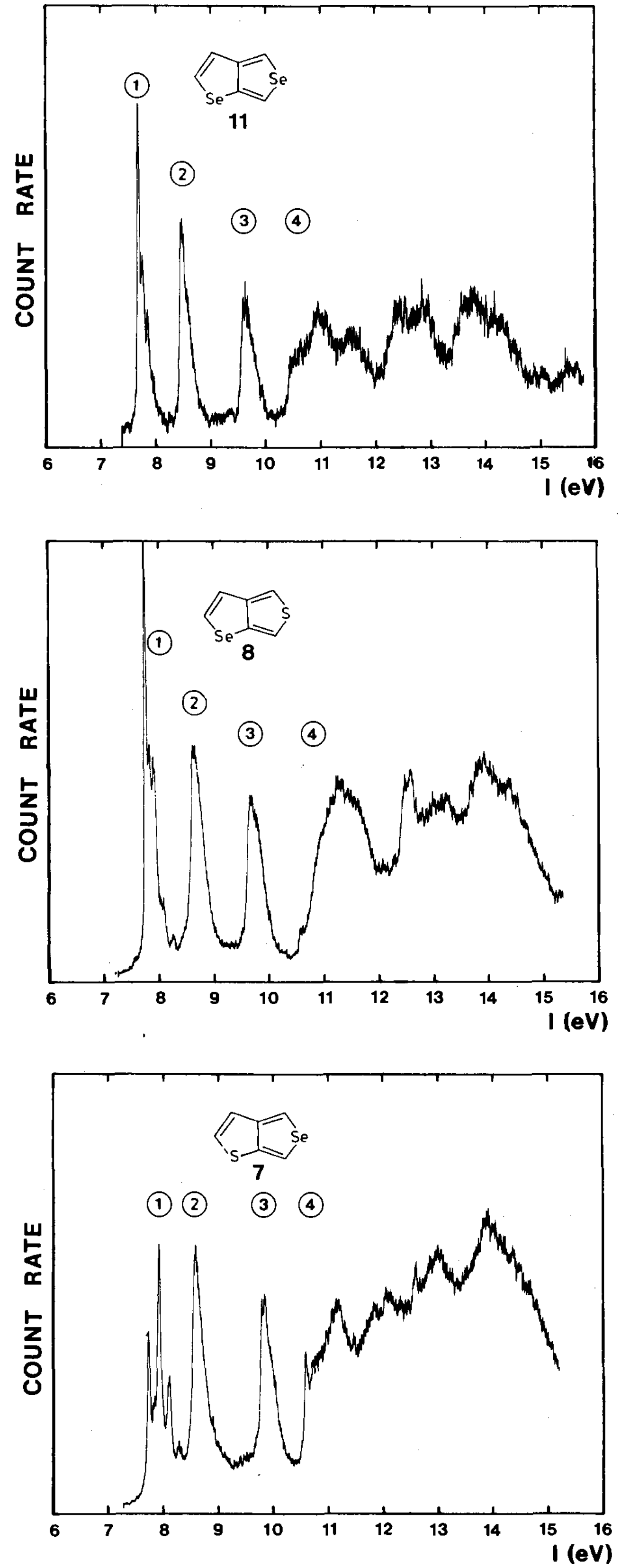


Fig. 2. He(I) PE spectra of **7**, **8**, and **11**

Table 1. Measured vertical ionization potentials ($I_{v,j}$) and orbital energies (ε_j) for **7**, **8**, and **11**. Values in eV

Compound	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$(HMO)	$-\varepsilon_j$(PPP)
	1	7.69	5a″(π)	7.72	8.44
	2	8.49	4a″(π)	8.68	9.62
11	3	9.63	3a″(π)	9.67	10.46
	4	10.9	2a″(π)	10.42	11.38
	1	7.76	5a″(π)	7.72	8.41
	2	8.64	4a″(π)	9.06	9.49
8	3	9.72	3a″(π)	9.71	10.40
	4	11.5	2a″(π)	10.89	11.50
	1	7.91	5a″(π)	7.86	8.22
	2	8.60	4a″(π)	8.71	9.58
7	3	9.85	3a″(π)	10.15	10.44
	4	10.8	2a″(π)	10.59	11.42

We will start our discussion with the PE spectrum of **11**. A comparison of the measured $I_{v,j}$'s with the calculated orbital energies (see Table 1) indicates that the first three ionization bands appearing below 11 eV correspond to an ionization from π orbitals. Such an assignment is in line with band shapes (steep onset) and is corroborated by the results of the spectroscopic investigations of selenoloselenophenes **9** and **10**[12]. The first σ band in the PE spectra of the latter compounds is found above 11 eV. Assignment of the particular ionization band to the ionization from the highest σ level in **11** is precluded owing to strong overlapping of the ionization bands around 11 eV.

Comparing the position of the first three PE bands (Table 1) in the series **11**, **8**, and **7**, we observe a gradual shift towards higher energy values for band ① and ③, while band ② moves first toward higher binding energy and then falls slightly down again. Perusal of the calculated orbital energies for the series reveals that theoretical results, particularly those obtained by using the HMO procedure, also reproduce this trend (see Figure 1).

Most of the observed shifts can be understood in terms of simple first-order perturbation theory[17] applied to the HMO's of **11**. Namely, the first- and the third-highest occupied MO's which have significantly smaller amplitudes on the selenium at position 5 than at position 1 (see Figure 1), are expected to be more affected by replacement of the selenium in the latter case. This is exactly what is observed in the measured spectra **7**, **8**, and **11**. In contrast, the SHOMO of **11** has a larger coefficient at position 5 than at position 1, resulting in a more pronounced stabilization on going from **11** to **8** than from **11** to **7**. The same approach was also successfully applied in rationalizing the changes in the measured $I_{v,j}$'s caused by successive replacements of one or both selenium atoms in **1** and **2**, respectively[12]. The satisfactory performance of the perturbed HMO model for the whole series of isomeric heteropentalenes **1**–**11** lends further support to its basic underlying concepts.

Finally, in view of the recent interest in reactivity[3] of selenophenes **9**, **10**, and **11**, it is of some importance to note that the latter compound possesses the highest-lying HOMO. The $I_{v,j}$'s of the first ionization event in **9** and **10** are 8.16 and 8.05 eV, respectively, which is approximately 0.5 eV higher than the first $I_{v,j}$ of **11**. The same holds for **7** and **8** and their counterparts in the series **1**–**5**–**9** and **2**–**6**–**10**, respectively. Hence, an enhanced reactivity of the [3,4-*b*]-annulated selenophenes (or their sulfur analogues) relative to the [2,3-*b*]- and [3,2-*b*]-fused systems in the frontier-orbital-controlled reactions could be expected[18].

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Experimental

The compounds **7**, **8**, and **11** were prepared according to the procedures described in the literature[7-9]. The PE spectra were recorded on a PS 18 photoelectron spectrometer equipped with a He(I) source (Perkin-Elmer, Ltd., Beaconsfield). The spectra were calibrated with argon and xenon, and a resolution of about 20 meV on the argon line was obtained. Each spectrum was recorded several times to ensure reproducibility of the results.

CAS Registry Numbers

7: 74070-00-1 / **8**: 33880-20-5 / **11**: 250-71-5

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[182/87]