Reversal in the Sequence of Two Highest Occupied Molecular Orbitals in the Series Thiophen, Selenophen, and Tellurophen†

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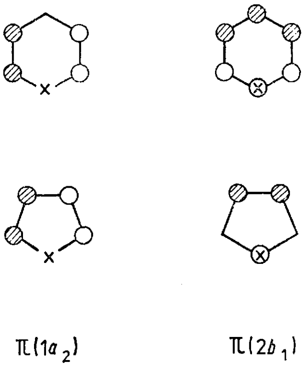
Summary It is shown by photoelectron spectroscopy that the two highest occupied MOs reverse their sequence from thiophen [$\pi(1a_2)/\pi)2b_1)$] through selenophen to tellurophen [$\pi(2b_1)/\pi(1a_2)$].

THE sequence of the two highest occupied MOs in pyridine and thiophen (**4**) is $\pi(1a_2)/\pi(2b_1)$ (*cf.* representation of the two MOs).[1,2] Recently we have detected and proved the inverse sequence $\pi(2b_1)/\pi(1a_2)$ for phosphorin (**1**) and arsenin (**2**);[3,4] this has also been confirmed for antimonin[5] (**3**). We report here the photoelectron (PE) spectra of (**4**), selenophen (**5**), and tellurophen (**6**) which show that there is a similar reversal in the sequence of the two highest occupied MOs in this series (Figure).



The broad resolved band (A) in the PE spectrum of (**4**) corresponds to the $\pi(1a_2)$ MO while the narrow band (B) is due to ionization from the $\pi(2b_1)$ MO. Band (C) was assigned to the lowest occupied $\pi(1b_1)$ MO (*cf.* representation of this MO).[2] On inspection of the bandshapes we must assume that broad bands (A) in the PE spectra of (**5**) and (**6**) and band (A) [attributed to ionization from the

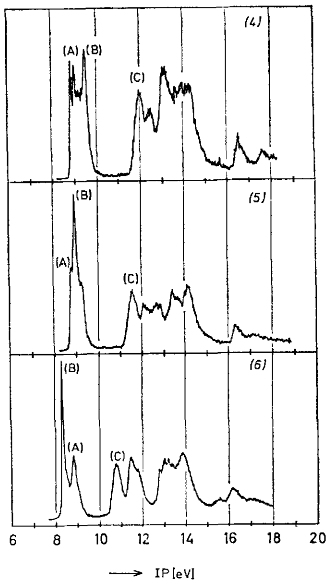


FIGURE. *Photoelectron spectra of thiophen* (**4**), *selenophen* (**5**), *and tellurophen* (**6**). *Measured vertical ionization potentials* (*in* eV):

(**4**): (A) 8·87, (B) 9·52, (C) 12·1;[2]
(**5**): (A) 8·80, (B) 8·95, (C) 11·6;
(**6**): (A) 8·81, (B) 8·27, (C) 10·8.

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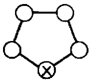
† For previous papers in the series: 'Theory and Application of Photoelectron Spectroscopy,' see: C. Müller and A. Schweig, *Tetrahedron*, in the press.

$\pi(1a_2)$ MO] in the spectrum of (**4**) are equivalent. Similarly we must assign the narrow bands (B) to the $\pi(2b_1)$ MO. Finally we assume bands (C) in the spectra of (**5**) and (**6**) to correspond to band (C) [attributed to ionization from the $\pi(1b_1)$ MO] in the spectrum of (**4**). This assignment implies (i) that in tellurophen (**6**) the two highest occupied π MOs have the inverse sequence $\pi(2b_1)/\pi(1a_2)$ to those in thiophen (**4**) and (ii) that in selenophen both MOs are nearly degenerate. Our arguments for this assignment and thereby for the reversal of the two highest occupied MOs in the series of compounds (**4**)—(**6**) are as follows:

(i) Narrow bands (B) are characteristic for MOs with a high p_π contribution on X (X = S, Se, Te).[6,7]‡

(ii) The assignment of the broad band (A) to ionization from the $\pi(1a_2)$ MO is in agreement with the observed constant position of this band throughout the spectra of (**4**)—(**6**). The $\pi(1a_2)$ MO has a node at X (X = S, Se, Te) and thus can be influenced only by at best a small inductive effect from the heteroatoms.

(iii) In contrast to the $\pi(1a_2)$ MO the energy of the $\pi(2b_1)$ and $\pi(1b_1)$ MOs may be directly influenced by the energy of the conjugative coupled p_π AOs on the heteroatoms. The ionization potentials corresponding to the narrow band (B) [due to ionization from the $\pi(2b_1)$ MO] and those corresponding to bands (C) [due to ionization from the $\pi(1b_1)$ MO in (**4**)] can be plotted against the first ionization potentials of the compounds H_2X (X = S, Se, Te) (due to ionization from the p_π lone pair MOs).[7] In both cases straight lines are obtained with nearly the same slopes. This result clearly supports the assignment of the narrow bands to the $\pi(2b_1)$ MOs and of the bands (C) to the $\pi(1b_1)$ MOs.



$\pi(1b_1)$

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‡ According to a CNDO/2[8] calculation the $\pi(2b_1)$ MO is already 80% localized on the sulphur atom in (**4**).

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