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# IONIZATION ENERGIES OF SELENOPHEN, TELLUROPHEN AND SOME OF THEIR DERIVATIVES

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The ionization energies of selenophen, tellurophen and a number of derivatives have been determined by the electron impact technique. Comparison of the values obtained for tellurophen with those referring to the other 5-membered rings reveals two major differences: (1) the IP of the unsubstituted tellurophen is significantly lower than that of its congeners; (2) the sensitivity to substituent effects is much smaller. The peculiar behaviour of tellurophen with respect to the other congener systems can be explained by admitting that a different molecular orbital is involved in the first ionization process of this ring. This is confirmed by photoelectron spectroscopy measurements.

## 1. Introduction

Tellurophen, a novel interesting heterocyclic system recently synthesized [1–3], has been the object of numerous investigations in our and other laboratories.

Studies concerning the geometry [4–6], the dipole moment [7], the reactivity [2,8,9], the "ground state aromaticity" [10], the spectral properties [2,5,6,11] and the sensitivity of this ring to substituent effects [12] have been published in the last two years. Many of these studies have been of comparative nature and have shown that many properties of tellurophen can be predicted by knowing the properties of the other congener rings: furan, thiophen, and selenophen.

In the present paper, the ionization energies (IP) of tellurophen and a number of its derivatives are reported and compared with those of analogous derivatives of furan, thiophen and selenophen, previously published [13]. Data on some additional selenophen derivatives are also reported.

## 2. Results and discussion

The ionization energies, determined by the electron impact technique, are reported in table 1.

Comparison with the data [13] referring to furans, thiophens and selenophens reveals two major differences.

(1) As concerns the unsubstituted rings, thiophen, furan and selenophen exhibit ionization energies of comparable value (9.12, 8.99 and 9.01 eV, respectively). On the contrary, the value observed for tellurophen is significantly lower, 8.60 eV.
(2) The sensitivity to substituent effects is much less pronounced in tellurophen than in the other rings.

Plots of the IP's of furans, selenophens and telluro-

Table 1
Ionization energies of tellurophen and selenophen derivatives obtained by electron impact (eV)

| No. | Substituent | Selenophen | Tellurophen |
|---|---|---|---|
| 1 | $SCH_3$ | – | 8.15 |
| 2 | $CH_3$ | 8.38 | 8.25 |
| 3 | H | 9.01 a) | 8.60 |
| 4 | $CO_2CH_3$ | 9.30 a) | 8.64 |
| 5 | $CO_2H$ | 9.25 | 8.80 |
| 6 | CHO | 9.47 a) | 8.88 |
| 7 | $COCF_3$ | 9.64 a) | – |
| 8 | $COCH_3$ | 9.30 a) | 8.60 |

a) Ref. [13].

phens against the IP's of thiophens have slopes of 1.22, 1.14 and 0.52, respectively.

The latter two are reported in fig. 1, the former one was reported in a previous paper [13].

The different behaviour of tellurophen can be explained by admitting that a different molecular orbital is involved in the first ionization process of this ring.

To a first approximation, neglecting the contribution of the d-orbital of sulphur, selenium and tellurium, the three occupied $\pi$-molecular orbitals of 5-membered heterocyclic compounds arise from the interaction between the heteroatom p orbital and the orbital of the butadiene moiety having the correct symmetry. They have the form illustrated below [14].

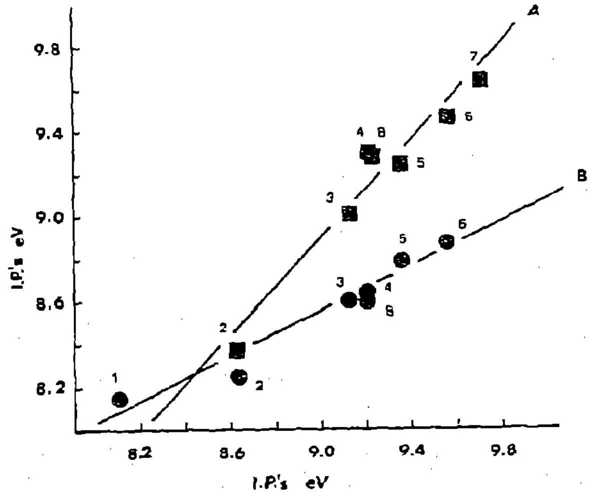
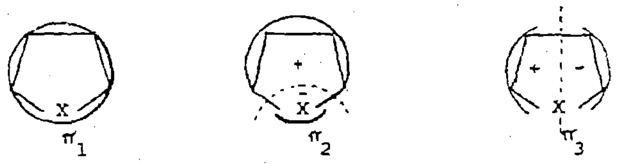


Fig. 1. Plots of ionization energies of monosubstituted selenophens (A) [and tellurophens (B)] versus those of monosubstituted thiophens. The numbers identify the substituents (see table 1).



The orbital $\pi_1$ is that of lower energy for all the systems considered and surely it is not involved in the first ionization process.

The $\pi_2$ orbital has, besides the molecular plane, another nodal surface perpendicular to it, being bonding between the carbon atoms and anti-bonding between the carbons and the heteroatom. Its energy depends markedly on the nature of the heteroatom and in particular *increases as the electronegativity decreases* [14].

The $\pi_3$ orbital has a nodal plane passing through the heteroatom and, unlike the $\pi_2$ one, extends exclusively over the carbon atoms. Consequently, its energy should be approximately independent of the electronegativity of the heteroatom. The experimental data can therefore be interpreted assuming that:

(i) In furan, thiophen and selenophen the $\pi_3$ orbital is that of higher energy and the electron is expelled from it in the first ionization process. This is in agreement with the fact that the first ionization energies and the substituent effects are similar for the three rings.

(ii) In tellurophen, because of the smaller electronegativity of tellurium atom, the energy associated with the $\pi_2$ orbital becomes higher than that associated with the $\pi_3$ orbital. Consequently, the less firmly bound electron pertains to the $\pi_2$ orbital and therefore its IP is appreciably lower. The lower sensitivity to substituent effects is in agreement with a relevant participation of the tellurium lone pair to this orbital.

The inversion of the highest filled orbitals in tellurpohen is confirmed by the comparison of the photoelectron energy spectra of the four congeners. The furan and thiophen spectra have been previously reported [15, 16], those of selenophen and tellurophen are shown in figs. 2a and 3a, respectively. Figs. 2b and 3b show the first two bands in enlarged scale.

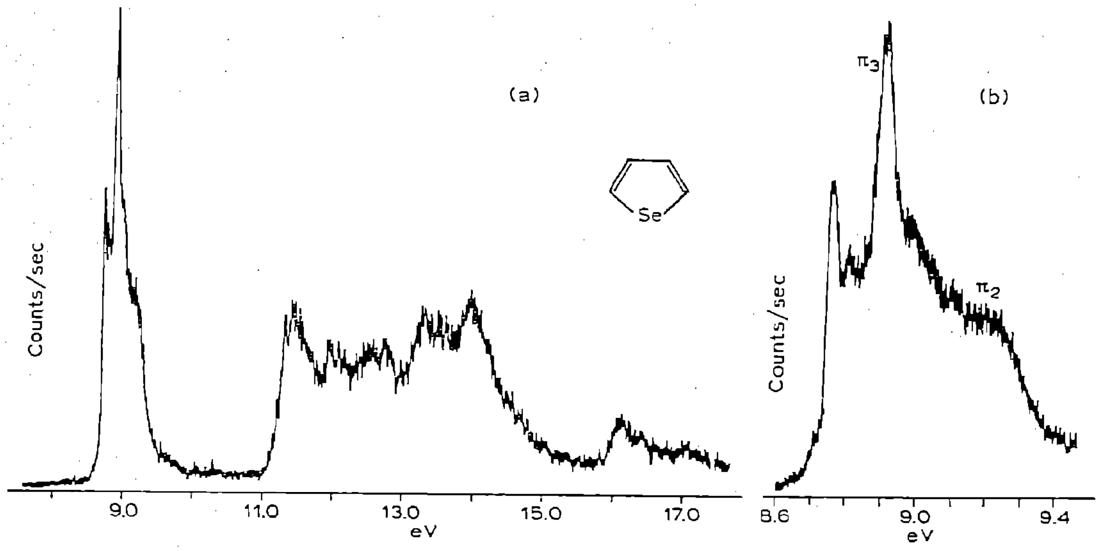


Fig. 2. (a) Photoelectron spectrum of selenophen (21.21 eV). (b) First and second photoelectron bands of selenophen (21.21 eV).

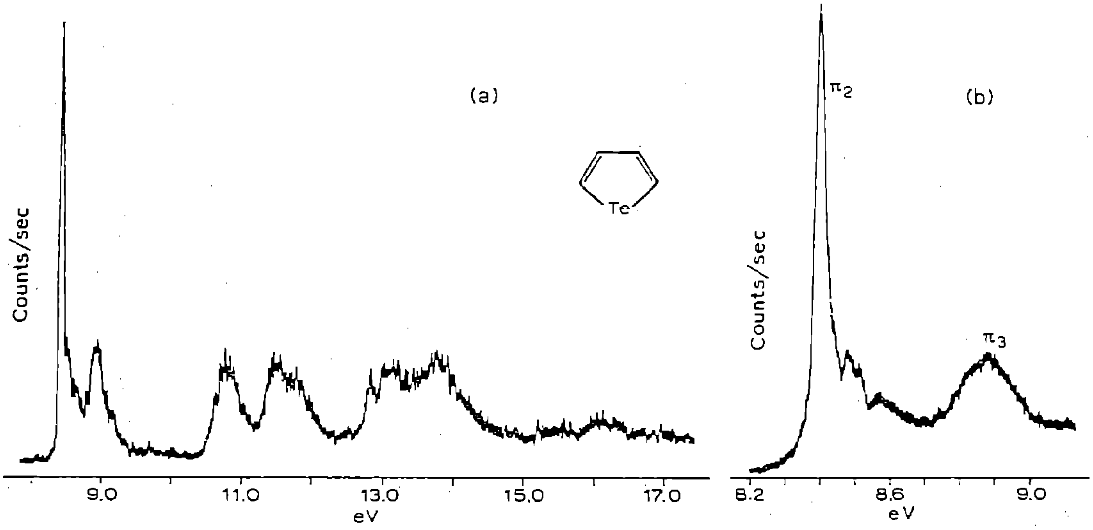


Fig. 3. (a) Photoelectron spectrum of tellurophen (21.21 eV). (b) First and second photoelectron bands of tellurophen (21.21 eV).

A comparison of the photoelectron data for the first two bands of these four compounds shows that the energy of one of those is constant, while the other changes with the heteroatom. On the ground of the previous discussion these bands have been quoted as $\pi_3$ and $\pi_2$, respectively, in table 2. The values are reported against Pauling's electronegativities in fig. 4. These data clearly confirm that the highest occupied orbital in tellurophen is the $\pi_2$ one. The shape of the corresponding photoelectron band is in agreement with an orbital having pronounced lone pair character. It is interesting to note * that the inversion of the highest orbitals in tellurophen can be predicted even by using the simple assumption of a constant interaction parameter $B$ (equal to 1 eV) and Coulomb inte-

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* We would like to thank Dr. D.W. Turner for having suggested this type of calculation.

Table 2
Ionization energies (eV)

| | Photoelectron spectr. | | E.I. d) first IP |
|---|---|---|---|
| | $\pi_3$ | $\pi_2$ | |
| furan | 8.89 a,b) | 10.25 a)<br>10.32 b) | 8.99 |
| thiophen | 8.87 b) | 9.49 b) | 9.12 |
| selenophen | 8.92 c) | 9.18 c) | 9.01 |
| tellurophen | 8.88 | 8.40 | 8.60 |

a) Ref. [15]; (b) ref. [16].

c) Due to the overlapping of the $\pi_2$ and $\pi_3$ bands (see fig. 2b) this figure should be considered as an upper limit for the "vertical" ionization energy. Work is in progress in this laboratory to obtain a more accurate value.

d) As generally found the electron impact values are 0.1 – 0.2 eV higher than the more accurate photon impact values.

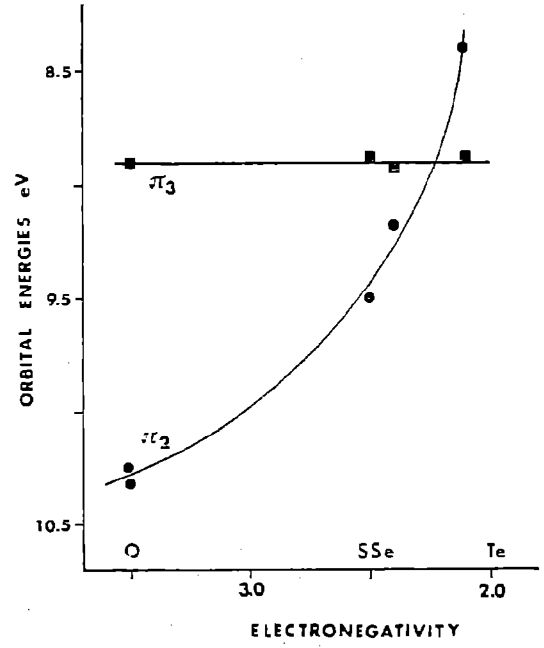

Fig. 4. Plots of the energies of the $\pi_2$ and $\pi_3$ orbitals of furan, thiophen, selenophen and tellurophen versus the electronegativities of the heteroatoms. (Koopmans' theorem is assumed to be valid.)

grals derived from the photoelectron spectrum of butadiene and the atomic p ionization energies, in the manner described by Maier and Turner [17].

The assignment of the complete photoelectron spectra of selenophen and tellurophen, and the comparison with the other five-membered congeners will be published elsewhere.

## 3. Experimental

### *3.1. Materials*

Tellurophen, selenophen and most of their derivatives were available from previously related studies [2].

2-thiomethyltellurophen was synthesized as follows. To an ethereal solution of 2-lithium tellurophen prepared from tellurophen (9g) in dry ether (80 ml) and a 20% solution of *n*-butyllithium in hexane (23.4 ml) a solution of dimethyldisulphide (4.7 ml) in dry ether (40 ml) was added dropwise under nitrogen and with stirring at room temperature. The mixture was allowed to stand for 4 h under stirring and then ice-water was added. The mixture was extracted three times with ether and the combined extracts were washed two times with 2N NaOH aq. water and dried ($Na_2SO_4$). The solvent was eliminated under reduced pressure and the residue distilled at 10 mmHg to give 4 g of pure product; p. eb. 116°–118°, NMR (100 MHz, $CDCl_3$; TMS internal standard) $\tau$ 7.47 (3H, Me), 2.54 (1H, m, H-3, $J_{34}$ 4.10, $J_{35}$ 1.60), 2.40 (1H, q, H-4, $J_{45}$ 6.70, $J_{43}$ 4.00), 1.22 (1H, q, H-5, $J_{54}$ 6.80, $J_{53}$ 1.60). Found: C, 26.82; H, 2.71; S, 14.02. $C_5H_6STe$ requires C, 26.60, H, 2.68; S, 14.20%.

### *3.2. Ionization energy determinations*

A conventional Atlas CH-4 mass spectrometer was used for the mass spectrometric measurements.

In order to minimize the experimental error in the plot of fig. 1, two samples of thiophen and tellurophen (or selenophen) derivatives bearing the same substituent have been introduced in the apparatus at the same time and the IP's of tellurophens and selenophens have been calculated relative to those of the thiophens [13], taken as reference standards.

The IP of 2-thiophencarboxylic acid has been also determined (9.35 eV). The reproducibility of the measurements was better than ± 0.1 eV. The photoelectron spectra have been recorded by using a Perkin Elmer PS 18 spectrometer. The estimated error in the

IP's is ±0.03 eV except for the $\pi$ orbitals of selenophen (see footnote c) of table 2).

## Acknowledgement

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