Photoelectron Spectra of the α-Substituted Derivatives of Furan, Thiophen, Selenophen, and Tellurophen. A Comparative Study of the Molecular Orbital Energies

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Vertical ionization energies of the two highest molecular orbitals and of orbitals mainly localized on the substituent of 31 α-substituted derivatives of furan, thiophen, selenophen, and tellurophen are discussed. The substituent effects confirm the reversal in the energy sequence of the two highest occupied π-MOs of tellurophen with respect to other five-membered heteroaromatic congeners and permit the assignment of the ionization energy values of the π_2 and π_3 MOs in selenophen. Assignments for some of the bands other than the first two in the photoelectron spectra of tellurophen and selenophen are proposed. The effect of the ring on the orbitals mainly localized on the substituent is briefly discussed.

SEVERAL authors[1-4] have discussed in some detail the photoelectron spectra of furan and thiophen and to a lesser extent those of some of their derivatives. Recently[5,6] the photoelectron study has been extended to selenophen and tellurophen and the comparison of the spectra has made it possible to obtain some interesting information. In particular it has been suggested that there is a reversal in the sequence of ionization energies (I) of the two highest occupied orbitals of tellurophen [$I(\pi_3) > I(\pi_2)$] with respect to the other congeners [$I(\pi_2) > I(\pi_3)$].

In order to confirm this hypothesis and contribute to the solution of some other problems raised in the preliminary study, we have undertaken a systematic photoelectron spectral investigation of the substituent effects on the molecular orbital energies of the five-membered heteroaromatic Group VI congeners.

RESULTS AND DISCUSSION

The photoelectron spectra of 31 α-derivatives of furan, thiophen, selenophen, and tellurophen, containing substituents of varying electronic type, have been recorded on a Perkin-Elmer PS 18 photoelectron spectrometer.

Vertical ionization energies (I_1, I_2) of the two highest MOs (π_2, π_3) and orbitals mainly localized on the substituents, are reported in Tables 1 and 3 respectively.

(1) *Sequence of the Two Highest Occupied* π-MOs *in Tellurophen.*—The reversal in the energy sequence of the π_2- and π_3-MOs of selenophen with respect to furan,

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[1] J. H. D. Eland, *J. Mass Spectrometry Ion Phys.*, 1969, **2**, 471.

[2] D. W. Turner, A. Baker, A. D. Baker, and C. R. Brundle, Molecular Photoelectron Spectroscopy, Wiley–Interscience, New York, 1970, p. 329.

[3] P. J. Derrick, L. Asbrink, O. Edqvist, B. O. Johnson, and E. Lindholm, *Internat. J. Mass. Spectrometry Ion Phys.*, 1971, **6**, 177.

[4] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1970, **42**, 1064.

[5] G. Distefano, S. Pignataro, G. Innorta, F. Fringuelli, G. Marino, and A. Taticchi, *Chem. Phys. Letters*, 1973, **22**, 132 and references cited therein.

[6] W. Shafer, A. Schweig, S. Gronowitz, A. Taticchi, and F. Fringuelli, *J.C.S. Chem. Comm.*, 1973, 541.

thiophen, and tellurophen, hypothesized in previous papers[5,6] has now been definitely confirmed from the photoelectron data of α-monosubstituted derivatives.

Table 1 shows that α-methyl substitution causes an increase in the separation of the first two bands ($I_2 - I_1$) in furan, thiophen, and selenophen and a decrease in tellurophen, in agreement with the expectation that electron-releasing substituents in the α-position exert a more pronounced destabilization effect on the energy of π_3- (which has a nodal plane passing through the heteroatom and the middle point of C-3–C-4 bond) than on that of π_2-orbital (mainly localized on the heteroatom and the C-3–C-4 bond). Analogous effects are observed for halogen substitution.

TABLE 1

Vertical ionization energies (eV) of π_3- and π_2-MOs of α-substituted five-membered heteroaromatic Group VI congeners

	Heteroatom							
	Oxygen		Sulphur		Selenium		Tellurium	
Substituent	$I_1(\pi_3)$	$I_2(\pi_2)$	$I_1(\pi_3)$	$I_2(\pi_2)$	$I_1(\pi_3)$	$I_2(\pi_2)$	$I_1(\pi_2)$	$I_2(\pi_3)$
CH_3	8.37	10.13	8.43 [c]	9.23 [c]	8.40	8.96	8.20	8.43 [b]
H	8.89 [a]	10.32 [a]	8.87 [a]	9.49 [a]	8.92	9.18	8.40	8.88
$CON(CH_3)_2$	8.86	10.41	8.84	9.40	8.85	9.10	8.39	8.89
Cl			8.89 [c]	9.63 [c]	8.83	9.34	8.68	8.89 [b]
Br			8.82 [c]	9.58 [c]			8.59	8.84 [b]
I			8.52 [c]	9.47 [c]			8.34	8.52 [b]
CO_2H	9.16	10.72	9.14	9.73	9.19	9.45 [b]	8.62	9.15
CO_2CH_3	9.00	10.56	8.98	9.61	9.05	9.26 [b]	8.51	9.00
NO_2	9.75	11.13	9.73	10.21	9.64	9.88 [b]		
CH_2Cl			8.89	9.49				
CHO			9.37	9.87				
CN	9.47	10.99						
SCH_3	8.58	10.32	8.63	9.37				

[a] Ref. 2. [b] Shoulder. [c] Values in good agreement with those reported in ref. 4.

More conclusive support for the 'reversed sequence hypothesis' in tellurophen is clear from an examination of the correlations reported in Table 2.

TABLE 2

Correlations between the ionization energies of the two highest π-MOs of furans, selenophens, and tellurophens against those of thiophens [a]

	Correlation [b]	β [c]	h [d]	s [e]	r [f]	n [g]
(1)	I_1^{Fur} *vs.* I_1^{Thi}	1.06	−0.55	0.03	0.998	7
(2)	I_1^{Sel} *vs.* I_1^{Thi}	0.95	0.43	0.06	0.988	7
(3)	I_2^{Fur} *vs.* I_2^{Thi}	1.01	0.87	0.06	0.984	7
(4)	I_2^{Sel} *vs.* I_2^{Thi}	0.96	0.12	0.03	0.997	7
(5)	I_1^{Tel} *vs.* I_1^{Thi}	0.55	3.61	0.11	0.790	8
(6)	I_2^{Tel} *vs.* I_2^{Thi}	1.25	−3.08	0.15	0.818	8
(7)	I_2^{Tel} *vs.* I_1^{Thi}	1.02	−0.19	0.02	0.999	8
(8)	I_1^{Tel} *vs.* I_2^{Thi}	0.95	−0.61	0.07	0.920	8

[a] Calculated by least square analysis. [b] Variables in the regression analysis: the second is the independent variable. [c] Slope of the straight line. [d] Intercept. [e] Standard error of the estimate in eV. [f] Correlation coefficient. [g] Number of points.

Slopes close to 1, very high correlation coefficients, and low values of standard error are obtained when I_1 and I_2 values for substituted furans and selenophens are plotted against the corresponding values for substituted thiophens (correlations 1—4). On the contrary, slopes differing greatly from unity, with very poor correlation coefficients, and high standard errors are observed when the energies of the first and second bands of substituted tellurophens are plotted against the corresponding energies of thiophen derivatives (correlations 5 and 6). However, very good correlations (7 and 8) with unitary slope are again obtained if the first ionization energies of tellurophens are plotted against the second ionization energies of thiophens and *vice versa*. The correlations of Table 2 clearly show that the substituent effect on $I(\pi_2)$ and $I(\pi_3)$ does not depend on the nature of the heteroatom. This result is foreseeable and in agreement with previous results[5] obtained by using the electron impact technique considering that the energy of π_3 is independent of the heteroatom. On the other hand it shows that the substituent effect on π_2 is mainly inductive.

The inversion of the highest filled orbitals in tellurophen has previously been justified.[5]

(2) *Assignment and Ionization Energy Values of the Two Highest Occupied* π-MOs *in Selenophen*.—The first two bands in the photoelectron spectrum of selenophen are in part overlapped indicating that the corresponding MOs are close in energy.* The vibrational structures are only partly resolved so that there is some doubt[5,6] about the assignment of $I(\pi_3)$ and $I(\pi_2)$ and their precise values [not in the sequence $I(\pi_3) < I(\pi_2)$ which is well established].

A contribution to the solution of this problem can be obtained by utilizing the correlations of $I(\pi_2)$ and $I(\pi_3)$ of substituted selenophens against the corresponding values of the other congeners.† Average interpolated

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* It is interesting to note that, due to this overlapping, selenophen is the only congener showing only one charge transfer band with tetracyanoethylene[7a] the other congeners showing[7b] two charge transfer bands assigned to charge transfer involving π_3 and π_2 as donors.

† The regression parameters of the correlation of I_1 and I_2 of selenophens against those of thiophens are reported in Table 2 (correlations 2 and 4). The regression equations coming from the correlations against those of furans and tellurophens are: $I_1^{Sel} = 0.90I_1^{Fur} + 0.88$ (*s* 0.04; *r* 0.995; *n* 6); $I_2^{Sel} = 0.91I_2^{Fur} - 0.31$ (*s* 0.07; *r* 0.981; *n* 6); $I_1^{Sel} = 1.10I_2^{Tel} - 0.90$ (*s* 0.05; *r* 0.988; *n* 6); $I_2^{Sel} = 0.94I_1^{Tel} - 1.22$ (*s* 0.06; *r* 0.944; *n* 6).

[7] (*a*) G. G. Aloisi, S. Santini, and G. Savelli, *J.C.S. Faraday I*, in the press; (*b*) S. Pignataro and G. Aloisi, *Z. Naturforsch.*, 1972, **27a**, 1165; G. Aloisi and S. Pignataro, *J.C.S. Faraday I*, 1973, 584.

values of 8.88 ± 0.01 for $I_1(\pi_3)$ and 9.14 ± 0.05 eV for $I_2(\pi_2)$ are obtained which are in excellent agreement with the values and the assignment reported in ref. 5.

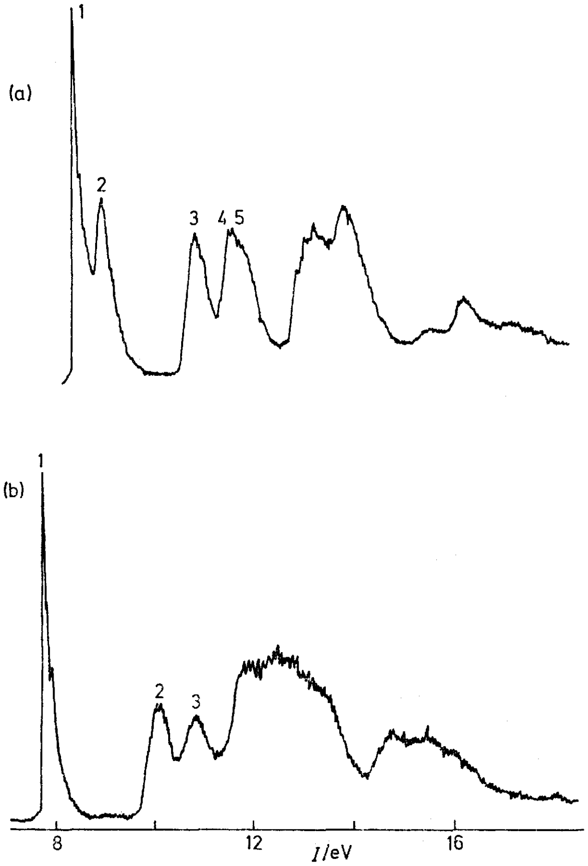

FIGURE 1 Photoelectron spectra (a) of tellurophen and (b) its tetrahydro-derivative

(3) *Assignment of the Bands Other than the First Two in the Photoelectron Spectra of Tellurophen and Selenophen.*—The third band in the spectra of selenophen and tellurophen was previously assigned[6] to the π_1-MO (the lower energy occupied π-MO without a node) by analogy with the thiophen spectrum.[3]

We now attempt an alternative assignment of the bands other than the first two in tellurophen, based on a comparison of its photoelectron spectrum with that of the non-aromatic tetrahydro-derivative[8] (Figure 1).

The two spectra look very similar: in particular, the first three bands of the tetrahydro-derivative resemble in intensity and energy separation the first, third, and fourth of tellurophen. They are assigned to π_2, and to the two (a_1 and b_2) $\sigma_{\text{Te–C-2}}$-MOs which are expected to be equivalent in both molecules.

The second and fifth bands in the aromatic compound spectrum do not seem to have counterparts in the saturated derivative. On this basis, they have been attributed to the π_3- and π_1-MOs respectively.

To sum up, according to this new assignment, the ionization energies of the uppermost occupied MOs of tellurophen are in the order: 8.40 (π_2), 8.88 (π_3), 10.8 ($\sigma_{\text{Te–C-2}}$); 11.5 ($\sigma_{\text{Te–C-2}}$), 11.8 eV (π_1).

The shift toward higher ionization energy values observed in passing from the bands of the saturated derivative to the corresponding bands in the aromatic compound, should be due mainly to the greater inductive effect of the C_4H_8 chain with respect to C_4H_4 and to the higher *s*-character of the σ-framework in tellurophen.

If this assignment is correct, then the interpretation of the photoelectron spectrum of selenophen[6] should probably be modified in a similar manner. By analogy with tellurophen, the bands at 11.4 and 12.0 eV in the selenophen spectrum should be due to $\sigma_{\text{Se–C-2}}$ and π_1 orbitals.

According to this assignment, the ionization energies of the π_1-MOs of the congener five-membered compounds are as follows: furan[3] 14.4, thiophen[3] 12.1, selenophen 12.0, and tellurophen 11.8 eV.

It is interesting to observe that the differences (Δ) between $I(\pi_2)$ and $I(\pi_1)$ parallel the 'ground state aromaticities' of the congener systems[9] as estimated from several different approaches, in the sense that a smaller energy difference corresponds to higher 'aromaticity': thiophen (Δ 2.61) > selenophen (Δ 2.85) > tellurophen (Δ 3.40) > furan (Δ 4.08 eV).

(4) *Substituent Bands*.—The spectra of the halogen-containing compounds show, as expected, two bands due to the halogen lone pairs which are non-equivalent as a consequence of the different interaction of the p_x and p_y orbitals with the π-electron system of the aromatic ring (Table 3). The peak at lower ionization energy is sharper, which suggests a lower bonding character and it has therefore been assigned to the electrons occupying

TABLE 3

Vertical ionization energies (eV) of MOs mainly localized on the substituent

R	Furan		Thiophen		Selenophen		Tellurophen	
$CON(CH_3)_2$	9.65		9.63		9.63		9.54	
Cl	12.2[a]	12.7[a]	11.53[b]	11.93[b]	11.34	11.70	10.86	11.24
Br			10.87[b]	11.39[b]			10.43	10.96
I			9.98[b]	10.65[b]			9.71	10.40
CO_2H			10.61	11.67	10.58	11.81	10.41	11.23
CO_2CH_3	10.56	11.1	10.37	11.03	10.33	11.00	10.21	11.00
NO_2	~10.9 ——	11.50	~10.80 ——	11.40	~10.65 ——	11.22		

[a] A. D. Baker, *Accounts Chem. Res.*, 1970, **3**, 17. [b] Values in good agreement with those reported in ref. 4.

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[8] S. Pignataro and G. Distefano, *Chem. Phys. Letters*, 1974, **26**, 356.

[9] F. Fringuelli, G. Marino, A. Taticchi, and G. Grandolini, *J.C.S. Perkin II*, 1974, 332.

the orbital p_x coplanar with the ring. The wider band at higher ionization energy is then due to the p_y-electrons [2,10] (the p_y orbital is perpendicular to the ring plane and overlaps the ring π-orbitals).

Very good straight lines are obtained for halogenothiophens and -tellurophens when the energies of the lone pair orbitals of Cl, Br, and I are plotted against the Pauling electronegativities of the corresponding halogen atoms, in perfect analogy with the observations for halogenobenzenes [11] (Figure 2).

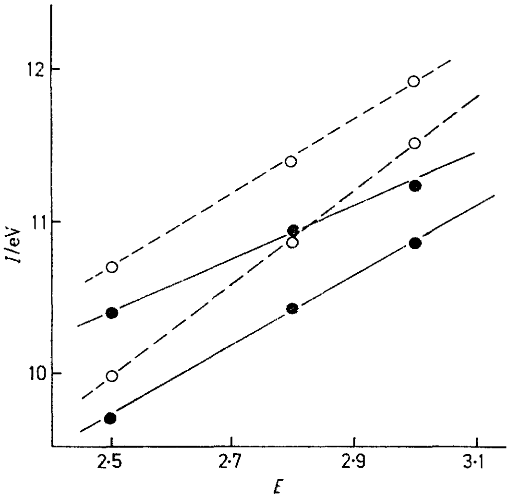

FIGURE 2 Plot of halogen p_x and p_y lone pair ionization energies (I) of halogenothiophens (dashed line) and halogenotellurophens (full line) against the Pauling electronegativity (E) of the halogen atom

The ionization energies of the halogen lone pairs vary with the ring, decreasing in the series, furan > thiophen > selenophen > tellurophen, probably as a consequence of the decreasing electronegativity of the heteroatoms.

The energy separation between the two halogen lone pairs (Table 3) is constant for a given halogen (0.38, 0.53, and 0.68 eV for Cl, Br, and I, respectively) and does not depend on the nature of the heteroatom. This is consistent with the fact that the p_y-orbital interacts with the π_3-orbital, the energy of which is constant (*ca.* 8.9 eV) for the four five-membered compounds. Such energy separations are very close in value to those observed for halogenobenzenes [10] (0.34, 0.55, and 0.84 eV).

Similar effects are also observed for MOs mainly localized on other substituents like CO_2H, CO_2CH_3, and NO_2. Also for these substituents the energy splitting of the substituent bands is independent of the heteroatom and it is close to values reported for other compounds.[12-14] Furthermore the corresponding ionization energy values increase with the electronegativity of the heteroatom.

EXPERIMENTAL

Furans,[15,16] thiophens,[17-19] and selenophens [16,20] were prepared by well known procedures and the tellurophens were synthesized as previously reported.[21-23]

Photoelectron measurements were made using a Perkin-Elmer PS 18 photoelectron spectrometer. The estimated error in the reported figures is ±0.05 eV unless overlapping of the bands occurs. Vibrational structures were often observed. The spacing in $I(\pi_3)$ is generally larger (160—170 mV) than in $I(\pi_2)$ (90—120 mV). For the ionization energy values of unresolved bands an error equal to the vibrational spacing should be taken into account.

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[10] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

[11] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Internat. J. Mass Spectrometry Ion Phys.*, 1970, **4**, 90.

[12] D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, 1972, **94**, 5592.

[13] A. Catrib and J. W. Rabalais, *J. Phys. Chem.*, 1973, **77**, 2358.

[14] O. S. Khalil, J. L. Meeks, and S. P. McGlynn, *J. Amer. Chem. Soc.*, 1973, **95**, 5876.

[15] S. Gronowitz, G. Sörlin, B. Gestblom, and R. A. Hoffman, *Arkiv. Kemi*, 1962, **19**(**34**), 483.

[16] S. Gronowitz, A. B. Hörnfeldt, and K. Petterson, *Chemica Scripta*, in the press.

[17] R. A. Höffman and S. Gronowitz, *Arkiv Kemi*, 1960, **16**(**43**), 515.

[18] S. Gronowitz and R. A. Höffman, *Arkiv Kemi*, 1958, **13**(**31**), 279.

[19] S. Gronowitz and B. Hòlm, *Chemica Scripta*, 1972, **2**(**5**), 245.

[20] J. Morel, C. Paulmier, M. Garreau, and G. Martin, *Bull. Soc. chim. France*, 1971, **12**, 4497.

[21] F. Fringuelli, S. Gronowitz, A. B. Hörnfeldt, J. Johnson, and A. Taticchi, submitted for publication.

[22] F. Fringuelli and A. Taticchi, *J.C.S. Perkin I*, 1972, 199.

[23] S. Caccamese, F. Fringuelli, G. Montaudo, R. Recca, and A. Taticchi, *Tetrahedron*, 1974, 4129.