Molecular Core Binding Energies for Thiathiophthens; Distinction between Symmetrical and Unsymmetrical Structures by *X*-Ray Photoelectron Spectroscopy

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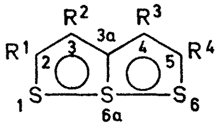
Summary Molecular core binding energies have been measured for some thiathiophthens and are interpreted in terms of SCF-MO calculations.

THE electronic structure of 6a-thiathiophthen (Ia) represents an interesting topic in both experimental and theoretical chemistry.

We present here experimental measurements, for some 6a-thiathiophthens, of sulphur (2*s* and 2*p*) molecular core binding energies determined by *X*-ray photoelectron spectroscopy and an interpretation in terms of all-valence-electron SCF-MO calculations.



(I)

a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = R^4 = Me$; $R^2 = R^3 = H$
c; $R^1 = R^4 = H$; $R^2 = R^3 = Ph$
d; $R^1 = Me$; $R^2 = R^3 = R^4 = H$

Spectra have been recorded on an A.E.I. ES100 electron spectrometer using Mg-$K\alpha_{1,2}$ radiation. The measured core binding energies are given in the Table; for comparison purposes the binding energies for thiophen[1] are also included. (For the 2*p* levels the binding energies for the $2p_{3/2}$ components only are given and for all cases a spin–orbit splitting of 1·0 eV was observed).

Molecular core binding energies (eV)

Compound	Atom	S(2*s*)	S($2p_{3/2}$)	q_i	$\sum\limits_{j\neq i}\frac{q_j}{r_{ij}}$
Thiathiophthen (Ia)	6a	228·5	164·1	−0·035	0·15
	1,6	227·0	162·6	−0·122	0·78
2,5-Dimethyl-thiathiophthen (Ib)	6a	228·7	164·2	−0·048	0·03
	1,6	227·1	162·7	−0·155	0·99
3,4-Diphenyl-thiathiophthen† (Ic)	6a	228·3	163·8	−0·032	0·13
	1	227·8	163·3	−0·080	0·59
	6	226·5	161·9	−0·143	0·80
2-Methyl-thiathiophthen (Id)	6a	228·5	163·7	−0·042	0·09
	1	227·6	163·0	−0·146	1·03
	6	226·4	161·7	−0·133	0·75
Thiophen	1	228·6	164·3	−0·061	0·08

† The longer of the S–S bonds is considered to be between S(6) and S(6a).

The crystal structure of 2,5-dimethylthiathiophthen is in some doubt but the balance of available evidence indicates a symmetrical structure with equal S–S bond lengths.[2] In accord with this the sulphur core levels are split into a 2:1 doublet indicating that the central sulphur core electrons are considerably more tightly bound than those for the terminal sulphur atoms. The same basic structure is shown by the parent thiathiophthen which suggests a symmetrical structure for this compound as well.

By contrast the sulphur molecular core binding energies for the 3,4-diphenyl derivative indicate three types of sulphur and is thus only consistent with an unsymmetrical structure in agreement with the recent *X*-ray crystallographic study.[3]

It may be shown[4] that the binding energy of a given core level for an atom within a molecule is related to the charge distribution by a relationship of the form equation (1) where E_i° is a reference level and the second term is the potential at the atom considered provided by the local valence electron distribution. The third term (an intramolecular Madelung type potential) is the potential at the atom provided by charges centred on other nuclei in the molecule. We have used this relationship previously to interpret measured core binding energies in acetyl compounds[5] and

$$E_i = E_i^\circ + kq_i + \sum_{j\neq i}\frac{q_j}{r_i} \qquad (1)$$

substituted aromatic compounds[6] in terms of both non-empirical and semi-empirical (CNDO/2) charge distributions. To make assignments of core levels for the thiathiophthens we have carried out all-valence-electron CNDO-SCF-MO calculations on thiathiophthen and its 2,5-dimethyl derivative. Since the phenyl groups in the 3,4-diphenyl derivative have been shown to be considerably twisted with respect to the thiathiophthen ring skeleton, conjugative interactions are expected to be quite small and as a first approximation therefore we have taken the electron distribution calculated for the unsubstituted unsymmetrical thiathiophthen skeleton. As a point of interest the calculated energy difference with respect to a symmetrical structure is *ca.* 5 kcal mol^{-1} with the symmetrical structure being the lower in energy. This supports the view that the thiathiophthen structure is likely to be sensitive to both intramolecular and intermolecular effects.[2] Using equation (1) the assignments of sulphur core levels have been made as given in the Table. In all cases the binding energies are dominated by the potentials at the atoms concerned and the potential from other atoms is quite small. Qualitatively therefore the higher binding energy of the central sulphur in the symmetrical thiathiophthens reflects the much lower electron population on the atom compared with the terminal sulphurs. Comparison with thiophen indicates that the local electronic environment around the central sulphur in the symmetrical thiathiophthens is very similar to that in thiophen. By contrast in the unsymmetrical 3,4-diphenyl derivative, the binding energy of the terminal sulphur involved in the long S–S bond is considerably lower than that for the termial sulphur involved in the short S–S bond and thus reflects the much greater electron population on the former. By plotting measured binding energies corrected for the intramolecular Madelung potentials against the charge on an atom a good straight line is obtained giving a value for *k* of 26·8 eV/unit charge. This should approximately represent the one-centre coulomb interaction between a core and valence electron on sulphur and appears to be entirely reasonable.

We have now examined a large number of both symmetrically and unsymmetrically substituted compounds and to illustrate the power of *X*-ray photoelectron spectroscopy as a tool for structural studies in this field we present data for one further compound for which structural data are not yet available. In the Table the measured core binding energies for 2-methylthiathiophthen are given. These indicate three different types of sulphur atom which could possibly be interpreted as being due to a structure with unequal S–S bonds or due to electronic perturbation of a symmetrical structure by the methyl substituent. To differentiate between these two possibilities we have carried out calculations on the methyl substituted thiathiophthen with a similar ring geometry to that for 2,5-dimethylthiathiophthen. The calculated S(2*s*) binding energies from equation (1) are S(1) 226·8, S(6a) 228·5, S(6) 227·0. The calculated effect of replacing H by CH_3 in a symmetrical thiathiophthen structure is thus quite small. This is clearly not compatible with the experimental results and we conclude therefore that 2-methylthiathiophthen has a structure with unequal S-S bonds.

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