CNDO/2 Calculations on 6a-Thiathiophthens; the Effect of Methyl and Phenyl Substituents on the Sulphur–Sulphur Bonding

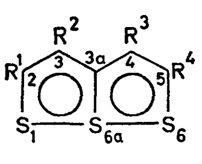
By L. K. Hansen, A. Hordvik,* and L. J. Saethre

(*Chemical Institute, University of Bergen, N-5000 Bergen, Norway*)

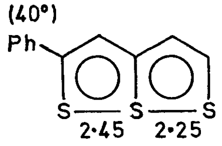
Summary The effect of methyl and phenyl substituents on the sulphur–sulphur bonding in 6a-thiathiophthen can be described by the results from CNDO/2 calculations.

It is well known from structural data on 6a-thiathiophthens that different substituent groups perturb the bonding in the three-sulphur sequence to different degrees. We have studied this problem from a theoretical point of view, and have carried out CNDO/2 calculations on the 6a-thiathiophthen molecule and on its 2- and 3-methyl and 2- and 3-phenyl derivatives.

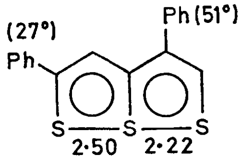
The following model structure of the 6a-thiathiophthen system, taken from a recent structure study of compound (I), was used in the calculations:[1] A planar molecule, symmetric about S(6a)–C(3a), with S(1)–S(6a) 2·350, S(1)–C(2) 1·673, C(2)–C(3) 1·347, C(3)–C(3a) 1·401, and S(6a)–C(3a) 1·737 Å. A bond length of 1·52 Å was used for the exocyclic C–C bond in (II) and (III), and the length of the C–C bond between the phenyl group and the 6a-thiathiophthen system in (IV) and (V) was set equal to 1·50 Å. The C–C bonds in the phenyl group, the C(sp^2)–H bonds, and the C(sp^3)–H bonds were taken to be 1·397, 1·08, and 1·09 Å, respectively.



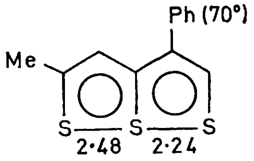
(I) $R^1 = R^2 = R^3 = R^4 = H$
(II) $R^1 = Me, R^2 = R^3 = R^4 = H$
(III) $R^2 = Me, R^1 = R^3 = R^4 = H$
(IV) $R^1 = Ph, R^2 = R^3 = R^4 = H$
(V) $R^2 = Ph, R^1 = R^3 = R^4 = H$



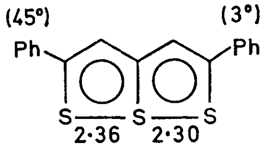
(IV)



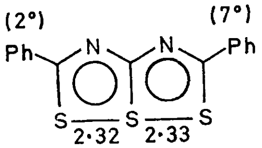
(VI)



(VII)



(VIII)



(IX)

Sulphur *d*-orbitals were included in the calculations, which were carried out using the program CNINDO distributed by the QCPE organisation.[2]

The CNDO/2 total energy[3] for (I), (II), (III), (IV), and (V), respectively, has been calculated as a function of a displacement of the central sulphur atom towards the terminal sulphur atoms keeping the geometry of the rest of the molecule constant, and the change in this energy as a function of the S(1)–S(6a) bond length for (I), (II), and (III) is given in Figure 1. Similar energy curves for (IV) and (V) are given in Figure 2. The three curves for (IV) correspond to this molecule with the phenyl group at twist angles 0, 45, and 90°, respectively. For (V), the S(1)–(6a) distance corresponding to energy minimum did not change with the twist angle of the phenyl group; the curve given corresponds to the phenyl group at 90° twist.

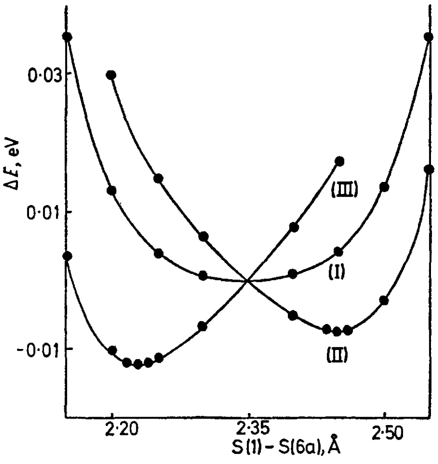


FIGURE 1. *The change* ΔE *in CNDO/2 total energy for compounds* (I), (II), and (III) *as a function of the* S(1)–S(6a) *bond length.*

The electronic structure for the symmetric configuration of (I) found from the present calculations agrees closely with that found from the calculations by Clark and Kilcast;[4] the total energy for (I) was found to be −71·4560 and −71·4564 a.u. in the respective studies.

The energy curve for (I), *cf.* Figure 1, has a flat, broad "minimum", about 0·3 Å. This should be emphasized because the sulphur–sulphur bond lengths in 6a-thiathiophthens are usually found in the range 2·20—2·50 Å.

An energy curve for 6a-thiathiophthen, roughly similar to that given in Figure 1, was obtained by Gleiter and Hoffman from extended Hückel calculations.[5] The EHT curve, however, has two minima, one at S(1)–S(6a) 2·25 Å and another at S(1)—S(6a) 2·45 Å with a barrier of about 0·05 eV between them.

From the energy curves in Figure 1, one notes that a methyl group in 2-position causes a lengthening of the S(1)–S(6a) bond, and a 3-methyl group a shortening of it. The curves in Figure 2 indicate that a 2-phenyl group has a lengthening effect on S(1)–S(6a) which varies with the twist angle of the phenyl group, and that a 3-phenyl group shortens this bond, but to a small degree only.

One may compare the CNDO/2 results with the known molecular dimensions of methyl and phenyl substituted 6a-thiathiophthens where there is no intramolecular strain which may perturb this bonding. From the structures of (IV),[6] (VI),[7] and (VII)[8] one gets the impression that a 2-methyl group and also a twisted 2-phenyl group causes a lengthening of S(1)–S(6a), and that a 4-phenyl group affects the S–S bonding to a small degree only. Furthermore, the structures of (VIII)[9] and (IX)[10] indicate that a twisted phenyl group has a greater lengthening effect on the neighbouring S–S bond than has a phenyl group which is coplanar with the central ring system. Thus, the observed effects of methyl and phenyl substituents on the sulphur–sulphur bonding in 6a-thiathiophthens are consistent with the results of the CNDO/2 calculations.

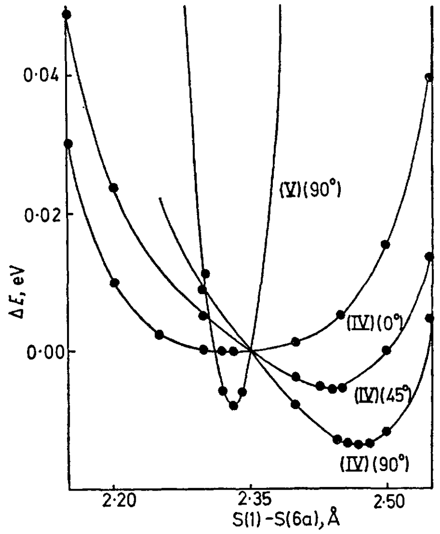


FIGURE 2. *The change* ΔE *in CNDO/2 total energy for compounds* (IV) *and* (V) *as a function of the* S(1)–S(6a) *bond length. The twist angle of the phenyl group is indicated.*

Clark, Kilcast, and Reid have measured the molecular core binding energies for S(2*s*) in (II) by *X*-ray photoelectron spectroscopy.[11] The energies found for the three sulphur atoms are 228·5, 227·6, and 226·4 eV.

We have calculated the S(2*s*) binding energies for the sulphur atoms in (II) according to equation (1)[12] with $E_i^0 = 229{\cdot}3$ eV and $k = 23{\cdot}3$ eV/unit charge. The values for

$$E_i = E_i^0 + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}} \qquad (1)$$

E_i^0 and k were found from a least-squares treatment of the energies, the atomic charges, and the intramolecular Madelung potentials reported by Clark, Kilcast, and Reid for 6a-thiathiophthen, 2,5-dimethyl-6a-thiathiophthen, 3,4-diphenyl-6a-thiathiophthen, and thiophen.[11]

From the electronic structure of (II) corresponding to the minimum in the CNDO/2 curve in Figure 1, the charges on the atoms S(6a), S(6), and S(1) were found to be −0·044, −0·089, and −0·185, respectively, and the intramolecular

Madelung potentials 0·15, 0·59, and 1·17 eV, mentioned in the same order. These values and equation (1) give the energies 228·4, 227·8, and 226·2 eV for S(6a), S(6), and S(1), respectively, in agreement with the experimental results.

A.H. thanks the Norwegian Research Council for Science and the Humanities for economic aid.

(*Received, 8th December* 1971; *Com.* 2091.)

---

[1] L. K. Hansen and A. Hordvik, *Acta Chem. Scand.*, 1970, **24**, 2246; and to be published.

[2] Quantum Chemistry Program Exchange, No. 141, Chemistry Department Indiana University, Bloomington, Indiana 47401.

[3] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

[4] D. T. Clark and D. Kilcast, *Tetrahedron*, 1971, **27**, 4367.

[5] R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899.

[6] S. Bezzi, *Gazzetta*, 1960, **92**, 859.

[7] A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, 1966, **20**, 2001; 1969, **23**, 1852.

[8] A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, 1969, **23**, 3611; 1971, **25**, 1835.

[9] A. Hordvik, *Acta Chem. Scand.*, 1968, **22**, 2397; 1971, **25**, 1583.

[10] A. Hordvik and L. Milje, *J.C.S. Chem. Comm.*, 1972, 182.

[11] D. T. Clark, D. Kilcast, and D. H. Reid, *Chem. Comm.*, 1971, 638.

[12] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, D. F. Heden, K. Hamrin, W. Gelius, T. Bergmark, L. O. Werne, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North Holland, Amsterdam, 1969.