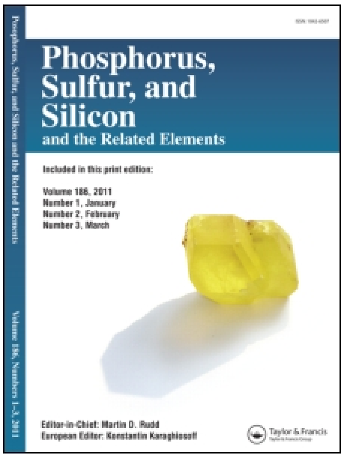

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A NON-EMPIRICAL LCAO MO SCF INVESTIGATION OF SOME ASPECTS OF STRUCTURE AND BONDING IN THE THIATHIOPHTHEN RING SYSTEM

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A NON-EMPIRICAL LCAO MO SCF INVESTIGATION OF SOME ASPECTS OF STRUCTURE AND BONDING IN THE THIATHIOPHTHEN RING SYSTEM

by

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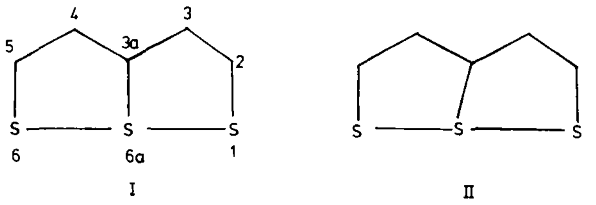
ABSTRACT

Non-empirical LCAO MO SCF calculations have been performed on prototype symmetrical and unsymmetrical thiathiophthen ring systems to investigate structure and bonding as a function of change in geometry. Substituent effects have been investigated and it is shown that within the theoretical limitations the energy differences between symmetrical and unsymmetrical structures are quite small. Comparison has been made with UPS and ESCA data pertaining to valence and core levels respectively and some consideration given to the thiathiophthen radical anion and dianion ring systems.

I. Introduction

Discussion centering on the electronic structure, bonding and reactivity of the 6a-thiathiophthen ring system has had a chequered history. The basic structure of the ring system **I** was only unequivocally established as recently as 1958 by Bezzi and coworkers[1] through an X-ray crystallographic study of the 2,5-dimethyl derivative. The reaction product of diacetyl acetone with P_2S_5 had until that time been assumed to have a 1,2-dithiophthen structure.[2] Since that date considerable crystallographic data[3] has been accumulated on a wide variety of substituted thiathiophthens and the salient features which emerge from such studies are as follows. In all cases the S–S–S system has been found to be essentially linear with S–S bond lengths being substantially less than the sum of the covalent radii. Depending on the substitution pattern the basic ring structure can be either symmetrical, **I**, or unsymmetrical, **II**, with substantial differences in S–S bond lengths (Figure I). For example in the symmetrical 2,5-dimethyl derivatives, equal S–S lengths of 2.358 Å have been reported, however for unsymmetrically substituted derivatives a range of values from 2.16 Å to 2.56 Å have been established. From this data it is evident that the thiathiophthen basic ring system is readily perturbed although it is not clear whether in some cases this arises from lattice effects. In the light of the lack of data on the free molecule (gas phase studies) this feature may best be studied by a theoretical treatment.



I

II

FIGURE I

Symmetrical and unsymmetrical skeletons for the thiathiophthen ring systems (schematic)

The reactivity of the thiathiophthen ring system has also been the subject of some considerable interest in recent years. Studies have been made of electrophilic and nucleophilic substitution and extensive studies also made of the electro-chemistry of the ring system.[3] Several interesting features emerge from these investigations which suggest together with the structural data, a delocalized 10π electron system with some typical aromatic characteristics.

Until 1972 all theoretical discussion pertaining to the electronic structure of the thiathiophthen ring system had been on the basis of π only or all valence electron semi-empirical (CNDO/2)[4] or empirical extended Hückel (EHT) calculations.[5] The EHT calculations, complemented by electronic polarization studies,[5c] predicted an unsymmetrical structure with a double minimum for the parent molecule in direct contradiction to the results of the less approximate CNDO/2 studies which suggest a broad potential minimum centered about the symmetric structure. The latter calculations in addition successfully account for many aspects of the available experimental data.[4, 6] A non-empirical study by Palmer and Findley has been reported[7] but no discussion has been given other than a partial population analysis. It is thus of some importance to undertake a theoretical study at the non-empirical level of this most interesting molecule to investigate the following:

i) The potential energy curve for the S–S–S bond system for the parent molecule.

ii) Electronic perturbation in the isolated parent ring system by various substituents.

iii) The role of d orbitals on the central and terminal sulfur atoms.

iv) The electronic structure of the ring system.

v) Aspects of the chemistry of the ring system.

vi) The core and higher valence energy levels to complement ESCA (sulfur molecular core binding energies) and UPS studies which have proved a valuable tool in studies of the ring system.

A preliminary report has been made of this work at the International Symposium on Organic Sulphur Chemistry (Lund, 1972).[8]

II. Computational Details

Thiathiophthen is a 12 atom 41 electron molecule. It is clear that even with a minimal basis set, computations at the non-empirical level require considerable expenditures of cpu and comprehensive facilities for the handling of the large number of integrals produced in the SCF procedure. Since the prime interest is in the interpretation of relative rather than absolute energies and differences of properties in general, the investigations reported in this work refer to minimal STO-3G basis sets suitably augmented by d polarization function of sulfur ($\zeta = 1.2$). Computations were performed employing the ATMOL series of programs implemented on an ICL 1906a. Typical run times for the symmetrical thiathiophthen **I** (222 primitive gaussians contracted to 74 basis functions) were 12 hr for integral evaluation and 3 hr for the SCF. Extensive use was thus made of MOVE and MERGE facilities for production of non-redundant integral lists involved in the subsequent studies with changes of geometry and basis set. Computational expense necessitated a very limited study of the PE surface for distortion of the S–S–S bond system. To simplify the calculations therefore a prototype unsymmetrical structure (II) was generated by displacing the central sulfur 0.1 Å towards S6 along the line of the three sulfur atomic centres. This asymmetry of 0.2 Å between the S6a–S6 and S6a–S1 bond lengths corresponds quite closely to that found in 3,4-diphenylthiathiophthen. An extreme distortion of the central sulfur of 0.2 Å was also considered, **III.**

III. Results and Discussion

A. Molecular Structure

The variation in total energy with changes of basis set (Table I) emphasizes the very small energies that are likely to be involved in distortion of the central sulfur. Further comment cannot be made on the basis of the energies, however as the geometry for the remainder of the molecule is unoptimized since displacement of the central sulfur will certainly result in second order changes, noticeably in the C3a–S6a bond length. This result, taken in conjunction with the semi-empirical[4,6] calculations mentioned previously indicates that not only intra-molecular perturbations but also inter-molecular forces in the crystal lattice may produce non-symmetrical structures. The X-ray crystallographic results, together with the majority of ESCA data refer to bulk properties and as such can only measure the combined effect of these two forces. Spectroscopic studies in the gas plane, where inter-molecular interactions are greatly reduced, are therefore required to experimentally determine the structures of the free molecules. At present the accuracy required is difficult to attain.

TABLE I

Total Energies of I, II, III as a function of Basis Set

Structure	Basis set*		Energy (a.u.)
I	Minimal	(1)	1368.0253
I	Minimal + 5d on S	(2)	1368.2207
I	Minimal + 6d on S	(3)	1368.3092
I	Minimal + 6d on S6a only	(4)	1368.1093
II	Minimal + 5d on S	(2)	1368.2207
III	Minimal + 5d on S	(2)	1368.2196

* Basis set type in parenthesis.

In investigating substituent effects on the electronic structure there are two well established approaches.

i) A complete calculation for the substituted molecule with appropriate changes in geometry. For molecules of this size this is at present not feasible.

ii) Considering only the substituted molecule with the geometry of the parent the bond overlaps may be computed and a detailed examination carried out of

TABLE II

Sulfur-Sulfur bond overlap populations with variation of Nuclear Charge at H5

	0.97		1.0	1.03	
Nuc. charge:	S6a–S6	S6a–S1	S6a–S6(1)	S6a–S6	S6a–S1
Total	0.1756	0.1747	0.1745	0.1735	0.1748
π–π	0.0840	0.0839	0.0839	0.0839	0.0840
pσ–pσ	0.1178	0.1164	0.1171	0.1164	0.1178

bond order-bond length relationships. This still involves recalculation of a large number of new integrals involving the substituent group.

For molecules of this size therefore, an alternative approach is required. This has been based on approximating the effective potential of the substituent by variation of the nuclear charge of one of the ring hydrogens at the site of substitution. Recomputation of the new 1-electron integrals followed by a new SCF procedure enables a bond overlap analysis of the S–S bonds to be made as outlined in (ii). This presumes the predominant bonding interaction is *via* the σ system. This is not in general unreasonable since hyperconjugation involving, for example, methyl substituents is small in the ground state and at least in some of the phenyl substituted compounds steric considerations dictate orthogonal π systems. However the prime consideration in this work is to qualitatively investigate substituent effects rather than attempt a quantitative discussion (which is not at this stage computationally feasible). This approach has considerable merit in that differences are being interpreted and that many of the approximations inherent in this analysis are minimized. The model substituents were effected at H5 with nuclear charges of 1.03 and 0.97 in both the symmetric (**I**) and unsymmetric (**II**) ring structures. These charges should then simulate substituents of respectively greater or lesser electronegativity than hydrogen.

The effect of substituents is most readily apparent from a Mulliken population analysis. Calculations have been carried out for the symmetric structure **I** and the bond overlap populations for the sulfur-sulfur bonds are given in Table II. It is readily apparent that the largest component arises from the pσ-pσ interaction. For a substituent at C5 less electronegative than hydrogen (simulated by a nuclear charge of 0.97) the bond overlap population for S6-S6a is larger than that for S6–S1 employing a shorter bond length for the former. The opposite should be true with respect to a substituent more electronegative than hydrogen. This is satisfyingly in agreement with experiment where the available experimental data indicate[9] that methyl or phenyl substituents at C5 lead to an increase in bond length of S6a–S6 compared with S6a–S1. (The effective sigma orbital electronegatives for phenyl C(trtrtrπ 17.58) and methyl C(tetetete 15.95) taken from Jaffe and Hinze's tables[10] are considerably greater than that of hydrogen (14.34).

From a wealth of available data it can be concluded that structure and bonding in organo sulfur compounds in cases where sulfur is formally dicovalent can be well understood without invoking 3d orbital participation. The now standard analysis for analyzing the participation has been applied to the symmetric thiathiophthen and the results are displayed in Table I. Addition of the contracted five d basis functions (d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, $d_{3z^2-r^2}$) to the minimal basis produces a significant energy lowering (0.1953 a.u.). This is mainly due, however, to the increased variational freedom of the sp basis as is shown by the further lowering in energy of 0.0835 a.u. upon addition of the symmetric d functions ($d_{x^2+y^2+z^2}$). The result from a Mulliken population analysis (Table III) indicates however a somewhat greater apparent d orbital contribution from the central sulfur. Although calculations at the CNDO/2 level greatly overestimate the extent of d orbital participation on sulfur a similar trend is also apparent from

TABLE III

Mulliken Population Analysis with Basis Set (2) for I and II

Center	I		II	
	σ	π	σ	π
S6a	12.307	3.870	12.303	3.873
S6	12.406	3.756	12.311	3.817
S1	12.406	3.756	12.527	3.683
C3a	5.039	0.786	5.033	0.793
C2	5.093	0.822	5.111	0.800
C5	5.093	0.822	5.069	0.854
C3	4.954	1.094	4.969	1.068
C4	4.954	1.094	4.969	1.068

Total Electron Density Map in Molecular Plane Thiathiophthen.

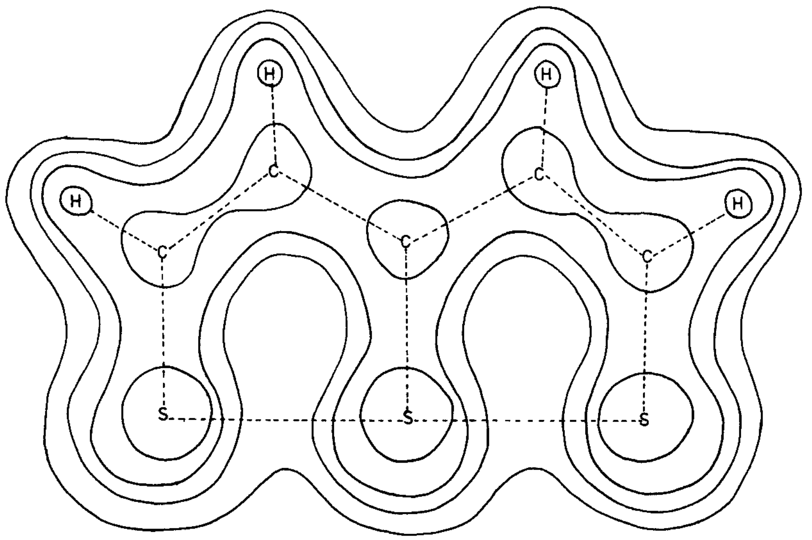


FIGURE II

In-plane density contour map for the symmetric thiathiophthen ring system

such calculations.[4] Comparison of the total energies computed for I with a minimal basis and augmented by d type functions on all three sulfurs or just on S6a reveals however that the improvements in energy are roughly additive.

The Mulliken population analysis (I, II) reveals quite strikingly the transfer of σ charge density from S6 to S1, as the S6a–S6 bond length is decreased. This is accompanied by a drift of π electrons in the opposite direction from S1 to S6. Thus although the difference in total population at the two terminal sulfurs is only 0.08e the net difference in σ electron density is approximately twice as large supporting the concept of the longer bonded terminal sulfur being much more nucleophilic in II than in the symmetrical species.

The electronic structure of I is well described by a density contour map (Figure II) in the molecular plane. The weak S–S bonds are well reproduced in comparison with the C–C and C–S bonds. The bond, no-bond resonance theories[3] which have been applied with much vigour to these compounds in the past are not readily rationalized by these results. It is perhaps better to consider the central sulfur atom residing in a two-dimensional potential well bounded by the terminal sulfurs. An extension of the three-center 4-electron bond model is then capable of explaining the nature of the electronic structure in a more realistic manner.[5a] This orbital interaction scheme for the higher occupied molecular orbitals of I is shown schematically in Figure III and is similar in concept to that proposed from an Extended Hückel analysis by Gleiter and Hoffmann (where the relative ordering of the orbitals is determined from the orbital energies calculated for I). The orbital SS_2 is seen to be destabilized due to the interaction with the occupied 3s orbital of the central sulfur. Further support that no appreciable d orbital participation operates at S6a to lower the energy of this orbital is given by comparing the differences in the SS_2 $(a_1\sigma)$ and $a_2\pi$ (AA, not shown) orbital energies of I for basis sets 1 and 2. The differences of 0.55 eV and 0.61 eV for basis sets 1 and 2 respectively indicate no appreciable stabilization by d orbitals on the central sulfur.

It is possible to account straightforwardly for the opposing drift in σ and π electron densities in going from I to II. The highest occupied orbital (SS_2) is essentially from the lone pairs on S1 and S6 with the S3s and $S_{dx^2-y^2}$ orbitals of the central sulfur. A

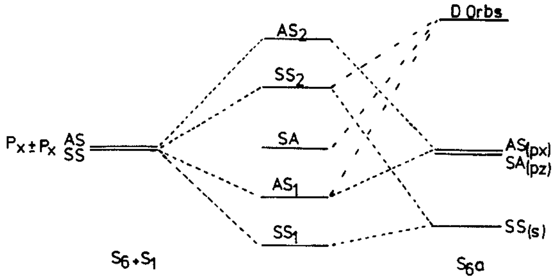


FIGURE III

Orbital interaction scheme for the symmetric thiathiophthen ring system for the higher occupied and lower virtual orbitals

TABLE IV

Orbital Energies of I and II with Basis Set (2) (4 in parenthesis)

Orbital	I (eV)	II (eV)	Orbital	I (eV)	II (eV)
$a_1\sigma$	6.27(5.87)	6.27	$a_2\pi$	6.39(6.41)	6.28
$b_1\pi$	8.58(8.40)	8.57	$b_1\pi$	9.24(9.17)	9.29
$b_2\sigma$	11.00(10.67)	11.00	$a_2\pi$	11.60(11.39)	11.59
$S6a_{2p}$	176.41(175.41)	176.39	$S6_{2p}$	173.25(172.52)	174.21
$S1_{2p}$	173.25(172.52)	172.35			

population analysis shows that as the S6–S6a bond length decreases in going to **II** the σ population on S1 decreases at the expense of S6. The mutual polarization of the sigma and pi electrons then dictates a drift of π electron density from this center. It is of some importance then to emphasize that π- only calculations will not account for this opposing drift and may lead to improper conclusions concerning the structural properties of these molecules.

To some extent therefore this analysis suggests that the triatomic sulfur system may be considered as an almost separate entity in so far as deformations in the structure are concerned. This is dramatically indicated by comparing the x and y components of the dipole moment in **I** and **II**. As anticipated the x dipole in **II** of 1.18D is directed along the axis in a manner in accord with population analysis data. The striking feature however, is the constancy of the y component (3.541D in **I**, 3.543D in **II**).

B. Core and Valence Energy Levels

High resolution (HeI) UPS studies have been reported on the higher occupied orbitals of thiathiophthen and some simple derivatives.[5b] On the basis of comparison with the orbital sequence and spacing produced by EHT calculations, Gleiter and coworkers assigned an unsymmetrical structure for the isolated thiathiophthen ring system. However, as we have previously noted, any theoretical model which does not accommodate the mutual interaction of the sigma and pi systems is likely to lead to erroneous results. That this is the case with respect to thiathiophthen is readily apparent from comparison with the results of CNDO/2 SCF MO investigations.[4] These calculations indicated that the valence energy levels were relatively insensitive to distortion of the basic ring system.

By contrast, ESCA studies of the sulfur 2p core levels show that the molecular core binding energies are sensitive functions of the structure and on this basis a distinction between symmetrical and unsymmetrical could be made.[12]

The calculated core and valence energy levels (from Koopmans' Theorem) of **I** and **II** are shown in Table IV. The notable feature is that there is little overall difference in the energies for the symmetrical or unsymmetrical structures thus confirming the CNDO/2 results. This is not surprising however, as the majority of the higher levels are either weak or non-bonding in the sulfur unit. The results correlate well with the (**I**) photoelectron spectra in the literature[5b] but indicate that an analysis of UPS spectra is unlikely to aid in the elucidation of the molecular structure.

By contrast the theoretical calculations indicate quite large differences in the sulfur 2p core levels for the terminal sulfurs in agreement with experiment. Previous experience has shown that with this small basis a scaling factor is required to quantitatively interpret the shifts in binding energy to accommodate for the fact that the basis is a considerable way from the Hartree-Fock limit.[13] With this correction the shift in binding energy for the $S_{2p_{3/2}}$ core levels in Table V between the central and terminal sulfur for **I** obtained from the S_{2p} core level eigenvalues is determined to be ~1.55 eV. This is in good agreement with previously reported measurements in this laboratory.[12] For the model unsymmetrical structure, **II**, there is a marked change in the core level eigenvalues of the terminal sulfur, that at S6 moving to higher energy. These theoretical results for the shifts are again in good agreement with results taken from 3,4-diphenylthiathiophthen.

TABLE V

Sulfur 2p Core Binding Energies with Basis Set (2) for I and II

	I		II	
Center	Exp.	Calc.	Exp.[12]	Calc.
S1	(0)	(0)	−0.7	−0.43
S6	(0)	(0)	0.7	0.48
S6a	1.5	1.55	1.5	1.55

It is of some interest to note that a very recent gas phase high resolution ESCA study by Siegbahn and coworkers,[14] has confirmed the original ESCA data[12] with respect to thiathiophthen as regards its symmetrical structure but in addition has revealed significant differences in linewidths for the core levels associated with the terminal and central sulfurs. This has been rationalized in terms of population of several of the vibrational levels in going to the terminal sulfur hole states in the Franck-Condon transition between the electronic ground state and the sulfur 2p core ionized hole state.

Electronic structures of the radical anion and dianions

There are two main points of interest in a study of the radical anion. Firstly, the lowest unoccupied molecular orbital (π) of thiathiophthen is anti-bonding in the triatomic sulfur unit. This change in bonding might be expected to alter the shape of the potential energy curve for the motion of the central sulfur. Secondly, the actual distribution of the unpaired electron is of interest as ESR studies are unable to give a direct measurement.

TABLE VI

Spin Densities in I and III with Basis Set (2) for Thiathiophthen Radical Anion

Center	Spin (I)	Spin (III)	Center	Spin (I)	Spin (III)
S6a	0.106	0.098	S6	0.068	0.064
S1	0.068	0.086	C3a	0.423	0.406
C2	0.119	0.107	C5	0.119	0.132
C3	0.001	0.011	C4	0.001	0.001

Total energy I −1368.1480 a.u.
Total energy III −1368.1454 a.u.

The results shown in Table VI indicate that there is a slight lowering in energy of the symmetrical radical structure and this is supported by the observation of the symmetric 2,5-diphenylthiathiophthen radical anion compared with the slightly unsymmetrical parent.[15] The unpaired electron distribution displays a much larger density at C2 and C5 than C3, C4 and is in qualitative agreement with results for the 2,5-diphenylthiathiophthens. The largest density is at C3a with ~0.25*e in the triatomic* sulfur sequence.

Dianion

Two electron transfer to thiathiophthen produces the closed shell dianion. It is of some interest then to examine the feasibility of a proposed scheme for the rearrangement of thiathiophthens by attack from sulfide nucleophile by a mechanism involving the possible intervention of the dianion. The proposed mechanism (Figure IV) involves uptake of 2 electrons producing a transient intermediate before rearrangement and loss of sulfur to form the six-membered ring structure.[15] The critical feature is the stability of the dianion which has now been demonstrated to be quite stable by polarographic studies. Calculations were performed on I, II and III with the lowest unoccupied π orbital of the thiathiophthen doubly occupied. The striking feature (Table VII) is the increased stability of the S—Ṡ—S 3-centre bond even though the π orbital is antibonding in the triatomic sulfur system. Though this π overlap is indeed reduced, the rearrangement in the σ system concomitant with uptake of two electrons strengthens the σ S—S bonds. Of the increase in σ electron density at the central and terminal sulfurs in the dianion, no more than 20% can be attributed to d orbital participation. Protonation at either the central or terminal sulfurs will weaken the σ bond and the monocyclic ring structure might reasonably be anticipated to result. Again it is

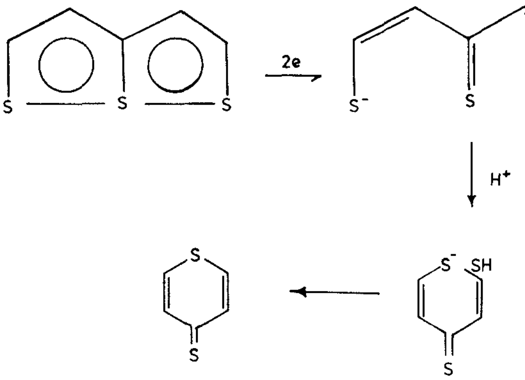


FIGURE IV

Proposed reaction scheme for rearrangement of the thiathiophthen ring system by reaction with sulfide anion

TABLE VII

Mulliken Population Analysis with Basis Set (2) of I and II for Thiathiophthen Dianion

	I		II	
Center	σ	π	σ	π
S6a	12.455	4.170	12.364	4.151
S6	12.491	4.087	12.340	4.173
S1	12.491	4.087	12.647	4.013
S6a—S6	0.200	0.074	0.240	0.036
S6a—S1	0.200	0.074	0.144	0.024

Total energy I − 1367.8391 a.u.
Total energy II − 1367.8382 a.u.

interesting to note that the unsymmetrical dianion structure is of comparable energy to the symmetrical species. There is, however, a considerable difference in the overlap and hence the bonding between S6a–S6 and S6a–S1. This will almost certainly have an important bearing in any differences in reactivity etc. with respect to the ring opening reaction for unsymmetrical as compared to symmetrical thiathiophthen ring system.

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