

ALL VALENCE ELECTRON SCF MO CALCULATIONS ON THE ELECTRONIC STRUCTURES AND REACTIVITIES OF SOME 6A-THIATHIOPHTHENES

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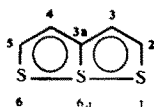
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Abstract—All valence electron CNDO/2 SCF MO calculations have been performed on 6a-thiathiophthene and some simple derivatives. The electronic structure is discussed and compared with available experimental data. Localization energies for prototype electrophilic (H^+) and nucleophilic (H^-) substitution of the parent molecule have been calculated. Relative acidities of the methyl protons in 2 and 3 methyl thiathiophthenes have also been investigated.

INTRODUCTION

THERE HAS BEEN a great deal of discussion recently concerning the structure of 6a-thiathiophthenes (I).¹ Experimental evidence favours a symmetrical structure in solution (with equal S—S distances) for symmetrically substituted compounds.



However, X-ray diffraction investigations suggest that in certain derivatives in the solid phase the S—S distances may be unequal. Studies of the 2,5-dimethyl derivative² indicate a symmetrical structure with S—S distances of 2.358 Å, however the 3,4-diphenyl derivative³ has an unsymmetrical structure with unequal S—S distances of 2.232 Å and 2.434 Å. The asymmetry of the 3,4-diphenyl derivative in the solid state has also been supported by X-ray photoelectron spectroscopy studies.⁴ Unsymmetrically substituted derivatives also have structures with unequal S—S bond lengths.

There have been few attempts to quantitatively describe the bonding in the thiathiophthene ring system. Extended Hückel calculations⁵ and PPP—SCF—MO calculations⁶ have been performed, but both suffer from serious drawbacks. For polar molecules, the approximations inherent in EHT are theoretically unsound⁷ and this is particularly so for molecules which by symmetry have σ - π separability. Whereas in a CNDO SCF MO treatment the off-diagonal elements of the F matrix depend on the total charge on a given atom, in an EHT treatment the σ and π systems are treated as essentially non-interacting. For systems such as the thiathiophthenes, therefore, where a strongly polarized σ framework exists EHT cannot give an adequate description of the bonding. In a PPP—SCF—MO π -electron only treatment, the assumption of a non-polarizable σ core is again questionable.⁷

In this work, we have performed all valence electron CNDO/2 SCF MO calculations on I, with the inclusion of 3d orbitals on the sulphur atoms. In order to investigate the

influence of substituents on the electronic structure, we have performed calculations on the 2- and 3-methyl derivatives. We also present the results of calculations on the reactivity of I with prototype electrophiles (H^+) and nucleophiles (H^-), and compare the results with experimental data. The calculated relative acidities of the 2- and 3-methyl derivatives are also discussed.

ELECTRONIC STRUCTURE OF THE THIATHIOPHTHENES

Calculations

The ring geometry as found² from the X-ray structure of the 2,5-dimethyl derivative was used for I and for the 2- and 3-methyl derivatives. A calculation was also performed on I with the ring geometry of the 3,4-diphenyl derivative in order to estimate the energy difference between the two forms. The molecules were taken to lie in the X—Y plane with the S_{6a} — C_{3a} bond along the positive Y axis.

Results

Energies. The total energy calculated for I is -71.4564 a.u., compared with the value -71.4484 a.u. calculated for the distorted form. This difference, of the order of 5 Kcal/mole, supports the idea that intermolecular effects may be at least as important as intramolecular effects in determining the thiathiophthene structure in the solid state.¹

Molecular orbitals. The orbital energies, orbital symmetries and predominant bonding characteristics of the orbital are given in Table 1. The most notable features of these results are the existence of the low-lying π -orbitals at 17.65 eV and 22.93 eV, and the prediction that the highest occupied orbital should be a σ -orbital.

The CNDO/2 calculations are known to exaggerate σ - π mixing; for instance, CNDO/2 calculations performed by us on thiophene predict the orbital order ($A_{1\sigma}$)($A_{2\pi}$)($B_{2\pi}$) with a $A_{1\sigma}$ — $A_{2\pi}$ separation of about 0.3 eV, whereas *ab initio* calculations predict a corresponding σ - π separation of ~ 3 eV.⁷ It is possible, therefore, that the positions of the $A_{1\sigma}$ and $A_{2\pi}$ orbitals in thiathiophthene may be reversed, but the separation of 1.8 eV would seem to preclude reversal of the $A_{1\sigma}$ and $B_{2\pi}$ orbitals. In general, the orbitals have negligible d-orbital coefficients on all sulphurs, except for the high energy $A_{1\sigma}$ lone pair orbital, which has a 13% $3d_{x^2-y^2}$ contribution on the central sulphur.

The appearance of this high energy σ orbital among the π orbitals casts some doubt on the validity of correlating measured ionisation potentials with the π orbital energies as calculated by the PPP—LCAO—SCF method.³ Either the first or the second ionisation potential would be expected to correspond to a lone-pair ionisation.

The only major effect of introducing distortion by taking the two S—S lengths unequal is to make the top two orbitals degenerate, with a higher energy of -10.260 eV. Introduction of a methyl group in the 2 position causes little reorganisation of the orbitals, apart from a shift of all the eigenvalues towards higher energies. However, introduction of a methyl group in the 3 position causes a reversal of the top $A_{1\sigma}$ and $A_{2\pi}$ levels, having energies -10.384 eV and -10.327 eV.

Populations and bond orders. The orbital populations calculated for I are given in Table 2. Several interesting points arise for these values. Firstly, the σ framework is strongly polarized; for instance, σ charges of -0.319 and $+0.718$ on S_1 , S_6 and S_{6a}

TABLE 1.

Orbital energy (eV)	Symmetry	Bonding characteristics
-10.498	$A_{1\sigma}$	lone pair on S_1, S_6
-10.658	$A_{2\pi}$	S-S, C_2-C_3, C_4-C_5
-12.340	$B_{2\pi}$	C-S
-12.816	$B_{2\pi}$	S-S
-13.556	$B_{1\sigma}$	S-S
-13.932	$A_{1\sigma}$	C-S
-15.331	$A_{1\sigma}$	C-S
-15.543	$B_{1\sigma}$	S-S, C_2-S_1, C_5-S_6
-16.819	$B_{1\sigma}$	C-C
-17.652	$A_{2\pi}$	$S_1-C_2, C_2-C_3, C_4-C_5, C_5-C_6$
-21.053	$A_{1\sigma}$	C-C, C-H
-21.246	$B_{1\sigma}$	C-C, C-H
-22.931	$B_{2\pi}$	C-C (+ some S-S)
-23.815	$A_{1\sigma}$	lone pair on S_{6a}
-24.258	$A_{1\sigma}$	C-S
-27.962	$B_{1\sigma}$	C-S, C-C
-28.373	$B_{1\sigma}$	C-C, C-H
-32.653	$A_{1\sigma}$	$C_{3a}-S_{6a}$
-34.394	$A_{1\sigma}$	C-C, C-S
-42.212	$B_{1\sigma}$	C-C
-46.498	$A_{1\sigma}$	C-C

TABLE 2.

Position	s	p	Populations			Total
			d	σ	π	
S_1, S_6	1.826	3.951	0.345	4.319	1.803	6.122
C_2, C_5	1.081	2.878	—	3.097	0.862	3.959
C_3	0.993	3.000	—	2.949	1.044	3.993
C_{3a}	1.044	2.845	—	3.059	0.830	3.889
S_{6a}	1.822	3.531	0.682	4.282	1.753	6.035

TABLE 3.

S_1, S_6 S_{6a}	s	p_x	p_z	d_{xz}	$d_{x^2-y^2}$
s	—	—	—	—	0.111
p_x	0.194	0.637	—	—	0.182
p_z	—	—	0.237	0.207	—
d_{x^2}	—	0.219	—	—	—
d_{xz}	—	—	0.265	—	—
$d_{x^2-y^2}$	0.168	0.453	—	—	—

Only bond orders greater than 0.1 are tabulated.

respectively. The relatively low σ charges on the carbons show that these charges result from a shift of the σ electrons from the central sulphur on to the terminal sulphurs.

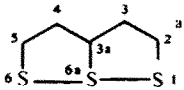
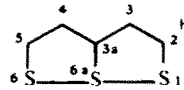
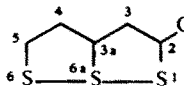
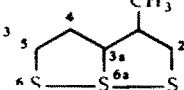
Secondly, although the π populations predict a positive charge on C_2 , C_5 , as predicted by EHT calculations,⁵ this is partly compensated by the σ charges of opposite sign. Consequently, both the C_2 , C_5 and the C_3 , C_4 positions have net positive charges, with the charge on C_2 , C_5 being the greater. The significant σ polarization again indicates the danger of using π -only calculations on this type of molecule.

Thirdly, the d orbital population on S_{6a} is significantly higher than on S_1 , S_6 . The relative importance of d orbitals on S_{6a} is also reflected in the S—S bond orders (Table 3). Although the main S—S bonding is of the p_σ — p_σ type with a bond order of 0.637, the bond orders between d orbitals on S_{6a} and the p orbitals on S_1 , S_6 are, in every case, larger than the corresponding bond orders between d orbitals on S_1 , S_6 and p orbitals on S_{6a} . Of particular interest is the value of 0.453 for the bond order between the $d_{x^2-y^2}$ orbital on $6a$ and the p_x orbital on S_1 , S_6 . This may be compared with the value of 0.182 for the $d_{x^2-y^2}$ orbital on S_1 , S_6 and the p_x orbital on S_{6a} .

The role of d-orbitals in the bonding in dicovalent organic sulphur compounds has been the subject of much controversy. Recent *ab initio* calculations on thiophene⁷ have indicated that inclusion of d orbitals has very little effect on the total energies, and that these orbitals are merely polarization functions. CNDO/2 calculations including d-orbitals almost certainly over-emphasize their importance, since an orbital exponent equal to that for the 3s and 3p orbitals is used. (It has been shown that a smaller d-orbital exponent does produce better results⁸). The above calculations demonstrate, however, the relative importance of the d-orbitals on the central sulphur as compared with the terminal sulphurs, although the absolute values cannot be taken too seriously.

The effect of distortion of I and introduction of methyl groups at C_2 and C_3 on the atomic charges is shown in Table 4. As can be seen, the effect of introducing different

TABLE 4

Position				
S_1	-0.122	-0.082	-0.146	-0.128
C_2	+0.041	+0.026	+0.094	+0.026
C_3	+0.007	+0.003	-0.019	+0.048
C_{3a}	+0.111	+0.104	+0.116	+0.103
C_4	+0.007	-0.021	+0.002	+0.009
C_5	+0.041	+0.048	+0.043	+0.041
S_6	-0.122	-0.143	-0.133	-0.125
S_{6a}	-0.035	-0.034	-0.042	-0.050

^a symmetrical

^b unsymmetrical: S_6 — S_{6a} is the longer bond

S—S bond lengths is to give the three sulphurs distinctly different charges. X-ray photoelectron spectroscopy studies have, indeed, shown three distinct sulphurs with different binding energies for the 3,4-diphenyl derivative.⁴ Introduction of methyl groups at the the 2- and 3-positions has very little effect on the charge distribution. In

the 2-methyl derivative there is an increased population on the 3-position, but in both cases there is very little change in the sulphur populations.

REACTIVITIES OF SOME 6a THIATHIOPHTHENES

Calculations

As we have previously noted discussion has been centred on the electronic structure of the parent thiathiophthene and much less attention has been paid to theoretical interpretations of the reactivity of this ring system. Experimentally, information is limited, but data is available for both electrophilic and nucleophilic substitution reactions for derivatives of the parent molecule.^{1, 9, 16}

Previous attempts at rationalising experimental data have been limited to static reaction indices, namely ground state π electron distributions calculated by PPP—SCF—MO and EHT methods. The deficiencies of these approaches have already been commented on in the previous section.

We have performed calculations using dynamic reaction indices, with a Wheland-type intermediate as a model. Thus, instead of using the calculated charges, which are very sensitive to parameter variation, as a guide to reactivities, the localization energies of the corresponding Wheland intermediates have been used.

The X-ray crystal structure of the 2,5-dimethyl derivative was used for the ring geometry, with S—S distances of 2.358 Å. The geometry about the appropriate atom in the Wheland intermediates was taken as approximately tetrahedral. For reaction at sulphur, calculations were also performed on the planar conformation.

Calculations were also performed on the relative acidities of the 2- and 3-methyl derivatives. The conformation of the $-\text{CH}_2^-$ group in the ion was taken as planar.

The total energies for 6a-thiathiophthene, benzene and the corresponding Wheland intermediates are given in Table 5. The LE values are the appropriate localization energies, and the Δ_{LE} values are the difference between the thiathiophthene localization energies and the corresponding benzene localization energies. (The energies are given in atomic units).

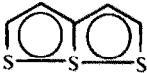
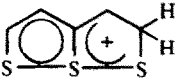
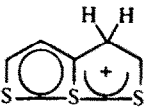
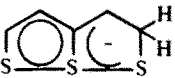
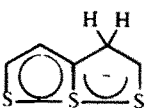
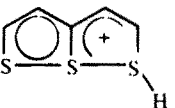
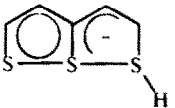
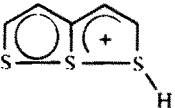
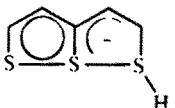

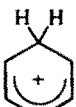
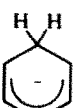
The calculations predict a pyramidal geometry for the intermediate in the reaction at sulphur; this geometry has been found from NMR data in some S-alkylthiophenium salts.¹⁰

The 3 position can be seen to be the preferred position for electrophilic attack, as is also predicted by the charge densities, and experimental evidence on derivatives of I indicates that bromination, nitration⁹ and formylation^{11, 12} can occur at this position. The Δ_{LE} value of about zero indicates that reaction should be about as facile as with benzene.

One interesting point is the similarity of the localization energies for attack at sulphur; this lies between those for attack at the two carbons, and indicate that electrophilic attack at sulphur may well be a competitive reaction. In fact, S-alkylations of unsymmetrical thiathiophthenes with MeI^{13} and with triethyloxonium fluoroborate¹⁴ have been reported.

The 2 position is predicted as the position for nucleophilic attack, as is also seen from the charges. The site is predicted to be more reactive than in benzene. Again, the similarity of the localization energy for attack at sulphur predicts that this could be a competitive reaction. Some evidence is available for nucleophilic attack at 2 by

TABLE 5.

	E_T	E_F	Δ_{LE}
	-71.4564	—	—
	-71.8200	-0.3636	0.0882
	-71.9052	-0.4488	0.0040
	-72.3522	-0.8958	-0.1755
	-72.0600	-0.6036	0.1167
	(planar) -71.8329	-0.3765	0.0147
	(planar) -72.1580	-0.7016	0.0187
	(pyramidal) -71.8633	-0.4069	0.0451
	(pyramidal) -72.2434	-0.7870	-0.0667
	-47.0924	—	—
	-47.5452	-0.4528	—
	-47.8127	-0.7203	—

HS^- ¹⁵ and by $\text{C}_2\text{H}_5\text{O}^-$ ¹⁶. The high positive localization energy for the 3 position indicates that nucleophilic attack at this position would be very unlikely.

The energies calculated for the 2- and 3-methyl derivatives, and for their conjugate bases, are given in Table 6. The ΔE values in the last column indicate that the 2-methyl derivative should be distinctly more acidic, the energy difference being about 0.17 a.u. The experimental evidence supports this; the thiathiophthene II condenses readily with 2 moles of benzaldehyde, while the thiathiophthene III is inert.¹⁷



TABLE 6.

	E_T	E_E
	-80.1670	
	-79.3074	0.8596
	-80.1489	
	-79.1250	1.0239

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