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Ultraviolet Spectra of, and SCF MO Calculations on 6a-Thiathiophthens

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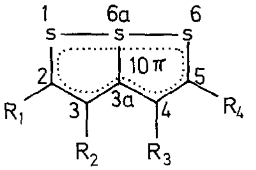
The nature of the bonding between the three sulphur atoms in 6a-thiathiophthen is discussed and considered from a group theory viewpoint. Ultraviolet spectra and ionisation potentials of some thiathiophthens have been calculated and measured, and the two sets of results are examined in relations to the sulphur bonding.

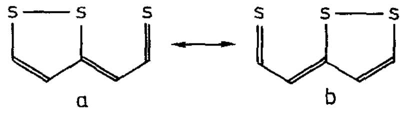
Introduction

The nature of the bonding in 6a-thiathiophthens (I) has attracted considerable attention from the time the first X-ray analysis of the structure of 2,5-dimethyl-6a-thiathiophthen (I; R_1=R_4=Me; R_2=R_3=H) ahowed that the molecule was planar with the three sulphur atoms colinear [1]. A monocyclic structure (IIa or b) can account satisfactorily neither for the general chemical aromaticity of the 6a-thiathiophthens [2], nor for the fact that both S–S distances are considerably less than the sum of the Van der Waals' radii and yet greater than normal single S–S bonds [3]. For these reasons, it may be supposed that some form of bonding between all three sulphur atoms occurs as in structure (I), which may then be regarded as a 10 π-electron system analogous to naphthalene. An early attempt to rationalise the structure (I) made use of a "one-bond, no-bond" resonance concept depicted by structure (IIa, b) and Hückel MO calculations were carried out on this basis [4]. Other workers have suggested that simple π-orbital overlap (8 π-electron system) would explain the bonding [5] but it is difficult to see how a stable molecule could result from such relatively weak forces. In a more elegant discussion [6], Maeda has suggested that the central sulphur atom of the 6a-thiathiophthens can bond to both of the adjacent sulphur atoms through digonal hybrids formed from $3p$, d-orbitals after promotion of a $3p$-electron to a $3d$-orbital. Maeda found that such hybrid orbitals on the central sulphur atom afforded only negative overlap with the adjacent sulphur $3p$ σ-orbitals. However, noting that 6a-thiathiophthen is a non-alternant heterocyclic having considerable charging around the molecule which could cause contraction of the $3d$-orbitals on the central sulphur atom, Maeda was able to show that strong positive overlap with the digonal hybrids could occur. Such sigma bonding could easily account for both the length and relative stability of the S–S bonds. Through calculations based on structure (I) and the Wheland-Mann ω-technique [7], we have shown that the reactivity of the 6a-thiathiophthens to electrophiles follows the calculated π-electron charge density distributions [8]. Recently, a suggestion that the structure of the thiathiophthens can be explained through electron-rich, three centre bonds involving the three sulphur atoms has been published [9].

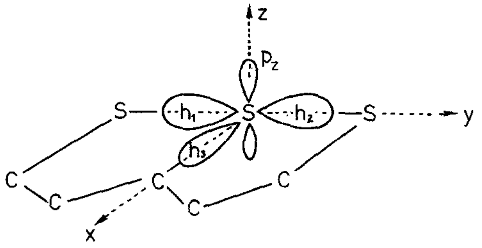
In order to gain further insight on the bonding in the thiathiophthens we have carried out SCF MO calculations to predict the π-electron transitions and ionisation potentials expected from structure (I). This approach is particularly useful as the thiathiophthens show intense absorption in the visible region of the spectrum which, as with azulene [10], is not predicted by simple Hückel MO theory.



I.



II.



	E	C_2	σ_{xz}	σ_{xy}
h_1	1	0	0	1
h_2	1	0	0	1
h_3	1	1	1	1
	3	1	1	3

$\equiv 2A_1 + B_2$

Fig. 1

The 6a-thiathiophthen structure (I, $R_1 = R_4$; $R_2 = R_3$) has C_{2v} symmetry and we have supposed the central sulphur is bonded to the two outer sulphur atoms and the central carbon through trigonal hybrids h_1, h_2, h_3 (the same final result is obtained by assuming only digonal hybrids h_1, h_2 and $3p$ bonding between central sulphur and carbon atoms). Under the operations of the C_{2v} group, the transformation properties of the hybrids h_1, h_2, h_3 are shown in Fig. 1. Reference to the C_{2v} table shows that the representation of h_1, h_2, h_3 is composed of the irreducible representations $2A_1 + B_2$. The B_2 representation corresponds to a p_y orbital, and the $2A_1$ representation is a combination of two from p_x, d_{z^2}, $d_{x^2} - y^2$ orbitals. Neglecting the high-energy combination $(d_{z^2}, d_{x^2-y^2})$, the trigonal hybrids may be composed from p^2d hybridised orbitals as envisaged by Maeda [6], although he was uncertain as to which d-orbitals might participate. Therefore, the configuration $3s^2 p_x p_y p_z d$ formed from $3s^2 p_x^2 p_y p_z$ by $p \rightarrow d$ promotion can give digonal or trigonal hybrids, and further, Maeda has shown that such hybrids can lead to bonding. Since the hybrid orbitals can be $p_x p_y d_{z^2}$ or $p_x p_y d_{x^2-y^2}$ they are degenerate but, the degeneracy can be removed in the molecule by distortion, which would also allow the use of d_{xy}-orbitals for bonding[1].

Method

The PPP adaptation of the Hartree-Fock SCF LCAO procedure [11] was used. The β_{CC}^{core}, one-centre, and two-centre repulsion integrals were evaluated by the Pariser-Parr [11], Paoloni [13], and Nishimoto-Mataga [14] methods respectively. Values for the empirical parameters involving sulphur ($\omega\ddot{s}$, $\omega\dot{s}$, βcs) were taken from the small range of values of these parameters found by us to yield the optimum results for the π-electron transitions of mono-, di-, and tri-sulphur heterocyclic systems [12]. The actual values used for $\omega\ddot{s}$, $\omega\dot{s}$, and βcs are shown in Tables 1–3. A value for βcs was obtained by assuming its proportion-

Table 1. I(R_1=R_2=R_3=R_4=H)

Parameters	E_{obs} (logε)	E_{calc} (f)
$\omega\ddot{s} = 10.5$	2.64 (3.68)	2.555 (0.21)
$\omega\dot{s} = -1$		3.757 (0.15)
$\beta ss = 0.4$		4.502 (0.09)
$\beta_{12} = 1.1$	4.89 (4.69)	4.772 (0.92)
$\beta_{3a6a} = 0.8$	5.42 (4.20)	5.607 (0.24)

All energies in Tables are given in electron-volts.

Table 2. I(R_1=R_4=Ph; R_2=R_3=H)

Parameters	E_{obs} (logε)	E_{calc} (f)
$\omega\ddot{s} = 9$	2.45 (4.14)	2.633 (0.18)
$\omega\dot{s} = 0$	3.63 (*sh*)	2.98 (0.42)
$\beta ss = 0.4$	4.04 (4.36)	3.66 (0.30)
$\beta^1{}_2 = 1.1$	4.80 (4.68)	4.79 (0.89)
$\beta_{3a6a} = 0.8$		

Table 3. I(R_1=Me, R_2=R_3=H, R_4=Ph)

Parameters	E_{obs} (logε)	E_{calc} (f)
$\omega\ddot{s} = 10.5$	2.51 (4.03)	2.563 (0.24)
$\omega\dot{s} = 0$	3.79 (4.05)	3.563 (0.41)
$\beta ss = 0.4$	4.58 (4.57)	4.326 (0.34)
$\beta_{12} = 1.1$	4.92 (4.61)	4.569 (0.73)
$\beta_{3a6a} = 0.8$		5.54 (0.35)

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[1] 2,5-Dimethyl-6a-thiathiophthen has been reported to have equal S–S bond lengths but accidental degeneracy of crystal and molecule symmetries means that the X-ray analysis would not reveal unequal S–S bond-lengths anyway [3]. Interestingly, both 2,5- and 3,4-diphenyl-6a-thiathiophthen have been reported to have unsymmetrical structures with unequal S–S bond-lengths [19, 20] in the crystal, thus removing the C_2 symmetry. These results however are probably due to distortion of the molecule in the crystal and so do not reflect the geometry of the isolated molecule.

ality to overlap and use of Mulliken's tables [15], but later calculations suggested the use of a smaller value. Values for two-centre integrals can be calculated readily since a considerable amount of X-ray data for bond lengths and angles in the 6a-thiathiophthens is now available [3]. For the calculations, the basic structure (I) was assumed with the σ-bonded skeleton shown and delocalised π-bonding provided by one $2p$-electron from each carbon, one $3p$ electron from the central sulphur atom, and two $3p$-electrons from each outer sulphur atom making a total 10 π-electron system. The ionisation potentials were determined by electron-impact using a modification of Warren's method [16, 17] and the results are shown in Table 4.

Table 4

Compound	*I.P.* (eV)		
	measured	calc.	Error
I(R_1=R_4=Me; R_2=R_3=H)	7.47	7.00[a]	−0.47
I(R_1=R_4=Me; R_2=H; R_3=Br)	7.49		
I(R_1=Me; R_2=R_3=H; R_4=Ph)	7.43	7.23	−0.20
I(R_1=R_4=Ph; R_2=R_3=H)	7.39		
I(R_1=SMe; R_2=R_3=H; R_4=Ph)	7.24		
Thiophthen	9.15	9.22	+0.07
Naphthalene	8.19	8.19	0

[a] *I.P.* calc for R_1=R_2=R_3=R_4=H (see text).

Results

The ultraviolet spectra of 6a-thiathiophthens [18] are characterised by strong absorption bonds nears 260 mμ and 500 mμ, the latter being responsible for the orange to deep-red colours of these compounds. Apart from the two main bands there are frequently observed other bands which require some comment. Simple alkyl derivatives of the 6a-thiathiophthens, as well as the parent molecule itself, show bands near 260 and 470 mμ but a shorter wavelength shoulder is usually observed near 240 mμ, and the 260 mμ band does not decay rapidly on its low wavelength side but suggests a further band near 300 mμ [18]. The presence of substituents capable of conjugating with the 6a-thiathiophthen nucleus leads to shifting of the 470 mμ band and the spreading of the bands near 260 mμ. In the spectrum of 2,5-diphenyl-6a-thiathiophthen at least four bands are discernable. As criteria of the success of the model of 6a-thiathiophthen based on structure (I), the SCF calculations of $\pi \rightarrow \pi$ transitions should follow the observed shifts in the ultraviolet spectra as well as predicting a long-wavelength maximum. The observed and calculated transition energies shown in Tables 1–3 for 6a-thiathiophthen, 2,5-diphenyl-6a-thiathiophthen, and 2-methyl-5-phenyl-6a-thiathiophthen are in reasonable agreement. The calculations based on the parameter values in Tables 1–3, correctly predict the intense long-wavelength maxima and the general spreading of peaks discussed above. The actual shift of the long-wavelength band with phenyl substitution is not so satisfactory, and, further, twisting of the phenyl ring out of the thiathiophthen plane does not affect this band greatly.

It is of interest that if $p-d$ or $d-d$ π-orbital overlap is important, the 6a-thiathiophthens may be regarded as Möbius strip molecules [21] and in terms of simple Hückel theory, a long-wavelength band should appear at about 2.78 eV, fortuitiously close to the observed value.

Before we obtained the small range of values for the parameters ωs and βcs [12] used in these calculations, we attempted to predict the $\pi \rightarrow \pi$ transitions in 6a-thiathiophthens using values for ωs and βcs suggested by earlier work [22]. These latter parameter values predicted no long-wavelength maximum in the visible spectrum and accordingly we considered the band might be due to a transition from the highest occupied molecular orbital into a vacant 3*d*-orbital on sulphur. Then, assuming the energy of the 3*d*-orbital to be little affected by substitution in the thiathiophthen, the transition energies obtained from ultraviolet spectra should be proportional to the ionisation potentials. The measured ionisation potentials are shown in Table 4 and there is a fair, linear correspondence between them and the energies of the long-wavelength bands (Fig. 2). However, the actual calculated ionisation potential for 2-methyl-5-phenyl-6a-thiathiophthen was not in good agreement with the observed value given in Table 4. It was later found [12] that the values for the parameters ωs and βcs which we had used did not predict the long-wavelength maximum in thiathiophthens, were equally unsatisfactory in calculating the electronic spectra of other sulphur heterocycles, and did not give a good value for the ionisation potential of thiophen. The values of the parameters developed by us [12] led to a prediction of the long-wavelength band in thiathiophthens and also gave good predicted values for the ionisation potentials of 2-methyl-5-phenyl-6a-thiathiophthen and thiophen. We therefore consider the long-wavelength band in 6a-thiathiophthens is in fact due to a $\pi \rightarrow \pi$ transition.

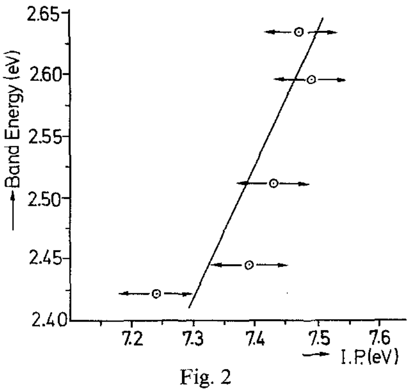

Fig. 2

Ionisation potentials were calculated by a modification of Koopmans' theorem [23]. It is well known that this theorem often gives values for ionisation potentials which are 1–2 eV to small and accordingly we used the equation, $I.P. = E_{\mathrm{HOMO}} + 1.77$ where E_{HOMO} is the energy of the highest occupied molecular orbital and the factor 1.77 is the difference between the observed ionisation potential and the calculated E_{HOMO} of naphthalene.

Conclusions

The observed $\pi \rightarrow \pi$ transitions and ionisation potentials of 6a-thiathiophthens can be predicted through SCF LCAO calculations based on structure (I) using parameters for sulphur derived from work on other sulphur compounds and this suggests that definite π-bonding exists between the three sulphur atoms.

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