

# A SELF CONSISTENT FIELD MOLECULAR ORBITAL TREATMENT OF THE REACTIVITY OF THIOPHENE AND THE ISOMERIC THIENOTHIOPHENES

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**Abstract**—The reactivity of thiophene and the isomeric thienothiophenes has been investigated using the semi empirical PPP SCF MO method.

## I. INTRODUCTION

IN CONNECTION with a recent study of the electronic spectra of the isomeric thienothiophenes<sup>1</sup> Fig. 1 the question of the reactivity of these molecules became of interest. Thieno[3.4b]thiophene (I),<sup>2</sup> has only recently been prepared and as yet there are no experimental data, as regards its reactivity in substitution reactions. Electrophilic substitutions in thieno[2.3b] (II) and [3.2b] (III)-thiophenes have been studied,<sup>3</sup>

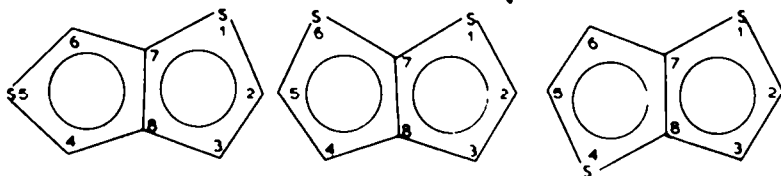


FIG. 1 Thieno[3.4b]thiophene

Thieno[2.3b]thiophene

Thieno[3.2b]thiophene

but there appears to be no previous SCF treatments of reactivity parameters for these compounds. A further isomer is also possible thieno[3.4c] Fig. 2 for which no classical structure may be written without involving a double bond to a sulphur atom; a calculation on the pi electronic structure of this compound is also of interest.

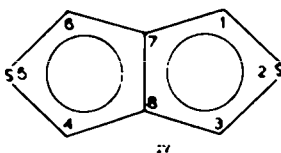


FIG. 2. Thieno[3.4c]thiophene

## II. METHOD OF CALCULATION

Detailed SCF Pople-Segal type calculations which we have carried out on thiophene,<sup>4</sup> including all valence electrons and taking into account 3s, 3p, 3d, 4s and 4p orbitals on sulphur, indicate that as far as the pi electronic energy of the system is concerned the 3d, 4s and 4p orbitals contribute to only a small extent. This is in agreement with the conclusion of Bielefeld and Fitts,<sup>5</sup> who considered only the pi

electronic system. Inclusion of the latter orbitals does affect the electron distribution to a significant extent. It is clear therefore that calculated localization energies should be reliable if 3d orbitals on sulphur are neglected, but charge densities must be treated with some reservations.

In a recent series of papers Dewar<sup>6</sup> and his co-workers have demonstrated that the Pariser-Parr-Pople treatment of pi electrons taken with empirical bond energies for the sigma system leads to very good estimates of heats of formation of aromatic hydrocarbons, oxygen and nitrogen heterocycles and localization energies for aromatic hydrocarbons. It has been pointed out elsewhere<sup>6</sup> that the main difficulty in the calculation of pi electron ground state properties is the estimate of the  $\beta$ 's which occur in the off diagonal elements of the F matrix. Using thermodynamic schemes, Dewar has made estimates of  $\beta$  for C-C, C-N and C-O bonds. There is a lack of thermodynamic data pertaining to aromatic sulphur compounds, thiophene<sup>7</sup> being one of the few compounds whose heat of formation is accurately known.

In discussing the electronic spectra of the thienothiophenes<sup>1</sup> the value of  $\beta$  for the C-S bonds was obtained from the empirical Wolfsberg Helmholtz<sup>8</sup> Eq. (1).

$$\beta_{\mu\nu} = K(I_{\mu\mu} + I_{\nu\nu}) S_{\mu\nu} \quad (1)$$

where  $K$  is a constant,  $I_{\mu\mu}$  and  $I_{\nu\nu}$  are the appropriate valence state ionization potentials for atoms  $\mu$  and  $\nu$ , and  $S_{\mu\nu}$  is the overlap integral.

This expression taken in conjunction with  $\beta_{C-C} = 2.371 \text{ eV}^9$  and the appropriate values of ionization potentials<sup>10</sup> and overlap integrals, gives a good account of the electronic spectra of thiophene and the isomeric thienothiophenes.<sup>1</sup> It seems worthwhile therefore to use Eq. (1) in conjunction with Dewar's ground state  $\beta_{C-C}$ <sup>6</sup> to evaluate  $\beta_{C-S}$  and hence attempt to calculate the heat of formation of thiophene. Taking the currently accepted heats of atomization of the elements, (carbon<sup>11</sup> 170.9 kcal/mole, hydrogen<sup>11</sup> 52.10 kcal/mole and sulphur<sup>12</sup> 65.90 kcal/mole), the heat of formation of thiophene from the gaseous atoms is  $-930.41$  kcal/mole. The heat of formation of the compound may be written as Eq. (2)<sup>6</sup>

$$\Delta H_f = -\sum E_{CC} - \sum E_{CH} - \sum E_{CS} - E_{\pi \text{ bonding}} \quad (2)$$

where  $E_{CC}$ ,  $E_{CH}$  and  $E_{CS}$  are bond energy terms for the relevant bonds and  $E_{\pi \text{ bonding}}$  is the calculated pi bonding energy as defined by Dewar. Reasonable estimates of carbon ( $sp^2$ )-hydrogen and carbon ( $sp^2$ )-carbon( $sp^2$ ) bond energies have been published.<sup>6</sup> Since the C-C bond lengths in thiophene alternate to a significant extent this must be taken into account. Compression energies were therefore calculated using the Morse formula (3)

$$\text{Compression Energy} = D_e[1 - \exp \alpha(r_e - r)]^2 \quad (3)$$

(Notation of Ref. 6)

The estimate of the bond energy term for the C-S bond is slightly more difficult. However, using the Laidler bond energy scheme<sup>13</sup> and the heat of formation of tetrahydrothiophene,<sup>12</sup> the bond energy  $E_{C(sp^3)-S}$  may be estimated as 69.20 kcal/mole. On the basis of increase in overlap integral in going to a  $C_{(sp^2)-S}$  bond, we may expect that the C-S bond energy should be higher in the latter case. It has been found empirically<sup>14</sup> that

$$E_{C(sp^2)-X} - E_{C(sp^3)-X} \approx 4 \text{ k cal/mole}$$

X = halogen

and this relationship is also probably reasonable for  $X = S$ . The value of  $E_{CS}$  for use in Eq. (2) was taken as 73.0 kcal/mole. For the calculation of the pi bonding energy by the Pariser-Parr-Pople SCF method the required one centre integrals were calculated from spectroscopic data,<sup>10</sup> and the two centre repulsion integrals evaluated using the uniformly charged sphere model. Full details of the method and parameters used will be published elsewhere.<sup>1</sup>

### III. RESULTS AND DISCUSSION

Table 1 shows the calculated contributions to the heat of formation of thiophene. The agreement between calculated and observed heats of formation is satisfactory and suggests that the value of  $\beta_{C-S}$  (-1.07 eV) is reasonable. For comparison the pi bonding energy calculated using the spectroscopic values<sup>1</sup> for  $\beta_{C-C}$  and  $\beta_{C-S}$  is included. This clearly emphasizes the need to use different parameters for ground state properties.

TABLE 1 CONTRIBUTIONS TO THE CALCULATED HEAT OF FORMATION OF THIOPHENE

Contribution	kcal
$\sum E_{CC}$	-268.19
$\sum E_{CH}$	-408.68
$\sum E_{CS}$	-146.00
$E_{\pi \text{ bonding}}$	-118.07
Total	-940.94
Expt. value	-930.41
$E_{\pi \text{ bonding}}$ (Spectroscopic $\beta$ 's)	-175.05

Having established a reasonable value for  $\beta_{C-S}$ , the electronic structure of the isomeric thienothiophenes was investigated. For these calculations the C-C bond lengths were taken to be 1.39 Å the average of the corresponding bond lengths in thiophene<sup>15</sup> and thieno[3.2b]thiophene<sup>16</sup> and the usual distance taken for an aromatic C-C bond. The C-S bond distances and C-S-C bond angles were taken to be those in thiophene (1.714 Å, 92°).<sup>15</sup> Tables 2 and 3 show the calculated eigen-

TABLE 2 CALCULATED EIGENVALUES FOR NAPHTHALENE, THIENO[3.2b]THIOPHENE AND THIENO[2.3b]THIOPHENE IN eV

Orbital number	II			III		
	Naphthalene	Thieno[3.2b]thiophene	Thieno[2.3b]thiophene	Naphthalene	Thieno[3.2b]thiophene	Thieno[2.3b]thiophene
10	2.451					
9	0.946					
8	0.126	1.630			1.939	
7	-0.881	0.515			0.003	
6	-1.692	-0.972			-0.682	
5	-9.648	-9.289			-9.566	
4	-10.459	-10.010			-9.756	
3	-11.466	-11.110			-11.065	
2	-12.286	-11.861			-11.861	
1	-13.791	-13.251			-13.254	

TABLE 3. CALCULATED EIGENVALUES FOR THIENO[3.4b]THIOPHENE AND THIENO[3.4c]THIOPHENE IN eV

Orbital number	I	IV
	Thieno[3.4b]thiophene	Thieno[3.4c]thiophene
10	-	-
9	-	-
8	1.864	2.109
7	0.215	0.5075
6	-1.086	-2.098
5	-9.055	-7.756
4	-10.196	-10.463
3	-10.933	-10.525
2	-11.866	-12.021
1	-13.261	-13.145

values for the isomeric thienothiophenes and for comparison those of naphthalene. For compounds I, II and III the  $10\pi$  electrons occupy the lowest five molecular orbitals giving a closed shell structure analogous to naphthalene. In the case of IV however the ground state is predicted to be a triplet, although the separation between singlet and triplet states is small  $\sim 0.11$  eV. (Since these calculations were completed a preliminary communication has appeared<sup>17</sup> on a derivative of the latter compound. The prediction of a triplet ground state would then explain the transitory existence of this compound and its facile addition reactions).

Applying Koopman's theorem, the predicted ionization potentials for I, II, III and naphthalene are 9.055, 9.289, 9.566, 9.648 eV. As is usual with the PPP SCF method ionization potentials tend to be overestimated but the values are all similar to that of naphthalene. Support for this comes from the fact that all four compounds form picrates. I is predicted to be the most susceptible to one electron oxidation.

No experimental heats of formation are available for the thienothiophenes, however if the reasonable assumption is made that the first three terms in Eq. (2) are the same for all four compounds, differences in heats of formation should be reflected in differences in  $E_{\pi\text{bonding}}$ . Table 4 gives the calculated differences in  $E_{\pi\text{bonding}}$  with respect to thieno[3.2b]thiophene II.

IV thieno[3.4c]thiophene is predicted to be much less stable in a thermodynamic sense, than the other isomers.

It has been pointed out previously<sup>6</sup> that the disappointing results experienced in early applications of SCF methods to the calculation of localization energies,<sup>18</sup> is a direct consequence of not allowing for core repulsion energies. This is particularly pertinent in the case of heterocyclic compounds. For example the calculated pi electronic energy for the Wheland intermediate cations for 2 and 3 substitution in thiophene are in the order  $3 > 2$ , however inclusion of the core repulsions reverses this order.

Table 5 gives the calculated localization energies for electrophilic, nucleophilic and free radical substitution in thiophene and the isomeric thienothiophenes.

For comparison the results for naphthalene are also included, these are essentially the same as those published by Dewar. The energies of the free radical intermediates were calculated in two ways using Koopman's theorem Eqs (4) and (5)

TABLE 4. CALCULATED DIFFERENCES IN  $E_{\pi}$  bonding IN eV FOR THE ISOMERIC THIENOTHIOPHENES

Compound	Differences in $E_{\pi}$ bonding in eV
thieno[3.2b]thiophene	0
thieno[2.3b]thiophene	0.054
thieno[3.4b]thiophene	0.313
thieno[3.4c]thiophene	2.000

TABLE 5. RELATIVE LOCALIZATION ENERGIES WITH RESPECT TO BENZENE AS STANDARD, FOR THIOPHENE, NAPHTHALENE AND THE ISOMERIC THIENOTHIOPHENES IN eV

Compound	Position of substitution	Type of substitution		
		Electrophilic	Radical	Nucleophilic
Thiophene	2	-1.205	-1.114	-0.460
	3	-0.057	-0.273	1.290
Thieno[3.2b]thiophene	2	-1.964	-0.915	-0.990
	3	-0.610	-0.025	1.172
Thieno[2.3b]thiophene	2	-1.685	-0.800	-0.365
	3	-0.7191	-0.005	-0.9884
Thieno[3.4b]thiophene	2	-1.430	-0.832	-0.737
	3	-1.069	-0.091	0.955
	4	-2.429	-1.245	-1.291
	6	-2.133	-1.084	-0.587
Naphthalene	1	-0.920	-0.410	-0.920
	2	-0.510	-0.14	-0.510

A negative value of localization energy indicates the site is more reactive than benzene

$$E_{\pi \text{ radical}} = E_{\pi \text{ cation}} + \epsilon + \quad (4)$$

$$E_{\pi \text{ radical}} = E_{\pi \text{ anion}} - \epsilon - \quad (5)$$

where  $\epsilon +$  and  $\epsilon -$  are the energies of an electron in the lowest unoccupied and highest occupied orbitals of the cation and anion respectively. The results show that these two approaches give identical answers.

For thiophene the 2 position is clearly favoured for all three types of substitution. As far as electrophilic substitution is concerned, thiophene is much more reactive than benzene, substitution occurring predominantly in the 2 position for a wide variety of electrophiles.<sup>19</sup> Comparison with Dewar's calculations show that the 2 position should be intermediate in reactivity to the 1 positions in naphthalene and anthracene, whilst the 3 position is almost identical to benzene. Quantitative data for electrophilic substitution in thiophene would suggest that this is a reasonable estimate of its reactivity.<sup>20,21</sup> Free radical substitution is predicted to occur more readily at both sites than in benzene, the 2 position again being favoured, phenylation for

example yields mainly the 2 isomer.<sup>22</sup> Nucleophilic substitution is again predicted to be more favourable in the 2 position, the 3 position being much less reactive than in benzene. Thieno[3.2b]thiophene and thieno[2.3b]thiophene have both been extensively investigated as regards electrophilic substitution reactions,<sup>3</sup> however, quantitative rate data is not yet available. The published observations leave little doubt that both of these compounds are very reactive, the 2 position being highly favoured as predicted. The 3 positions should be activated towards electrophilic substitution. Both free radical and nucleophilic substitution are predicted to favour the 2 substituted products. The substitution reactions of thieno[3.4b]-thiophene have not yet been reported.<sup>2</sup> This compound is of particular interest since the rings are non equivalent and there are four possible sites of substitution. The 4 position is highly activated and the most favoured site for electrophilic, nucleophilic and free radical substitution. Some interesting variations in localization energy seem worthy of note, concerning the order of reactivities of these compounds as given by the site of highest reactivity in each compound. For electrophilic substitution the order of decreasing reactivity is thieno[3.4b]thiophene > thieno[2.3b]thiophene > thieno[3.2b]thiophene > thiophene.

For free radical substitution

thieno[3.4b]thiophene > thiophene > thieno[3.2b]thiophene > thieno[2.3b]thiophene

For nucleophilic substitution

thieno[3.4b]thiophene > thino[3.2b]thiophene > thiophene > thieno[2.3b]-thiophene.

#### CONCLUSIONS

The extension of Dewar's SCF treatment of ground state properties of conjugated molecules to include sulphur compounds has been attempted and found to be satisfactory. In terms of PPP SCF MO calculations a reasonable interpretation of some of the chemistry of thiophene and the isomeric thienothiophenes has been presented.

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