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Commentationes

MO-SCF-LCAO Studies of Sulphur Compounds

III. Thiophene

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Results from an *ab initio* MO-SCF-LCAO study of the thiophene molecule, using an extended set of contracted Gaussian basis functions, are presented. The ordering of the molecular orbitals and the ionization energies are discussed in relation to experimental data from electron spectroscopy. A number of molecular properties have been computed in good agreement with available experimental information. The effect of $3d$ functions on sulphur for the description of the chemical bond and for the physical and chemical properties of thiophene is elucidated. Molecular potential energy maps are used in a discussion of the mechanism for electrophilic substitution reactions.

Es werden Resultate von *ab initio*-MO-SCF-LCAO-Studien des Thiophenmoleküls mit Hilfe eines erweiterten Satzes von kontrahierten Gauß-Basisfunktionen dargestellt. Die Reihenfolge der Molekülorbitale und die Ionisationsenergien werden diskutiert und mit experimentellen Daten aus elektronenspektroskopischen Messungen verglichen. Eine Anzahl molekularer Daten konnte in guter Übereinstimmung mit verfügbaren experimentellen Werten berechnet werden. Die Bedeutung der $3d$ Funktionen des Schwefels bei der Beschreibung der chemischen Bindungen und der physikalischen und chemischen Eigenschaften des Thiophens wird aufgezeigt. Zur Diskussion des Mechanismus elektrophiler Substitutionsreaktionen werden Diagramme der molekularen potentiellen Energie herangezogen.

Résultats d'un calcul *ab-initio* MO SCF LCAO de la molécule de thiophène, où l'on utilise une base étendue de fonctions gaussiennes contractées. L'ordre des orbitales moléculaires et les énergies d'ionisation sont discutés en fonction de données expérimentales de spectroscopie électronique. Un certain nombre de propriétés moléculaires calculées sont en bon accord avec les données expérimentales. On élucide l'effet des fonctions $3d$ du soufre sur la description de la liaison chimique et sur les propriétés physicochimiques du tiophène. Des cartes d'énergie potentielle moléculaire sont utilisées pour une discussion du mécanisme des réactions de substitution électrophile.

Introduction

Thiophene is one of the simplest conjugated cyclic systems which contain sulphur. The thienyl ring is an important building stone for many larger organic compounds. A detailed understanding of the sulphur-carbon bond in thiophene is therefore of great importance for the discussion of the chemistry of a large class of organic molecules. The electronic structure of thiophene has also interested theoretical chemists for many years. The early work was restricted to studies of the π-electron system. The first attempt to extend the Hückel molecular orbital method to heterocyclics was made by Wheland and Pauling [1] in a study of the thiophene molecule. Only the $3p_\pi$ orbital on sulphur was assumed to contribute to the π-electron wave function. The first suggestion that $3d$-orbitals might participate in the sulphur-carbon bond was made by Schomaker and Pauling a few years later [2]. A number of authors have later presented results from Hückel type calculations on thiophene and related sulphur containing systems using a $3p-3d$ hybrid atomic π-orbital on the sulphur atom.

Bielefeld and Fitts made a Pariser-Parr-Pople type calculation, where the basis set was enlarged with $3d_\pi$ and $4p_\pi$ functions on sulphur [3]. Their results showed that $3d_\pi$ atomic orbitals participate only to a small extent in the ground state. The electronic spectrum was, however, markedly influenced. The $3d_\pi$ orbitals also had a noticeable effect on the dipole moment.

Only the π-electrons were considered in these studies. The first attempt to give a description of the electronic structure of thiophene including all valence electrons was made by Clark [4]. He used the CNDO/2 method of Pople, Santry and Segal, modified in order to include $3d$, $4s$ and $4p$ atomic orbitals for sulphur in the basis set. The results showed a rather large participation of the $3d$-orbitals in the sulphur-carbon bond. The calculated population was 0.24 and 0.14 for $3d_\sigma$ and $3d_\pi$, respectively. Calculation of the dipole moment made it clear that the effect of the $3d$-orbitals was overestimated by the CNDO/2 method.

Clark and Armstrong have recently published results from an *ab initio* calculation on thiophene using contracted Gaussian basis functions [5]. A basis of 127 primitive Gaussians was reduced to 50 contracted functions; four *s*, two *p* and two *d* functions for sulphur, three *s* and one *p* functions for carbon and three *s* functions for hydrogen. The energy lowering due to the inclusion of the $3d$ functions was found to be 0.12 a.u. with a population of 0.72 electrons in S $3d$ orbitals. A large fraction of this population should, however, be attributed to S $3s$, since six *d*-type functions were used instead of five.

We report in this paper results from an *ab initio* calculation similar to the work of Clark and Armstrong. It is the third paper in a series discussing the electronic structure and molecular properties of sulphur compounds. Preceding papers have given results for the molecules H_2S and SO_2 [6] and the sulphate ion [7].

The basis set used here consists of 126 primitive Gaussians: ten *s*-type, six *p*-type and one *d*-type (exponent 0.5) functions for sulphur, seven *s*-type and three *p*-type functions for carbon and four *s*-type and one *p*-type Gaussian for hydrogen. This set was contracted to "double zeta", that is, two basis functions per atomic shell. The contracted set, thus obtained, consists of 76 contracted functions. Details of the choice of basis functions have been given previously and will not be further discussed here [6–8].

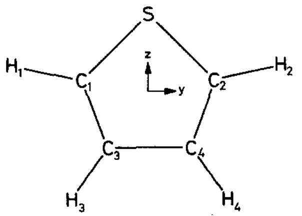


Fig. 1. Numbering of the atoms and the coordinate system for the thiophene molecule

All calculations were made at the experimental equilibrium geometry [9], using the IBMOL IV program system [10] and an IBM 360/91 computer. The coordinate system and the numbering of the atoms is shown in Fig. 1.

Results and Discussion

A. Total and Orbital Energies

Total energies are given in Table 1, where a comparison is made to the results obtained by Clark and Armstrong [5]. A lower total energy is obtained in the present work, since a larger set of contracted Gaussians has been used. The effect of adding polarization functions is, as expected, less pronounced with the larger basis set. The energy decrease due to the addition of $2p$ functions on hydrogen was found to be 0.023 a.u., while the addition of $3d$ functions on sulphur gives a further lowering of 0.030 a.u. The two effects are found to be completely independent of each other.

Orbital energies are reported in Table 2 together with experimental data for ionization energies. Lindholm *et al.* have recently presented an UV excited electron spectrum for thiophene measured up to 25 eV [11]. Their results together with the assignments made in [11] are given in the sixth column of Table 2. However, their assignment for three of the outer orbitals has been questioned by Gelius *et al.* on the basis of an intensity analysis of their ESCA results for thiophene [12]. This intensity analysis rather supported the present *ab initio* orbital assignment. The last column of Table 2 contains the ionization energies and the orbital assignments given in [12].

The structure of the outer molecular orbitals with respect to the distribution of charge and the bonding character is presented in Table 3. Mulliken's population analysis method has been used and the bonding properties have been obtained from the overlap populations.

The molecular orbitals corresponding to ionization energies below 27 eV can be divided into five well separated groups (Fig. 2). The same grouping of the levels is found experimentally as the results of Lindholm *et al.* show. The assignments made in their paper [11] is partly based on the present investigation, partly on experimental information and extended Hückel calculations including comparisons with spectra of related compounds. Both calculations and experiment predict the two outermost orbitals to be of π-type and give them in the

Table 1. Total energies for thiophene (in atomic units)

	T. E.	$-V/T$
Without pol. functions	-550.923	1.997
with H $2p$	-550.946	1.997
with S $3d$	-550.976	1.998
with H $2p$ and S $3d$	-550.999	1.998
Clark and Armstrong [5]:		
s, p basis on S	-550.417	—
s, p, d basis on S	-550.535	—

Table 2. Orbital energies and ionization energies for thiophene (in atomic units)

Orbital	no pol.	H 2*p*	S 3*d*	H 2*p* and S 3*d*	Ionization energies[a]	Ionization energies[b]
$1a_1$	−91.981	−91.980	−91.975	−91.974		
$1b_2$	−11.278	−11.279	−11.268	−11.269		10.68 (C 1*s*)
$2a_1$	−11.278	−11.279	−11.268	−11.269		
$3a_1$	−11.253	−11.253	−11.247	−11.248		10.67 (C 1*s*)
$2b_2$	−11.252	−11.252	−11.247	−11.247		
$4a_1$	− 8.988	− 8.987	− 8.977	− 8.976		
$3b_2$	− 6.680	− 6.679	− 6.669	− 6.669		6.29 (S 2*p*)
$5a_1$	− 6.679	− 6.678	− 6.668	− 6.668		6.24 (S 2*p*)
$1b_1$	− 6.675	− 6.674	− 6.666	− 6.665		
$6a_1$	− 1.198	− 1.199	− 1.183	− 1.185		0.959 ($6a_1$)
$4b_2$	− 1.001	− 1.001	− 0.995	− 0.995	0.820 ($7a_1$)	0.820 ($4b_2$)
$7a_1$	− 0.997	− 0.997	− 0.986	− 0.986	0.812 ($4b_2$)	0.812 ($7a_1$)
$8a_1$	− 0.767	− 0.766	− 0.764	− 0.762	0.673 ($8a_1$)	0.691 ($8a_1$)
$5b_2$	− 0.755	− 0.754	− 0.752	− 0.750	0.647 ($5b_2$)	0.654 ($5b_2$)
$9a_1$	− 0.709	− 0.707	− 0.703	− 0.702	0.610 ($9a_1$)	0.610 ($9a_1$)
$6b_2$	− 0.590	− 0.590	− 0.583	− 0.583	0.526 ($6b_2$)	0.526 ($6b_2$)
$10a_1$	− 0.546	− 0.544	− 0.541	− 0.540	0.511 ($10a_1$)	0.511 ($10a_1$)
$2b_1(\pi)$	− 0.531	− 0.530	− 0.524	− 0.524	0.489 ($7b_2$)	0.489 ($2b_1$)
$7b_2$	− 0.523	− 0.522	− 0.524	− 0.523	0.467 ($11a_1$)	0.467 ($7b_2$)
$11a_1$	− 0.471	− 0.471	− 0.476	− 0.475	0.445 ($2b_1$)	0.445 ($11a_1$)
$3b_1(\pi)$	− 0.350	− 0.350	− 0.342	− 0.342	0.349 ($3b_1$)	0.349 ($3b_1$)
$1a_2(\pi)$	− 0.339	− 0.338	− 0.333	− 0.332	0.327 ($1a_2$)	0.327 ($1a_2$)

[a] From Ref. [11]. — [b] From Ref. [12].

Table 3. Bonding character and populations for the outer molecular orbitals in thiophene[a]

Orb.	Gross atomic populations					Bonding character[b]				
	S	C_1	C_3	H_1	H_3	$S–C_1$	$C_1–C_3$	$C_3–C_4$	$C_1–H_1$	$C_3–H_3$
$6a_1$	0.50	0.36	0.35	0.02	0.02	b	b	b	nb	nb
$4b_2$	0.11	0.49	0.34	0.08	0.03	wb	sb	wab	wb	wb
$7a_1$	0.84	0.15	0.37	0.00	0.06	b	wb	sb	nb	nb
$8a_1$	0.30	0.36	0.28	0.20	0.02	ab	wb	b	sb	wb
$5b_2$	0.26	0.33	0.28	0.10	0.17	b	nb	wab	b	b
$9a_1$	0.18	0.24	0.40	0.08	0.19	nb	wb	wb	wb	b
$6b_2$	0.01	0.36	0.31	0.16	0.18	nb	b	ab	b	b
$10a_1$	0.06	0.21	0.57	0.12	0.07	nb	nb	sb	b	wb
$2b_1$	0.62	0.37	0.32	—	—	b	b	wb	—	—
$7b_2$	0.63	0.38	0.10	0.12	0.09	b	wab	wab	b	wb
$11a_1$	1.35	0.16	0.10	0.00	0.06	wb	wab	b	nb	nb
$3b_1$	1.12	0.00	0.43	—	—	wab	wb	sb	—	—
$1a_2$	0.03	0.70	0.28	—	—	nb	b	ab	—	—

[a] From the calculation including polarization functions.

[b] Nomenclature: b = bonding, a = anti, w = weakly, s = strongly and n = non.

same order. The next group consists of five orbitals. The present calculation gives them in the order: $11a_1 < 7b_2 < 2b_1 < 10a_1 < 6b_2$, where $2b_1$ is the third π-orbital. Lindholm *et al.*, on the other hand, predict the order to be: $2b_1 < 11a_1 < 7b_2 < 10a_1 < 6b_2$. This assignment is based on a comparison with

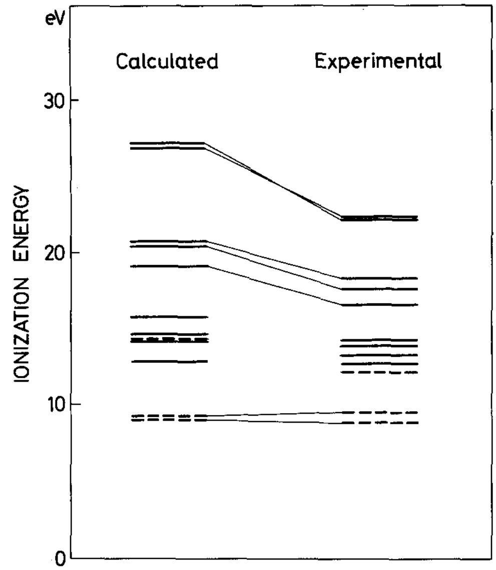


Fig. 2. A comparison between calculated and experimental ionization potentials for the outer molecular orbitals in thiophene. Experimental values and assignments are from the work of Lindholm *et al.* [11]. Dotted lines correspond to π-orbitals

benzene. The inner π-orbital ($1a_{2u}$) in this molecule has a vertical ionization energy of 12.3 eV [18]. Extended Hückel calculations give the values -15.0 and -14.8 eV for the orbital energies of the orbitals $1a_{2u}$ in benzene and $2b_1$ in thiophene [11]. Thus it is suggested that the ionization energy corresponding to $2b_1$ should be around 12.1 eV and the peak found at this energy is assigned to this orbital. A comparison with the results obtained by P. Siegbahn from an *ab initio* calculation on furan [15] is also made.

A series of *ab initio* calculations on azines with a basis set similar to the one used here has recently been performed by Roos *et al.* [16]. This study also includes benzene. It is therefore now possible to make a consistent comparison between experimental ionization energies and calculated orbital energies for the three molecules benzene, thiophene and furan. Ionization energies for the three π-orbitals in these molecules are given in Table 4. There is a good agreement between experimental and calculated shifts for the two outer π-orbitals. The calculations predict, in contrast to the extended Hückel calculations of Lindholm *et al.*, an increase in energy of around one eV for the inner π-orbital in thiophene compared to the corresponding orbital in benzene. If we use this shift to assign the photoelectron spectrum, we would expect to find the experimental value for the vertical ionization energy of $2b_1$ around 13 eV. This corresponds closely to the experimental ionization energy found at 13.3 eV, which has been assigned to $7b_2$ by Lindholm *et al.* Thus, following the same interpretation procedure as Lindholm but using *ab initio* instead of extended Hückel calculations in order to correlate the ionization energies of benzene and thiophene leads to an assignment for the fifth molecular orbital level in thiophene in agreement with the theoretical predictions made in this paper.

Table 4. Calculated and experimental ionization energies for the π-orbitals in C_6H_6, C_4H_4S and C_4H_4O (in eV)[a]

	C_6H_6	C_4H_4S	C_4H_4O
calc.	9.08	9.04	9.06
exp.	9.3	8.9	8.9
calc.	9.08	9.30	11.03
exp.	9.3	9.5	10.3
calc.	13.62	14.25	17.28
exp.	12.3	12.1 (13.3)	14.4 (15.6)

[a] Calculated values from [15, 16] and the present study. Experimental values were taken from the work of Lindholm *et al.* [11, 17, 18]. Values within parenthesis have been obtained with the assignments predicted by the calculations.

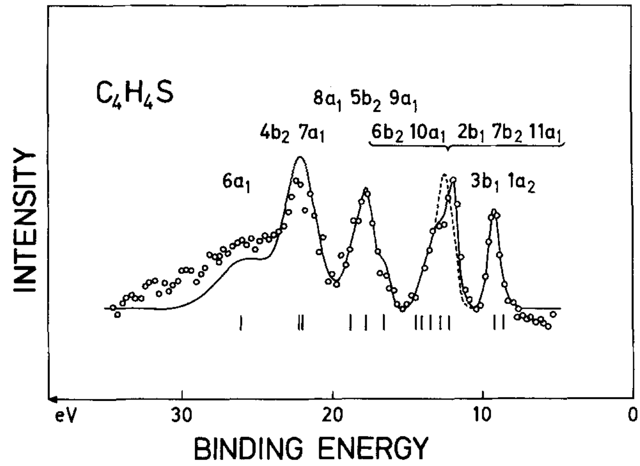


Fig. 3. The electron spectrum of the molecular orbital region in thiophene excited by Mg $K\alpha$. The solid and dotted lines are theoretically calculated intensities using different orbital assignments as discussed in the text. The positions of the orbitals are indicated by the vertical lines under the spectrum

It is assumed in the paper by Lindholm *et al.*, that the orbital $11a_1$ is nonbonding (lone-pair on the sulphur atom). It should therefore become impossible to explain the vibrational structure of the band at 12.1 eV with the assignments suggested here. The present results show, however, that $11a_1$ is delocalized with 67% of its charge on sulphur (cf. Table 3). It is found to be S–C_1 and C_3–C_4 bonding and C_1–C_3 antibonding. One should therefore expect to find "ring distorting" and "ring breathing" vibrational structure in the band due to the removal of an electron from $11a_1$.

Recently Gelius *et al.* have proposed a model, involving atomic subshell photoionization cross sections and gross atomic charges, for interpreting the molecular orbital intensities in electron spectra excited by soft X-rays [12]. The theoretical justification for this intensity model is discussed in [14]. The model has been applied to several molecules and the agreement with experimental intensities is generally good. Fig. 3 shows the electron spectrum of the valence electrons of thiophene excited by Mg $K\alpha$ together with the calculated intensity spectrum using the intensity model. The experimental spectrum has been corrected for a linear background and for the contribution from the Mg $K\alpha_{3,4}$ satellite lines. The gross atomic populations used in the intensity model were taken from the present calculation.Two different orbital assignments were examined, the *ab initio* assignment (solid line in Fig. 2) and the assignment proposed by Lindholm *et al.* (dotted line). From Fig. 3 it is obvious that the intensity analysis supports the present *ab initio* orbital assignment.

The ionization energy of the core electrons have also been studied by ESCA [12, 13, 19]. Particular attention has been paid to the chemical shift between the two different C 1*s* levels. Clark and Lilley reported an experimental value of 0.1 eV for this chemical shift [13]. Previously, however, Clark reported a broadening of 0.1 eV of the thiophene C 1*s* line relative to the corresponding line of benzene. Gelius *et al.* performed their ESCA measurements on gaseous thiophene, thereby achieving a somewhat better resolution. From an observed C 1*s* broadening of 0.13 eV relative to benzene they arrived at a C 1*s* chemical shift in thiophene of 0.34 ± 0.12 eV. This experimental shift is somewhat smaller than the 0.58 eV, which is the C 1*s* orbital energy difference in our best *ab initio* calculation. This is consistent with the general trend in MO-LCAO calculations of "double zeta" accuracy to give somewhat too large chemical shifts when Koopmans' theorem is used to estimate the ionization energies [15, 22–25].

B. Population Analysis

The result from a population analysis, using the method of Mulliken, is presented in Table 5. The population in the S 3*d* orbitals is found to be 0.18. Of this only 0.04 electrons is attributed to the 3*d*π-orbitals. The effect of back-bonding in the π-orbital $1a_2$ is thus found to be small (the 3*d*-population in this orbital is 0.01). It is interesting to compare these populations with the variation of the gross atomic charge on sulphur. The calculation without S 3*d* basis functions gives a charge of $+0.49$. With these functions the charge is reduced to $+0.00$. This decrease is much larger than the corresponding 3*d*-population. The effect of the 3*d* functions is to increase the populations in the S 3*s*- and S 3*p*-orbitals. Thus they act as *polarization functions* rather than as independent valence orbitals. An entirely different situation was found in SO_2 and SO_4^{-2} [6, 7]. The positively charged sulphur atom here stabilized the 3*d*-orbitals, so that they could act as additional valence orbitals. A large 3*d*-population was found with the S 3*s*- and S 3*p*-populations unaffected. Obviously there is a difference between systems like H_2S and C_4H_4S, where sulphur is the most electronegative atom, and systems where sulphur forms bonds with electronegative ligands like oxygen and fluorine. In the former case the 3*d*-functions will behave as polarization functions just as they do when they are added to the basis set for a first row atom. In the second case, however, the 3*d*-level is stabilized and is available for additional bonding as in SO_4^{-2}, SOF_2, SF_6, etc.

The large decrease in charge on the sulphur atom gives a corresponding decrease for the carbon atoms C_1 and C_2. In agreement with semi-empirical

Table 5. Gross atomic populations and charges for thiophene

	no pol.	H $2p$	S $3d$	H $2p$ and S $3d$
S (s-orb.)	5.790	5.787	5.804	5.806
S ($p\sigma$-orb.)	6.003	5.995	6.278	6.284
S ($p\pi$-orb.)	3.725	3.727	3.723	3.727
S ($d\sigma$-orb.)	—	—	0.143	0.143
S ($d\pi$-orb.)	—	—	0.038	0.037
q (S)	+0.482	+0.491	+0.016	+0.001
C_1 (s-orb.)	3.324	3.263	3.184	3.134
C_1 ($p\sigma$-orb.)	2.135	2.076	1.976	1.894
C_1 ($p\pi$-orb.)	1.109	1.105	1.085	1.080
q (C_1)	−0.568	−0.444	−0.245	−0.108
C_3 (s-orb.)	3.166	3.124	3.187	3.146
C_3 ($p\sigma$-orb.)	1.983	1.907	2.021	1.941
C_3 ($p\pi$-orb.)	1.028	1.025	1.035	1.032
q (C_3)	−0.177	−0.056	−0.243	−0.119
H_1 (s-orb.)	0.733	0.826	0.751	0.847
H_1 (p-orb.)	—	0.027	—	0.030
q (H_1)	+0.267	+0.147	+0.249	+0.123
H_3 (s-orb.)	0.764	0.864	0.768	0.869
H_3 (p-orb.)	—	0.028	—	0.028
q (H_3)	+0.236	+0.108	+0.232	+0.103

π-electron studies, these calculations also predict a somewhat larger π-electron density on the carbon atom C_1 than on C_3. This is, however, more than counterbalanced by the greater accumulation of σ-electrons on C_3. This is explained by the fact that the sulphur atom acts as an equally strong σ-electron acceptor as it is a π-electron donor. Thus the total negative charge is greater on C_3 than on C_1. The implications of this charge distribution in the double bond on the molecular potential in this region will be discussed below.

C. Molecular Properties

A number of molecular properties of the thiophene molecule have been computed. The results are presented in Table 6 together with available experimental data.

The inclusion of the $3d$S functions has a marked effect on the results. Thus the dipole moment decreases from 0.96 to 0.62 Debye. This change is caused by the reduction of the atomic charges, which results in almost non-polar bonds. The quadrupole moments exhibits a similar, but less pronounced effect. The expectation value $\langle z^2 \rangle_{CM}$ is decreased, due to the increased electron density around the sulphur atom. This in turn leads to the changes of the quadrupole moment components shown in Table 6. These results can be compared with the experimental values given by Sutter and Flygare [21]. Thus, the results for θ_{xx}, θ_{yy} and θ_{zz}, computed without $3d$S functions are, respectively, 91%, 103% and 48% of the experimental values. With $3d$S functions in the basis set these figures become 95%, 100% and 73%. The improvement is, as expected, greatest for θ_{zz}.

Table 6. Molecular properties of thiophene[a]

	no pol.	H $2p$	S $3d$	H $2p$ and S $3d$	exp.
Dipole moment (Debye)					
	0.959	0.973	0.606	0.619	0.54[b]
Quadrupole moment (10^{-26} esu · cm^2)					
Q_{xx}	−7.593	−7.597	−7.839	−7.847	−8.3 ± 2.2[c]
Q_{yy}	6.784	6.850	6.536	6.608	6.6 ± 1.5
Q_{zz}	0.809	0.747	1.303	1.239	1.7 ± 1.6
Diamagnetic susceptibility tensor (10^{-6} erg/G^2 mole)					
χ^d_{xx}	−440.64	−440.51	−439.78	−439.70	−438.1 ± 3.0[c]
χ^d_{yy}	−286.64	−286.58	−285.81	−285.78	−284.8 ± 3.0
χ^d_{zz}	−226.90	−226.75	−226.50	−226.38	−225.7 ± 3.0
$\chi^d_{\mathrm{av.}}$	−318.06	−317.95	−317.36	−317.28	−316.2 ± 3.0
Potential at the sulphur nucleus (a.u.)					
Φ(S)	−59.21	−59.21	−59.22	−59.22	
Electric field gradient at the sulphur nucleus (a.u.)					
q_{xx}(S)	1.606	1.601	1.520	1.514	
q_{yy}(S)	−1.930	−1.916	−1.929	−1.919	
q_{zz}(S)	0.324	0.315	0.410	0.404	
Quadrupole coupling constants for S^{33}, assuming $Q(S^{33}) = -0.062$ barns (MHz)					
$eq_{xx}Q(S^{33})$	−23.40	−23.32	−22.14	−22.06	
$eq_{yy}Q(S^{33})$	28.12	27.91	28.10	27.96	
$eq_{zz}Q(S^{33})$	−4.72	−4.59	−5.97	−5.89	
Other expectation values (a.u.)					
$\langle x^2 \rangle_{\mathrm{CM}}$	30.68	30.65	30.53	30.50	30.4 ± 4.3[c]
$\langle y^2 \rangle_{\mathrm{CM}}$	160.31	160.22	160.13	160.06	159.3 ± 4.3
$\langle z^2 \rangle_{\mathrm{CM}}$	210.60	210.58	210.06	210.06	209.3 ± 4.6
$\langle 1/r_{\mathrm{S}} \rangle$	66.11	66.11	66.12	66.12	
$\langle 1/r_{\mathrm{C}_1} \rangle$	25.66	25.66	25.67	25.67	
$\langle 1/r_{\mathrm{C}_3} \rangle$	25.04	25.04	25.05	25.05	
$\langle 1/r_{\mathrm{H}_1} \rangle$	11.19	11.20	11.19	11.20	
$\langle 1/r_{\mathrm{H}_3} \rangle$	10.76	10.77	10.76	10.78	

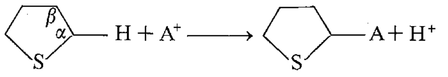
[a] The y and z axes are in the molecular plane and the z axis bisects the CSC angle.
[b] Ref. [20]. — [c] Ref. [21].

With a bulk magnetic susceptibility of -57.40×10^{-6} erg/G^2 mole, Sutter and Flygare obtain the elements of the diamagnetic susceptibility tensor. As can be seen in Table 6 the agreement with our calculated values is excellent. The effect of the $3d$S functions on this property is negligible.

There is, to our knowledge, no experimental determination of the quadrupole coupling constants for S^{33} in thiophene. The values given in Table 6 have been obtained with a value of -0.062 barns for the nuclear quadrupole moment of S^{33} [6]. In a previous work we have calculated the quadrupole coupling constants for S^{33} in SO_2 [6]. The results were in good agreement with experiment. We therefore believe that the results obtained in the present study are also close to the true values.

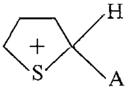
D. Molecular Potentials and Electrophilic Substitution

The five-membered rings pyrrole, furan and thiophene undergo electrophilic substitution preferentially at the α-position (C_1 in Fig. 1):



(1)

The orientation to the α-position seems to be more pronounced in furan and thiophene than in pyrrole [26]. It is generally assumed that the mechanism for aromatic electrophilic substitution proceeds via an intermediate addition complex [27]:



(2)

It is, however, also possible that complexes of π-type are involved in some reactions of this type. This possibility will be discussed below for the thiophene molecule.

The theoretical interpretation of the preferential position for electrophilic attack has traditionally been made by means of π-electron theory. Discussions based on frontier electron densities and localization energies have in many cases been able to give results in good agreement with experiments, while the orientation role of the total π-electron distribution seems to be less well established. Actually these three concepts refer to different steps in the reaction. The π-electron distribution is assumed to be related to the electrostatic potential in the C–C double bond. Therefore it should give information about the orientation of the electrophilic reagent in an intermediate π-complex. The frontier electron density and the localization energy give, on the other hand, information about the formation of the addition complex (2) where the double bond has been broken and a bond is established between the aromatic compound and the electrophile. Interpretations by means of frontier electron densities are quite straight forward for the five-membered heterocycles pyrrole, furan and thiophene. Semi-empirical π-electron calculations on these molecules show that the frontier orbital is of symmetry $1a_2$ (symmetric with respect to rotation about the symmetry axis) and with most of the charge located at the α-position. The present study also gives this (cf. Table 3) and a similar result was obtained for furan in a previous study [15].

Scrocco *et al.* have suggested that useful information about the reactivity of molecules can be obtained from a study of molecular potentials [28]. The electrostatic interaction energy between the molecule and a positive test charge was mapped. These maps showed well defined nucleophilic regions around the molecules and the results could be used to discuss the protonation of a series of three-membered ring systems [29]. Recently the same method has been used in a discussion of the protonation of formamide [30].

One might expect to gain some insight into the mechanism for electrophilic substitution reactions from a study of such molecular potential maps. The possibility for a π-complex intermediate, where the electrostatic interaction will be dominant, can be discussed. Preferential directions for electrophilic attack might also be elucidated from a study of such maps.

Such a study has been performed for the thiophene molecule. A computer program, constructed by Almlöf [31], was used. For computational reasons the calculations were made with the 3*d*S functions excluded from the basis set. This is, however, not a serious drawback since the influence of these functions on the wave function is small. Further, the potential energy, being a quantity which is optimized in a calculation based on the variational principle, is insensitive to small changes in the basis set. The potential energy at the sulphur nucleus has been computed with and without the 3*d*S functions and was found to change less than 0.02% (cf. Table 6).

The first map was made in the plane of the molecule. The potential was found to be positive everywhere except in the sulphur lone-pair region, where a minimum was found at a distance of 1.90 Å from the sulphur nucleus and with a depth of −9.4 kcal/mole. Next the potential was mapped in a plane through the C–C double bond and perpendicular to the molecular plane. The energy was found to be positive up to a height of 1.25 Å. A minimum of −14.0 kcal/mole occurred at a distance of 1.74 Å from the molecular plane. In order to investigate this region closer, a map was made in a plane parallel to the molecule at this distance. This potential energy map is shown in Fig. 4. The potential is negative

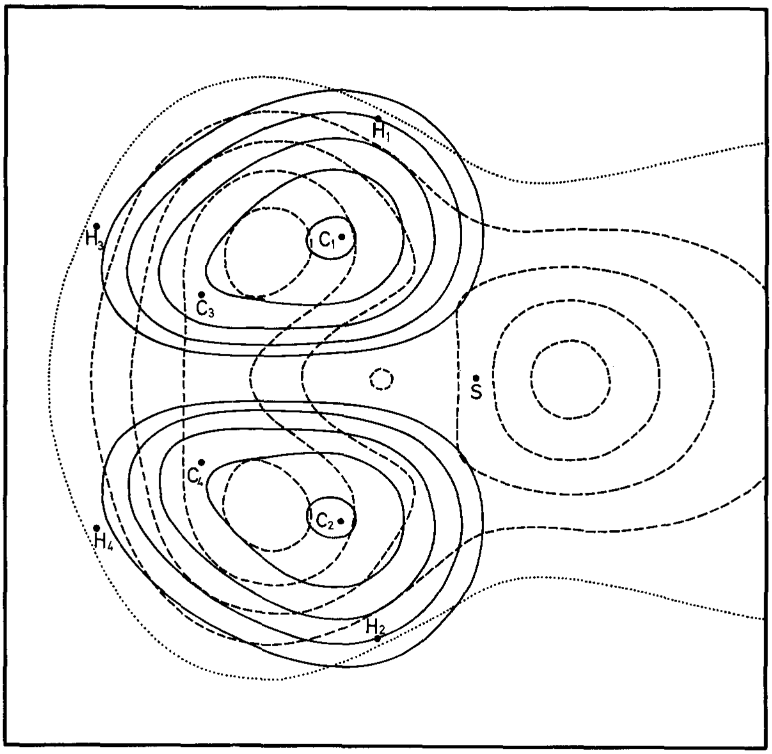


Fig. 4. Molecular potential surface in a plane parallel to the molecule at a distance of 1.74 Å (dotted lines). The following lines are plotted: 0, −0.005, −0.010, −0.015 and −0.020 a.u. Superimposed on this figure is an electron density map for the frontier orbital $1a_2$. The density lines are: 0.001, 0.002, 0.004, 0.008 and 0.016

everywhere, which illustrates the nucleophilic character of the π-electron system. Three distinct minima are found, one over each of the double bonds (−14.0 kcal/mole) and one in the sulphur lone-pair region, with the same energy. This region was investigated in more detail by means of a map in a plane through the symmetry axis and perpendicular to the plane of the molecule. The result is shown in Fig. 5. The energy minimum occurs at a distance of 1.95 Å from the sulphur nucleus and at a height above the plane of 1.59 Å.

These results indicate two possible pathways for an electrophilic attack on thiophene. If a π-complex intermediate is formed, a position of the reagent at the sulphur atom seems equally probable as a position above one of the double bonds. It is noteworthy that the energy minima occur at such large distances from the molecule that the overlap between the frontier orbitals and the electron accepting orbital of the electrophile can be assumed to be small. The electrostatic interaction is therefore dominant, and the minima found in the potential energy maps should correspond rather closely to minima in the true interaction energy. Thus, the results give some confidence to the idea that the reaction can proceed via weak intermediate addition complexes of π-type.

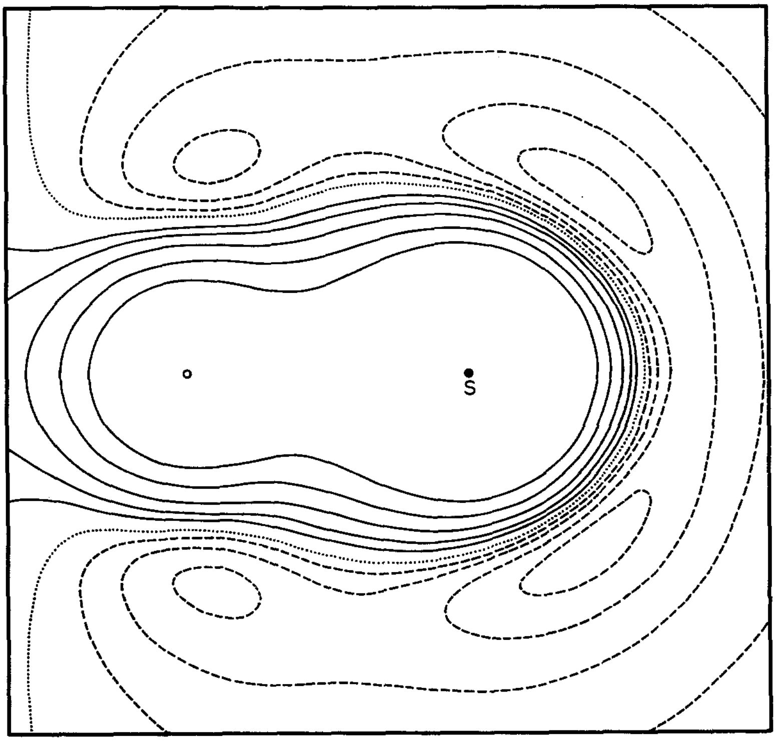


Fig. 5. Molecular potential surface in a plane perpendicular to the molecule and through the two-fold symmetry axis. The following lines are plotted: −0.020, −0.015, −0.010, −0.005, 0.0 (dotted line), 0.01, 0.02, 0.04, 0.08 and 0.16 a.u.

It is interesting to note that the distances from the energy minimum at the double bond to the two carbon nuclei are almost exactly equal. The population analysis data show that the α-carbon has a somewhat larger π-electron population than the β-carbon (cf. Table 5). This is consistent with results obtained from semi-empirical calculations [32]. It might therefore be dangerous to use only π-electron populations, which is often done, to draw conclusions about the orientation role of the electrostatic interaction between the π-electron system and the electrophile.

The results from the present study suggest another explanation for the orientation of the substitution to the α-carbon. The reaction coordinate would most probably go through regions of negative potential energy. Thus one can assume that the attack occurs either through the double bond or through the sulphur lone-pair. The results suggest the existence of outer complexes of π-type, but this is not necessary for the determination of the reaction path. An attack through the sulphur atom would most likely lead to substitution at the C_α-position. The intermediate (2) is formed by a charge transfer mainly from the frontier orbital $1a_2$, which has most of its electrons at C_α but also some population at sulphur due to $3d\pi - 2p\pi$ conjugation. Attack through the double bond could lead to substitution at both positions. The uneven charge distribution in the orbital $1a_2$ also in this case favours substitution at the C_α-position. The electron density distribution in this molecular orbital is illustrated in Fig. 4.

A quantitative estimate of the orientation, taking into account the pathway through the lone-pair region and the uneven charge distribution in $1a_2$, gives 85–90% C_α-substitution. Nitration of thiophene is known to give 70% α-substitution and only 5% β-substitution [26].

It should be remembered, however, that the discussion made above does only take into account first order interactions between the aromatic system and the electrophile. The results might be modified by polarization and solution effects. In a future work these effects will be studied by means of a comparison of potential energy maps and detailed computations of the reaction surfaces for protonation reactions.

Conclusions

The sulphur atom in thiophene forms almost non-polar bonds, with a gross atomic charge of zero on the sulphur atom and +0.02 on the adjacent CH group. The $3d$S functions have been found to behave as polarization functions rather than as an extra valence orbital. This is shown by the fact that the population of these functions in small. Instead, their introduction into the basis set causes considerable changes in the $3s$ and $3p$ population.

The orbital energy ordering has been found to be in agreement with the ordering obtained from an intensity analysis of the ESCA results, but to deviate slightly from the molecular level order suggested by Lindholm *et al.* from an analysis of the UV excited electron spectrum.

A number of molecular properties have been calculated and found to be in good agreement with available experimental data. The $3d$S functions gave a considerable improvement on the results for the dipole and quadrupole moments.

Molecular potential energy maps have been used to discuss the mechanism for electrophilic substitution reactions. The existence of weak intermediate complexes of π-type is suggested together with two possible explanations for the preferentiality of C_α-substitution. The molecular energy maps show a possible pathway for the reaction which goes through an energy minimum above the sulphur atom and leads to substitution at the C_α-positions. The other pathway, through the C_α–C_β double bond, might give substitution at both positions. However, also in this case C_α-substitution will probably dominate, due to the uneven charge distribution in the frontier orbital $1a_2$.

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