Tetrahedron Vol 24, pp 2663 to 2679 Pergamon Press 1968 Printed in Great Britain

A SELF CONSISTENT FIELD MOLECULAR ORBITAL INVESTIGATION OF THE IMPORTANCE OF d ORBITAL PARTICIPATION IN THE GROUND STATE OF THIOPHENE

D. T. CLARK
Department of Chemistry, The University, Durham

(*Received in the UK* 12 *September* 1967, *accepted for publication* 29 *September* 1967)

Abstract—The electronic structure of thiophene has been investigated using the Pople Segal Complete-Neglect of Differential overlap self consistent field theory and including all valence electrons. The effect of including 3d, 4s and 4p orbitals on sulphur is discussed in relation to calculated and experimental dipole moments and spin spin coupling constants. The evidence is that inclusion of 3d, 4s and 4p orbitals has a very small effect on the calculated total energy of thiophene, but a significant effect on the relative magnitude of proton–proton and directly bonded carbon 13-proton coupling constants, and calculated dipole moments.

INTRODUCTION

THE role of d orbital participation in the ground state of thiophene (Fig. 1) has interested chemists for many years.

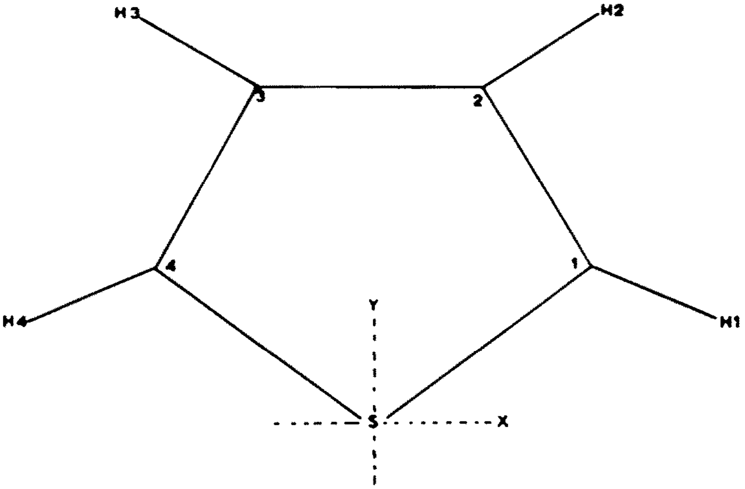


FIG. 1 Numbering system and co-ordinate system for thiophene.

The first suggestion that d orbitals might be important in thiophene was put forward by Schomaker and Pauling,[1] who on the basis of dipole moment and bond length data, inferred a 10% contribution from resonance canonicals involving d orbital participation on sulphur. This is based mostly on speculation, however, and cannot be considered as serious evidence for the importance of d orbital participation.

Longuet-Higgins showed[2] theoretically that an analogy might be drawn between —CH=CH— and —$\ddot{S}$— using 3p–3d hybrids of the latter, and this model has been extensively used[3] in Hückel type calculations on heterocyclic sulphur compounds. This model has been severely criticized by Zauli and his co-workers, who pointed out[4] that hybrid oribtals built with $3p_x$, $3d_{xz}$ and $3d_{yz}$ orbitals to give the required bond angle, would have too high an energy to contribute effectively.

Several SCF Pariser–Parr Pople calculations have been carried out[5–8] on thiophene, and with one notable exception[8] all have neglected participation of d orbitals on sulphur, and all to some extent or another agree with experimental data. The striking feature about these calculations, is the wide variation in charge distribution and calculated dipole moments. For example there is even disagreement as to the relative magnitudes of electron densities at the ring carbon atoms.[5–8] On the other hand the calculated electronic spectra are all very similar.[5–8]

The paper by Bielefeld and Fitts[8] is of considerable interest as it is the first to explicitly consider d orbital participation in thiophene, and raises some interesting points. Firstly the pi overlap integral between a 3d orbital on sulphur and a $2p_z$ orbital on carbon adjacent was calculated to be 0·473, at a distance of 1·714 Å. The distance to the non nearest neighbour carbon (2·556 Å) is still short enough for the overlap integral to have an appreciable value. Recent calculations[9] have shown that inclusion of non nearest neighbour β's has a substantial effect on charge distribution. Secondly in common with all the previous SCF treatments of thiophene, only the pi electrons were considered, this poses the question, if d orbitals have a significant effect on the pi electron distribution can the effect on σ electrons be ignored?

The importance of d orbital participation in neutral sulphur compounds has been discussed by Craig *et al.*[10, 11] on the basis of overlap integrals calculated using Slater orbitals. The effective nuclear charge calculated using Slater's rules[12] for a sulphur 3d orbital is small, and hence overlap integrals involving this orbital are also calculated to be small. This led Craig *et al.*[10, 11] to suggest that sulphur needs to be attached to electronegative groups to allow sufficient contraction of the d orbitals for effective overlap. However this result rests on the false premise that overlap integrals calculated using Slater orbitals are a good approximation to integrals calculated using SCF orbitals, *if* Slater's rules are used to obtain effective nuclear charges. These rules were devised to yield orbitals with reasonable energies. For orbitals with high principal quantum number, the energy is largely determined by the wave function close to the nucleus, whereas overlap integrals are determined by the magnitude of the wavefunction at distances further from the nucleus. This has led Burns[13] to produce a set of modified Slater's rules, which give overlap integrals very similar to those obtained using SCF orbitals.

Figures 2–4 show overlap integrals involving S and H and C using Slater orbitals and Burns modified Slater rules. The striking feature in Fig. 2 is the high value of the H(1s)-S(3d) overlap integral and its slow tailing off. The dotted lines indicate the overlap integrals involved in thiophene, for comparison C–C overlaps involved are also included. Figures 2–4 show quite clearly that d orbital participation on S cannot be rejected on the grounds of overlap integrals being too small.

It is the purpose of this paper to try and shed some new light on the electronic structure of thiophene and the importance of d orbitals therein, considering all the valence electrons in a Pople–Segal[14–16] type SCF calculation. Since the energies[17]

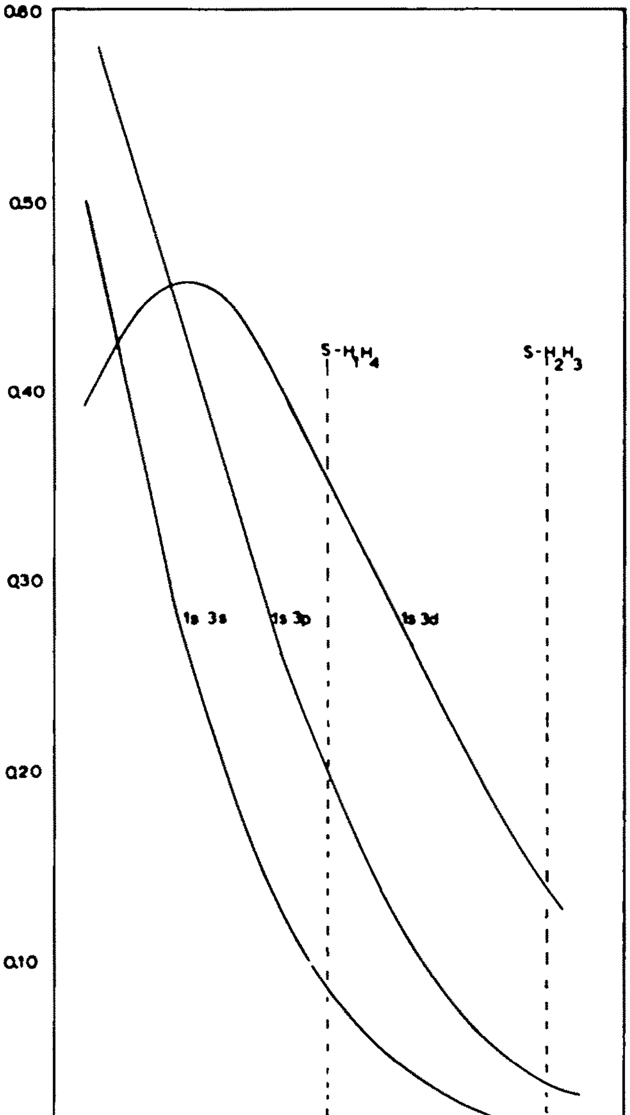


Fig. 2 Overlap integrals involving a hydrogen 1s orbital and 3s, 3p and 3d orbitals on sulphur.

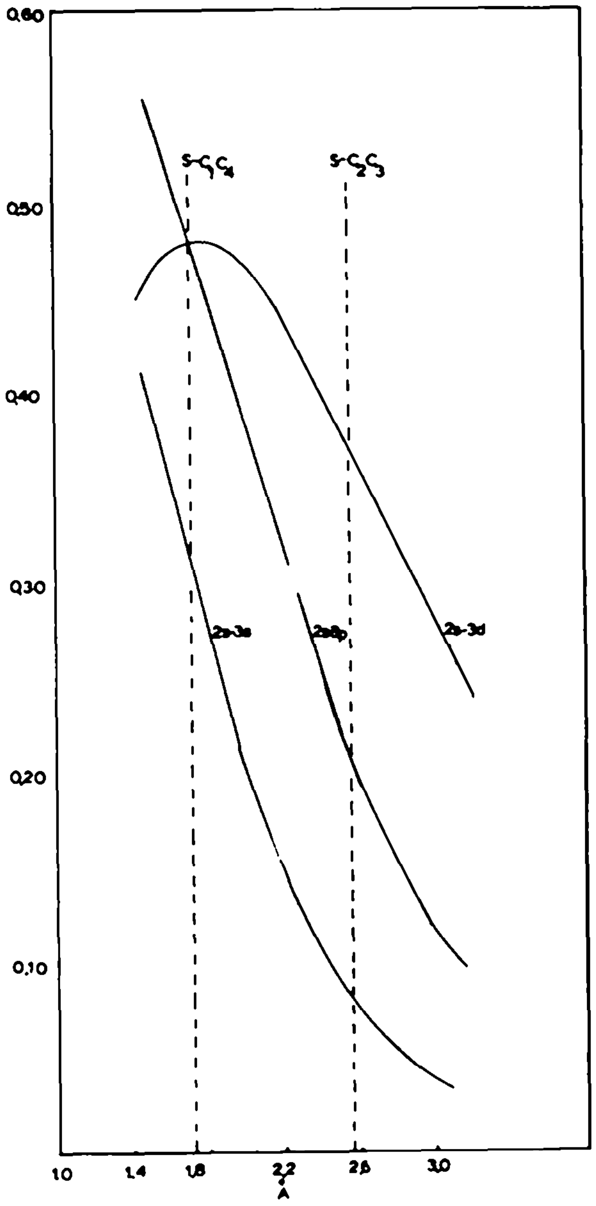


FIG. 3 Overlap integrals involving a carbon 2s orbital and 3s, 3p and 3d orbitals on sulphur.

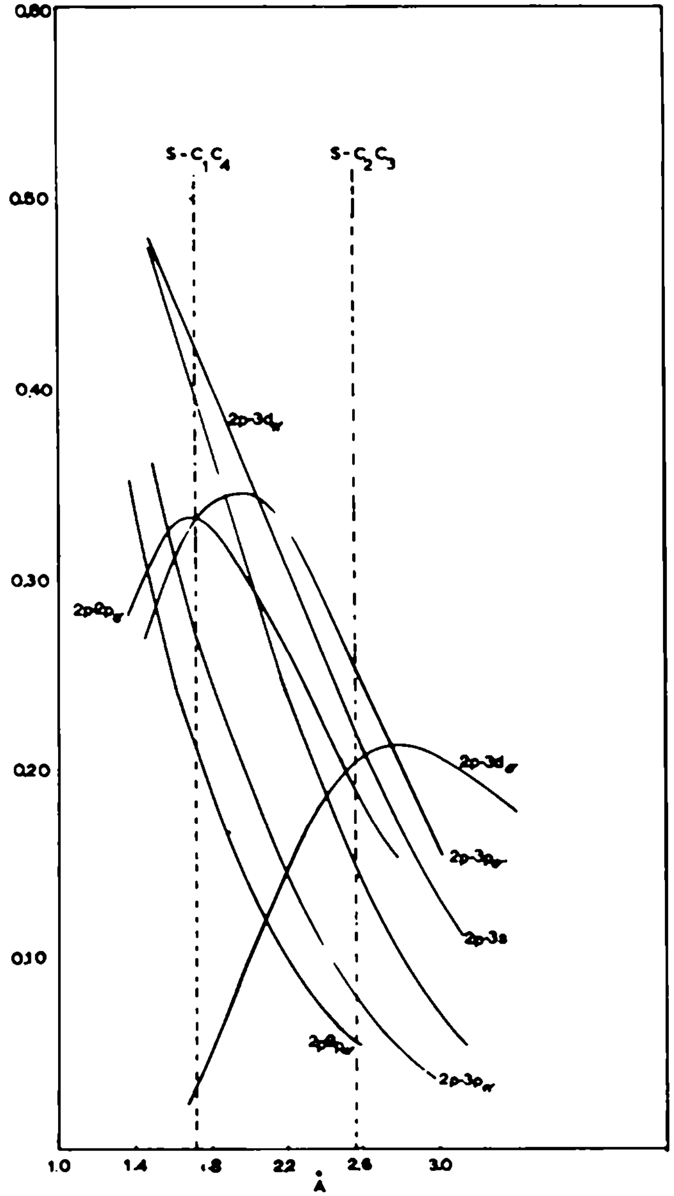


FIG. 4 Overlap integrals involving a carbon 2p orbital and 3s, 3p and 3d orbitals on sulphur.

of the 4s and 4p orbitals of sulphur are very similar to those of the 3d orbitals, calculations were also carried out including the latter.

Method of calculation

In a recent series of papers Pople *et al.*[14–16] have produced a new approximate method for calculating self-consistent molecular orbitals for all valence electrons, for molecules containing no atoms heavier than fluorine, i.e. excluding d orbitals, the so called Complete Neglect of Differential Overlap Method II[16] The theory has been applied to numerous small molecules with spectacular success, and it is therefore of considerable interest to apply this method to larger molecules, and to investigate the inclusion of d orbitals.

The elements of the F matrix are given by Eqs (1) and (2) (notation Ref. 15).

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB} \tag{1}$$

$$\text{where } U_{\mu\mu} = -I_\mu - (Z_A - 1)\gamma_{AA}$$

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \tag{2}$$

Eq. (1) neglects the penetration terms, the equations are formally similar to those used in the highly successful Pariser–Parr–Pople SCF theory[18, 19] of pi electronic structure of molecules.

As in the latter theory, the main problem is the estimation of the core and repulsion integrals and the β's which occur in the off diagonal elements of the F matrix. Pople *et al.*[16] have estimated the one centre core integrals from the average of valence state ionization potentials and electron affinities, however, valence state ionization potentials are in general more accurately known than electron affinities so we have approximated the core integrals as the average of valence state ionization potentials in the manner described by Sichel and Whitehead.[20] For the 3d, 4s and 4p orbitals of sulphur, the core integrals were approximated to the ionization potentials[17] for the processes

$$\text{(3d)}\ s^2p^33d \rightarrow s^2p^3$$

$$\text{(4s)}\ s^2p^34s \rightarrow s^2p^3$$

$$\text{(4p)}\ s^2p^34p \rightarrow s^2p^3$$

The 3d orbitals are highly directional giving rise to ligand perturbation effects, however for neutral compounds with elements in their normal covalency such a perturbation by the ligands is expected to be small, hence we have neglected this factor.

In their original paper Pople and Segal[14–16] assigned to γ_{AA} the analytic value of the electrostatic repulsion energy of two electrons in a Slater s orbital. This does not allow for correlation energy, and hence we prefer to use the method due to Pariser,[21] which has been applied so successfully in the P–P–P SCF method, of evaluating the γ_{AA} from Eq. (3).

$$\gamma_{AA} = I_{AA} - A_{AA} \tag{3}$$

where I_{AA} is the valence state ionization potentials of atom A.

A_{AA} is the valence state electron affinity of atom A. Whitehead[20] has investigated this method in detail and the parameters used here are taken from this paper.

If the results of the CNDO approximation are to be invariant to local transformations of the atomic orbital basis functions, then the same value of γ_{AA} must be taken for s, p and d orbitals on atom A. The 3s and 3p orbitals on sulphur will undoubtedly be more important as far as bonding is concerned than either the 3d or 4s and 4p orbitals, so that the average repulsion energy should approximate the average for the former orbitals (9·21 eV). This is probably not too serious an approximation to make as the one centre repulsion integral for a 3d orbital on S, for example, may be estimated as around 7 eV.

The two centre repulsion integrals γ_{AB} were calculated from the corresponding one centre repulsion integrals using the refined Mataga[22] procedure Eq (4)

$$\gamma_{AB} = \frac{14{\cdot}397}{(\alpha_{AB}^2 + r_{AB}^2)^{\frac{1}{2}}} \quad \text{where} \quad \alpha_{AB} = \frac{(2 \times 14{\cdot}397)}{\gamma_{AA} + \gamma_{BB}} \tag{4}$$

Since this work was essentially completed a publication has appeared in which Santry and Segal,[23] have included d orbitals on sulphur in the CNDO II method. Their approach differs from ours mainly in the evaluation of overlap integrals and γ's. They divide their γ_{AB}'s into three sets γ_{AB} (s,s), γ_{AB}(s,d) and γ_{AB}(d,d) and approximate each as the analytic value of the electrostatic repulsion energy of the two electrons in appropriate Slater s orbitals. This is necessary since the electron repulsion terms calculated in this way for the three sets differ considerably, so that a single value is no longer adequate. Their calculations therefore are not invariant to local transformations of the atomic orbital basis functions. The electron repulsion integrals calculated using Pariser's approximation as modified by Sichel and Whitehead[20] give electron repulsion integrals which are much smaller, and hence differences are smaller. The calculations reported here correspond most closely to those using the basis set spd[1] reported by Santry and Segal.[23]

The first term in the off diagonal elements of the F matrix (β's) were made proportional to overlap integrals (Eq 2) in the original Pople papers,[14–16] in order to maintain the invariance to the transformation of atomic orbital basis functions. However, the core potential experienced by an electron in a d orbital is quite different from that experienced by an s or p electron, so that direct proportionality of the β's to overlap integrals is likely to seriously overestimate the importance of d orbitals, because of the relatively large overlap integrals involved. In one of the first treatments of compounds in which d orbitals are important Wolfsberg and Helmholtz[24] proposed the relationship Eq. (5).

$$\beta_{\mu\nu} = \frac{-K(I_{\mu\mu} + I_{\nu\nu})\,S_{\mu\nu}}{2} \tag{5}$$

where $I_{\mu\mu}$ and $I_{\nu\nu}$ are appropriate valence state ionization potentials of atoms μ and ν, K is a constant and $S_{\mu\nu}$ is the overlap integral between atoms μ and ν. This relationship has also been used extensively in calculations using extended Hückel theory,[25] and more recently in detailed calculations[26] using a modified CNDO II method on transition metal compounds Eq (5) has been employed with considerable success with $K = 1$. In the latter paper[26] the $U_{\mu\mu}$ and $\gamma_{\mu\mu}$ were also calculated from spectroscopic data, in a manner analagous to that proposed by Whitehead[20] and hence we feel justified in using equation (5) at least as a starting point for estimating β's. The values of β obtained using Eq (5) are quite close in magnitude on the average for C—C and C—H bonds to those used by Pople so the effect of introducing Eq (5) is to reduce quite drastically the β's involving d (and 4s, 4p) orbitals whilst giving values of β's for the other overlaps in line with those predicted using the Pople relationship. It has been pointed out[14] that strictly speaking Eq (5) is not invariant to a transformation of atomic orbital basis functions. However, preliminary calculations showed that this effect is negligible compared with the total energy calculated for the molecule, and the latter should be reliable to the 2nd place of decimals. This is in line with calculations carried out using extended Hückel theory.[27]

TABLE 1

			One centre core integrals		
Orbital	Atom	Z_{eff}	$-I_{\mu\mu}$	$-U_{\mu\mu}$	$\gamma_{\mu\mu}$
1s	H	1·200	13·60	13·60	12·85
2s	C	3·150	20·07	50·69	10·207
2p	C	2·800	10·910	41·53	
3s	S	5·900	20·77	66·80	9·21
3p	S	4·551	11·98	58·01	
3d	S	3·00	2·00	48·03	
4s	S	1·950	3·75	49·78	
4p	S	1·300	2·40	48·43	

Table 1 lists the parameters employed in these calculations. Calculations were carried out according to three models.

Model I 3s and 3p orbitals on sulphur

Model II 3s, 3p and 3d orbitals on sulphur

Model III 3s, 3p, 3d and 4s, 4p orbitals on sulphur.

D orbital transformations were carried out according to the method described by Ballhausen.[28] Bond lengths and bond angles were taken from Ref. 29.

The calculations were carried out on the University of Newcastle's KDF9 computer using a program kindly supplied by Drs. P. G. Perkins and D. H. Wall. Limitations of storage capacity (16K) dictated that the initial H matrices should be calculated previously and used as input data, together with atomic co-ordinates, gammas and core charges. 25 iterations were sufficient to obtain density matrix elements self-consistent to seven decimal places. For the largest number of orbitals (33) Method III, the time taken was 45 min. For the calculation of atom-atom polarizabilities and spin–spin coupling constants (see later) a separate program was written for the University of Durham's Elliott 803 Computer. Overlap integrals were calculated from a compilation of master formulae kindly made available by Dr. P. G. Perkins.

RESULTS AND DISCUSSION

Since the eigenfunctions are expected to be markedly dependent on the model chosen (I, II or III), two ground state properties have been investigated, dipole moments and proton–proton and directly bonded carbon 13-proton coupling constants. In the latter case it was not expected that quantitative agreement between observed and calculated coupling constants would be obtained, but rather that relative magnitude and trends would be discernible. By investigating these properties and the total energy of the molecule it was hoped that it would be possible to determine whether the effect of d orbital participation was being over or underestimated and hence allow reasonable conclusions to be drawn as to the relative importance of d orbital participation in the ground state of thiophene.

The co-ordinate axes adopted are shown in Fig. 1. The orbitals available for bonding on sulphur are 3s, $3p_x$, $3p_y$, $3d_{xy}$, $3d_{z^2}$, $3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$ for σ bonds and $3p_z$, $3d_{xz}$, $3d_{yz}$ and $4p_z$ for π bonds.

A. *Dipole moments and charge distributions*

Tables 2 and 3 show the distribution of charge between the atomic orbitals in thiophene, and the total σ and π charge distributions for Methods I, II and III.

TABLE 2. THE DISTRIBUTION OF CHARGE BETWEEN THE ATOMIC ORBITALS IN THIOPHENE (THE *Z* AXIS IS PERPENDICULAR TO THE MOLECULAR PLANE)

Atom and orbital		Model I	Model II	Model III
$H_1(H_4)$	1s	0·9655	0·9477	0·9455
$H_2(H_3)$	1s	0·9716	0·9662	0·9649
$C_1(C_4)$	2s	1·0171	1·0145	1·0129
	$2p_x$	0·9499	0·9724	0·9691
	$2p_y$	1·0056	0·9994	1·0009
	$2p_z$	1·0848	1·0678	1·0682
$C_2(C_3)$	2s	1·0153	0·9980	0·9932
	$2p_x$	0·9912	0·9884	0·9885
	$2p_y$	0·9949	0·9698	0·9692
	$2p_z$	1·0710	1·0579	1·0619
S	3s	1·5689	1·5626	1·5618
	$3p_x$	1·1434	1·0616	1·0552
	$3p_y$	1·4657	1·4241	1·4219
	$3p_z$	1·6884	1·6108	1·6024
	$3d_{xy}$	·	0·1296	0·1288
	$3d_z^2$		0·0345	0·0333
	$3d_{xy}^{22}$	—	0·0750	0·0746
	$3d_{xz}$		0·0918	0·0907
	$3d_{yz}$	—	0·0458	0·0451
	4s	—	—	0·0285
	$4p_x$		—	0·0030
	$4p_y$		—	0·0046
	$4p_z$	—	—	0·0015

TABLE 3. TOTAL SIGMA, PI, ELECTRON AND CHARGE (δ) DISTRIBUTION IN THIOPHENE

Atom		Model I		Model II		Model III	
		Electron population	δ (charge)	Electron population	δ (charge)	Electron population	δ (charge)
$H_1(H_4)$		0·9655	+0·0345	0·9477	+0·0523	0·9455	+0·0545
$H_2(H_3)$		0·9716	+0·0284	0·9662	+0·0338	0·9649	+0·0351
$C_1(C_4)$	σ	2·9726	+0·0274	2·9863	+0·0137	2·9829	+0·0171
	π	1·0848	−0·0848	1·0678	−0·0678	1·0682	−0·0682
$C_2(C_3)$	σ	3·0014	−0·0014	2·9562	+0·0438	2·9509	+0·0491
	π	1·0710	−0·0710	1·0579	−0·0579	1·0619	−0·0619
S	σ	4·1780	- 0·1780	4·2874	0·2874	4·3117	−0·3117
	π	1·6884	+0·3116	1·7484	+0·2516	1·7397	+0·2603

Reference to Table 3, Method I shows that S is a σ electron acceptor and π electron donor and overall is positively charged. The sigma inductive effect is relayed to the adjacent C atoms (C_1, C_4) both of which are σ electron deficient, the non nearest neighbour C atoms (C_2, C_3) being approximately neutral as far as the σ electrons are concerned. All the carbons carry an excess of pi electrons, the electron density being highest for the C atoms (C_1, C_4) adjacent to S. An interesting point to note here is that the *total* electron density ($\sigma + \pi$) is largest for the C_2, C_3 carbon atoms. As far as the hydrogens are concerned all carry a net positive charge, that for the hydrogens (H_1, H_4) adjacent to S being the largest.

Inclusion of d orbitals has a dramatic effect (Method II, Table 3), the S atom now becoming overall negatively charged. This is a result of both σ and pi electron drift towards the S atom, the former being roughly twice as important as the latter. This in part answers one of the queries we started with concerning the importance of d orbitals in sigma and pi bonding. The evidence here is that d orbitals are at least as important in σ bonding as in pi bonding. Reference to Table 2 shows that the σ charge migration to S results largely from the mixing of $3p_x$, $3p_y$ and $3d_{xy}$ orbitals with smaller contributions from $3d_{x^2-y^2}$ and $3d_{z^2}$. The 3s orbital population remains roughly the same in all three models, this is to be expected since this orbital is much lower in energy than the other orbitals involved. Table 2 shows quite clearly that the increased σ electron charge on sulphur is largely at the expense of H_1, H_4 and C_2 and C_3.

The increased pi electron density on sulphur is at the expense of $C_1(C_4)$ and $C_2(C_3)$ the point of interest here being that the charge migration is much smaller than that obtained by Bielefeld and Fitts.[8] Indeed the charge migration found by the latter authors was solely at the expense of $C_2(C_3)$, the electron densities actually being increased at C_1 and C_4. This large discrepancy can be traced to the neglect of non nearest neighbour β's, some of which are quite large.

The introduction of 4s and 4p orbitals Method III shows very little change in charge distribution to Method II. The orbital populations (4s, 4p) are quite small (Table 2). Hence although the core potential experienced by the 4s and 4p electrons is larger than that for the d orbitals their contribution is very small because of the small overlap integrals.

The molecular dipole moment has three major contributions from:

(a) The net atomic charge densities;

(b) The atomic (sp) polarizations resulting from mixing of s and p orbitals on each atom;

(c) From the atomic (pd) polarization resulting from mixing of 3p and 3d orbitals on S.

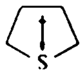
These three contributions and their total are listed for the three model calculations in Table 4. These calculations represent a rather crude approximation to the molecular dipole moment, nonetheless Pople[15, 16] has shown that the method gives useful results.

The experimental absolute value of the total dipole moment is 0·550 ± 0·040 Debye as determined in the gas phase by Harris, Le Fevre and Sullivan.[30] Convincing arguments that the dipole moment is +ve in the sense defined above have been presented.[6] The dipole moment calculated using Method I is fortuitously good. The dipole moments calculated for Methods II and III are considerably larger largely because of the charge migration to S. This suggests that the participation of d orbitals *may* be overestimated in this treatment, however, for such a large molecule as this it is perhaps good enough that the predicted dipole moments have the correct sign and order of magnitude.

TABLE 4. CALCULATED CONTRIBUTIONS TO THE MOLECULAR DIPOLE MOMENT OF THIOPHENE (DEBYES)

Model	Charge density	sp polarization	pd	Total
I	− 1·153	+ 2·048		0·895
II	+ 0·582	+ 2·258	− 0·947	2·258
III	+ 0·706	+ 2·104	− 0·974	1·836
			Exptl	0·550 ± 0·040

* Positive dipole moment contribution is in the sense



B. *NMR spin coupling constants*

The Pople–Santry theory[31] of nuclear spin–spin coupling based on delocalized molecular orbitals has been used[32-36] to estimate numerical values of couplings with a good deal of success. In general proton–proton and proton–carbon 13 couplings constants are predicted to have the correct sign but are generally smaller than those observed.[32-36] Most previous treatments have been based on extended Hückel theory or the Pople–Santry theory both of which are less sophisticated than the Pople–Segal SCF CNDO II method.

For spin–spin couplings involving hydrogen the most important term is the Fermi contact contribution, the terms involving the orbital and spin dipolar contributions being relatively unimportant.[31-36] Eq (6) gives the Pople–Santry formula[31] for the Fermi contact contribution to the spin–spin coupling constants.

$$J_{AB} = \left(\frac{\gamma_A \gamma_B \hbar}{2\pi}\right)\left(\frac{64\pi^2}{9}\right) \beta^2 S_A(O)^2 S_B(O)^2 \pi_{S_A . S_B} \qquad (6)$$

where $S_A(O)^2$ and $S_B(O)^2$ are the spin densities at the nuclei A and B of the valence s orbitals $\pi_{S_A . S_B}$[37] is the mutual polarizability of the s valence orbitals defined by Eq

$$\pi_{\mu\nu} = 4 \sum_{i}^{occ} \sum_{j}^{unocc} (\varepsilon_i - \varepsilon_j)^{-1} C_{i\mu} C_{i\nu} C_{j\mu} C_{j\nu} \qquad (7)$$

γ_A and γ_B are the magnetogyric ratios for nuclei A and B
β is the Bohr magneton.

Using the conversion factors based on $Z_{eff} = 1·2$ for hydrogen, calculated by Murrell[35] and the s orbital population numbers, eigenvalues and eigenfunction

TABLE 5 CALCULATED AND OBSERVED PROTON PROTON AND DIRECTLY BONDED CARBON 13 PROTON COUPLING CONSTANTS FOR THIOPHENE (IN C/S)

Model	Coupling constant in c/s						
	H_1-H_2	H_2-H_3	H_1-H_4	H_1-H_3	C_1-H_1	C_2-H_2	Δ(C_1-H_1) (C_2-H_2)
I	+2·22	+0·83	+0·31	+0·25	+59·76	+46·0	+13·76
II	+2·31	+0·45	+0·74	+0·17	+53·00	+56·00	−3·00
III	+2·41	+0·47	+0·82	+0·15	+51·90	+54·40	−2·50
Experimental[38]	+5·15	+3·45	+2·75	+1·05	+187·00	+180·00	+7·00

calculated according to the three models, the coupling constants are calculated to be as shown in Table 5.

The couplings are all predicted to have a positive sign, as is found experimentally,[38] and for the H–H couplings the trends are satisfactorily reproduced particularly by Model I. This is best illustrated by a graph (Fig. 5). Inclusion of d orbitals reverses the orders of the C–H coupling constants and the H_2–H_3 couplings. This again would seem to suggest that the effect of d orbital participation is being overestimated. It can be seen that a smaller contribution from the d orbitals would reduce the magnitude of the H_2–H_3 and H_1–H_3 couplings relative to H_1–H_4 and give improved agreement with the experimental results. This also applies to the C–H coupling constants.

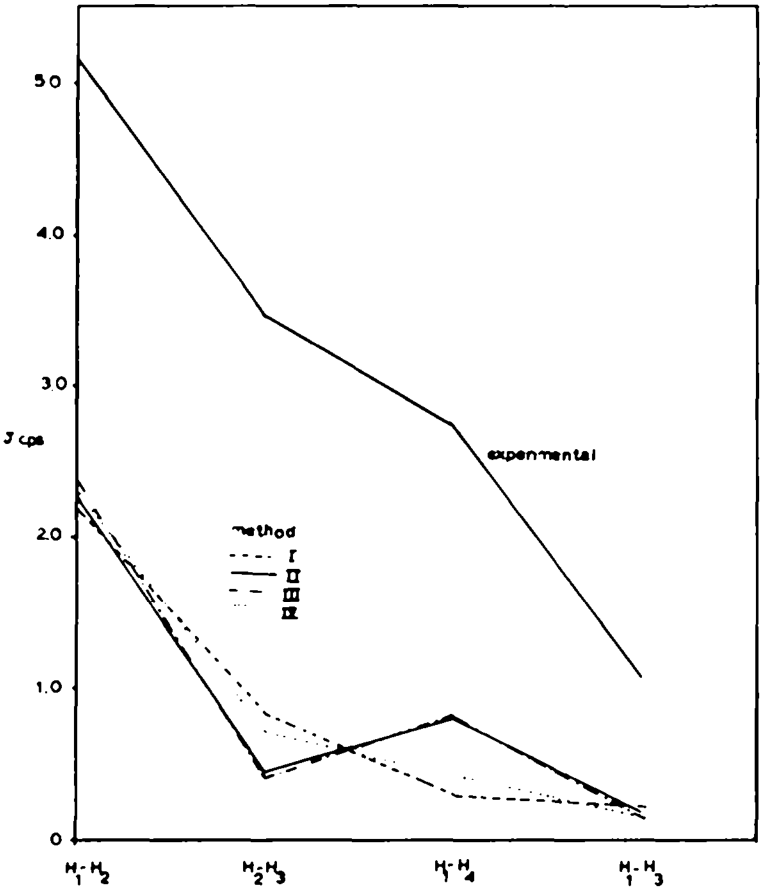


FIG. 5 Calculated and observed proton-proton spin coupling constants in thiophene.

C. *Total energies*

Table 6 shows how the total energy varies as 3d, 4s and 4p orbitals are included on S. The interesting feature here is the small extent to which inclusion of 3d, 4s and 4p orbitals contribute to the total energy. This is in marked contrast to the effect of these orbitals on dipole moments, charge distribution and coupling constants.

This emphasizes the fact that one must define carefully which property one is referring to, when discussing the importance of d orbital participation on sulphur. The dipole moment and coupling constant data taken together would seem to indicate that d orbital participation has been slightly overestimated in Method II, so that the percentage energy change (1·77 %) probably represents an upper limit to the energy lowering on inclusion of these orbitals.

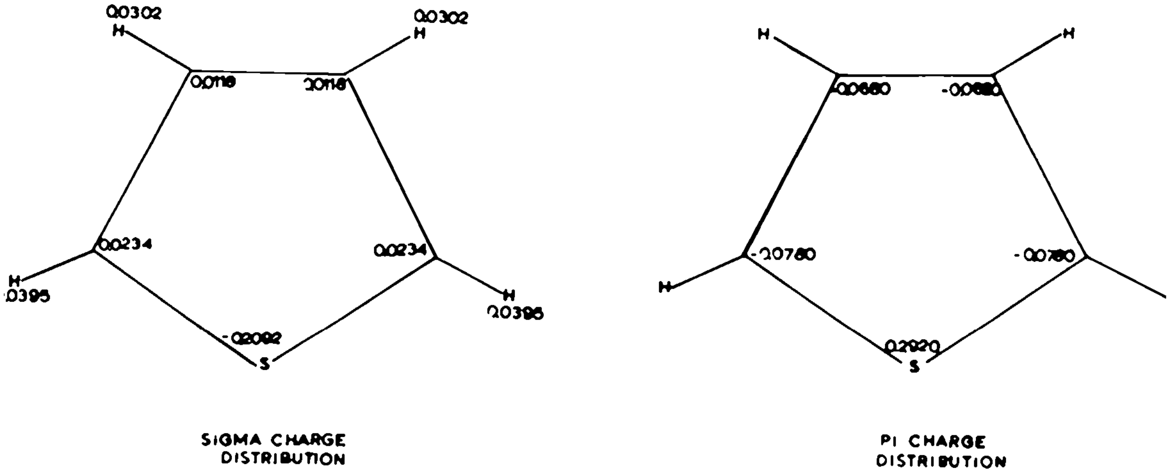
In the light of the foregoing discussion it seems worthwhile to modify the extent of the 3d, 4s and 4p orbital participation to obtain the best fit to the dipole moment and coupling constant data. This is most readily brought about by varying the parameter K Eq (5) for β's involving 3d, 4s and 4p orbitals.

TABLE 6. TOTAL ENERGY OF THIOPHENE ACCORDING TO THE THREE MODELS IN eV AND PERCENTAGE CHANGE IN ENERGY ON INCLUDING 3d, 4s and 4p ORBITALS

	I	II	III
	− 507·1483	− 516·1492	− 517·3881
% change	0	1·77	2·02

A value of $K = 0{\cdot}5$ (Method IV) gives a good overall fit to the dipole moment (calculated μ 0·69 Debye) and coupling constants (see Fig. 5) $J_{H_1-H_2}$ 2·29 c/s $J_{H_2-H_3}$ 0·71 c/s $JJ_{H_1-H_4}$ 0·45 c/s $J_{H_1-H_3}$ 0·18 c/s $\Delta(C_1-H_1) - (C_2-H_2) + 3{\cdot}4$ c/s. Fig. 6 shows the σ and π charge distribution.

The percentage energy change on inclusion of 3d and 4s and 4p orbitals relative to Method I is 0·62 %.



SIGMA CHARGE DISTRIBUTION

PI CHARGE DISTRIBUTION

FIG. 6 Sigma and pi electron distribution on thiophene according to Model IV.

CONCLUSIONS

The extent of 3d, 4s and 4p orbital participation in the ground state of thiophene has been investigated by the Pople–Segal SCF CNDO II Method. A good overall fit to the experimental dipole moment and relative magnitude of H–H and ^{13}C–H coupling constants is obtained when 3d, 4s and 4p orbitals are neglected. Inclusion of the latter orbitals using the constant $K = 1$ in the Wolfsberg–Helmholtz equation leads to an overestimate of the importance of these orbitals, however reducing the extent of participation ($K = 0{\cdot}5$) leads to a significant improvement in the overall fit to experimental dipole moment and relative magnitude of coupling constants. Inclusion of 3d, 4s and 4p orbitals on sulphur has a very small effect on the total energy of the molecule. As far as the electron distribution is concerned, inclusion of 3d, 4s and 4p orbitals has a larger effect on the sigma system than on the pi system of thiophene.

Acknowledgement The author is grateful to Dr. J. W. Emsley for helpful discussions.

REFERENCES

[1] V. Shomaker and L. Pauling, *J. Am. Chem. Soc.* **61**, 1769 (1939).
[2] H. C. Longuet-Higgins, *Trans. Faraday Soc* **45**, 173 (1949).
[3] A. Streitweiser, *Molecular Orbital Theory for Organic Chemists.* Wiley, N.Y. (1961).
[4] A. Mangini and C. Zauli, *J. Chem. Soc.* 2210 (1960).
[5] D. S. Sappenfield and M. M. Kreevoy, *Tetrahedron* Suppl. **2**, 157 (1963).
[6] A. J. H. Wachters and D. W. Davies, *Tetrahedron* **20**, 1841 (1964).
[7] N. Solony, F. W. Birss and J. B. Greenshields, *Canad. J. Chem.* **43**, 1569 (1965).
[8] M. J. Bielefeld and D. D. Fitts, *J. Am. Chem. Soc.* **88**, 4804 (1966).
[9] R. L. Flurry, Jr., and J. J. Bell, *Ibid.* **89**, 525 (1967).
[10] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.* 332 (1954).
[11] D. P. Craig and E. A. Magnusson, *Ibid.* 4895 (1956).
[12] J. C. Slater, *Phys. Rev.* **36**, 51 (1930).
[13] G. Burns, *J. Chem. Phys.* **41**, 1521 (1964).
[14] J. A. Pople, D. P. Santry and G. A. Segal, *Ibid.* **43**, S129 (1965).
[15] J. A. Pople and G. A. Segal, *Ibid.* **43**, S136 (1965).
[16] J. A. Pople and G. A. Segal, *Ibid.* **44**, 3289 (1966).
[17] P. Palmieri and C. Zauli, *J. Chem. Soc.* (A) 813 (1967).
[18] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953).
[19] J. A. Pople, *Trans. Faraday Soc* **49**, 1375 (1953).
[20] J. M. Sichel and M. A. Whitehead, *Theoret Chim. Acta* **7**, 32 (1967).
[21] R. Pariser, *J. Chem. Phys.* **21**, 568 (1953).
[22] N. Mataga and K. Nishimoto, *Z. Phys. Chem. Frankfurt* **13**, 140 (1957).
[23] D. P. Santry and G. A. Segal, *J. Chem. Phys.* **47**, 158 (1967).
[24] M. Wolfsberg and L. Helmholtz, *Ibid.* **20**, 837 (1952)
[25] R. Hoffman, *Ibid.* **39**, 1397 (1963).
[26] L. Oleari, G. De Michelis and L. Di Supio, *Mol. Phys.* **10**, 111 (1966).
[27] R. E. Davis and A. Ohno, *Tetrahedron* **23**, 1015 (1967).
[28] C. J. Ballhausen *Introduction to Ligand Field Theory.* McGraw-Hill, N.Y. (1962).
[29] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Adersen, *J. Mol. Spectry.* **7**, 58 (1961).
[30] B. Harris, R. J. W. Le Fevre and E. P. A. Sullivan, *J. Chem. Soc.* 1622 (1953).
[31] J. A. Pople and D. P. Santry, *Mol. Phys.* **8**, 1 (1964).
[32] J. A. Pople and D. P. Santry, *Ibid* **9**, 311 (1965).
[33] F. B. Van Duijneveldt, V. M. S. Gil and J. N. Murrell, *Theoret Chim. Acta Berlin* **4**, 85 (1966).
[34] G. T. Jones and J. N. Murrell, *J. Chem. Soc.* A 1421 (1966).
[35] J. N. Murrell, P. E. Stevenson and G. T. Jones, *Mol. Phys.* **12**, 265 (1967).

[36] R. C. Fahey, G. C. Graham and R. L. Piccioni, *J. Am. Chem. Soc.* **88**, 193 (1966).
[37] C. A. Coulson and H. C. Longeut-Higgins, *Proc. Roy. Soc.* A. **191**, 39 (1953).
[38] S. Cronowitz and R. A. Hoffman, *Arkw. Kerui* **15**, 45 (1959).
[39] A. D. Cohen and K. A. McLauchlan, *Discuss Faraday Soc.* **34**, 132 (1962).