Bonding Contribution of Sulfur d Orbitals in Thiophene. An Extension of the Self-Consistent Field Molecular Orbital Method[1]

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Abstract: The $3d_{xz}$ and $3d_{yz}$ atomic orbitals on sulfur are included in the linear combination of atomic orbitals in a semiempirical self-consistent field molecular orbital study of thiophene. The extension of the SCF MO method to include more than one atomic orbital per atomic site is accomplished by a point-charge model for the evaluation of two-center repulsion integrals. A comparison of the SCF molecular orbitals with and without the inclusion of these higher atomic orbitals shows that the d orbitals participate in the π-electronic structure of thiophene to only a small extent, but that their participation affects the calculated electronic properties to a great extent.

In a study which pioneered the extension of the Hückel molecular orbital (MO) theory[3] to include heterocyclic systems, Wheland and Pauling[4] applied the MO method to the thiophene molecule for the first time. Their treatment of thiophene implicitly assumed that the sulfur atom in the molecule contributes only a $3p_z$ atomic orbital (AO) to the π electronic MO wave functions when the latter are written as a linear combination of atomic orbitals (LCAO).

Schomaker and Pauling[5] later suggested that resonance forms contributing to the structure of thiophene include those in which the sulfur atom violates the octet rule and the M shell is expanded to hold ten electrons; *i.e.*, the 3d orbitals on the sulfur atom are partially occupied in the ground state of the molecule. Longuet-Higgins[6] incorporated this idea in a Hückel MO calculation on thiophene by employing $3p_z$–$3d_{xz}$–$3d_{yz}$ hybrid atomic orbitals on the sulfur atom. This approach with some variations has been further applied to thiophene and other sulfur-containing molecules by many authors.[7,8]

A controversy still exists as to whether d-orbital participation should be included in MO calculations on sulfur-containing heterocyclic molecules. Although the inclusion of the d orbitals on sulfur has proved useful in some cases,[7,8] many authors[8–12] believe that thiophene and related molecules may be successfully treated without their explicit consideration. Moreover, some authors feel that d-oribital participation has never been proved and state that calculations based on the Longuet-Higgins model are fallacious.[13]

Both of these approaches to the MO study of thiophene are somewhat unsatisfactory in that they bias the calculation either by omitting the d orbitals entirely or by including their participation arbitrarily. In an effort to overcome this difficulty, we present in this article an MO calculation on thiophene in which the possibility of d-orbital participation is admitted by including the $3d_{xy}$ and $3d_{yz}$ orbitals on the sulfur atom in the basis set of atomic orbitals in the LCAO approximation. Since the energy of an electron in a 4p orbital of atomic sulfur is comparable to that for an electron in a 3d orbital, we also include the $4p_z$ AO on sulfur in the basis set for thiophene.

For purposes of comparison, we make three separate LCAO MO calculations on thiophene. The first considers only the $2p_z$ orbitals on the carbon atoms and the $3p_z$ orbital on sulfur. The second includes two additional orbitals: the $3d_{xz}$ and $3d_{yz}$ atomic orbitals on the sulfur atom. The third calculation adds the $4p_z$ atomic orbital on sulfur to the basis set in the LCAO approximation. Hereafter, we refer to these three choices for the basis set as the five-orbital model, the seven-orbital model, and the eight-orbital model, respectively. Thus, the molecular orbitals ϕ_i for the π electrons of thiophene are written in the form

$$\phi_i = \sum_{j=1}^{n} c_{ij}\chi_j \quad n = 5, 7, 8 \tag{1}$$

where χ_2 and χ_5 are the $2p_z$ orbitals on the α-carbon atoms, χ_3 and χ_4 are the $2p_z$ orbitals on the β carbon atoms, and χ_1, χ_6, χ_7, χ_8 are the $3p_z$, $3d_{xz}$, $3d_{yz}$, $4p_z$ AO's, respectively, on the sulfur atom. When n is five, we have the five-orbital model; for n = 7 and n = 8, we have the seven- and eight-orbital models, respectively. The sites of the nuclear centers are numbered from 1 to

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[2] National Science Foundation Predoctoral Fellow, 1962–1964.

[3] E. Hückel, *Z. Physik*, **70**, 204 (1931).

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[7] J. Metzger and F. Ruffler, *J. Chim. Phys.*, **51**, 52 (1954); J. de Heer, *J. Am. Chem. Soc.*, **76**, 4802 (1954); L. Melander, *Arkiv Kemi*, **8**, 361 (1955); K. Kikuchi, *Sci. Rept. Tohoku Univ., First Ser.*, **40**, 133 (1956); **41**, 35 (1957); K. Maeda, *ibid.*, **43**, 203 (1959); *Bull. Chem. Soc. Japan*, **33**, 304 (1960); G. Milazzo and G. De Alti, *Gazz. Chim. Ital.*, **89**, 2479 (1959); J. Koutecký, *Collection Czech. Chem. Commun.*, **24**, 1608 (1959); M. K. Orloff and D. D. Fitts, *Biochim. Biophys. Acta*, **47**, 596 (1961).

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[10] D. S. Sappenfield and M. M. Kreevoy, *Tetrahedron Suppl.*, **2**, 157 (1963).

[11] A. J. H. Wachters and D. W. Davies, *Tetrahedron*, **20**, 2841 (1964).

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[13] A. Mangini and C. Zauli, *J. Chem. Soc.*, 2210 (1960).

5, as shown in Figure 1, in agreement with the numbering of the lowest AO on each site.

The coefficients c_{ij} in eq 1 determine the MO's, which in turn are calculated so as to minimize the π-electronic energy. For the seven- and eight-orbital models, the values of c_{i6} and c_{i7} for the occupied MO's (i = 1, 2, 3) are, then, an indication of the extent to which the 3d AO's on the sulfur atom participate in the ground state of thiophene. Similarly, for the eight-orbital model the values of c_{i8} (i = 1, 2, 3) indicate the $4p_z$-orbital participation.

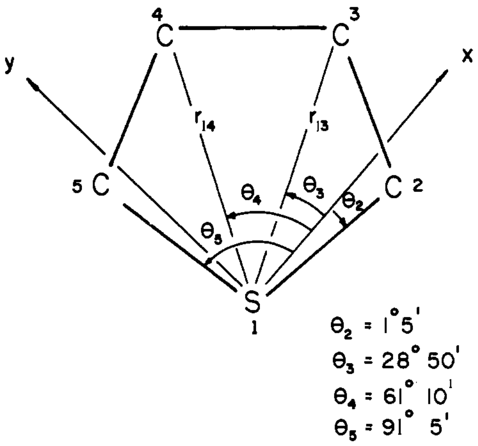

Figure 1. The numbering of atomic sites, the orientation of the sulfur-fixed coordinate system, and the geometry of thiophene. The positive z axis is perpendicular to the plane of the ring and points upward. The symmetry axes of the lobes of the $3d_{xz}$ atomic orbital on sulfur lie in the xz plane; those for the $3d_{yz}$ atomic orbital on sulfur lie in the yz plane.

Method of Calculation

The π-electronic structure of heteroaromatic molecules may be calculated most reliably by the self-consistent field (SCF) MO theory. Until now all SCF LCAO MO calculations on aromatic molecules have been limited to models in which only one AO per nuclear site is included in the LCAO basis set. In this section we write the Hartree–Fock (HF) operator[14] for the π electrons of thiophene in a form which allows more than one AO on sulfur. In the next section we evaluate the various one- and two-electron integrals that arise in this formation.

Working within the Born–Oppenheimer approximation[15] and the π-electron approximation,[16] we write the ground-state wave function for the six π electrons of thiophene as an antisymmetrized product of one-electron functions, *i.e.*, as a single Slater determinant. When we represent each one-electron MO by eq 1 and apply the variational principle, we obtain the standard form for the Hartree–Fock matrix H, whose elements are[17]

$$H_{ij} = \langle\chi_i(1)|H^{\text{core}}(1)|\chi_j(1)\rangle + \sum_{k=1}^{n}\sum_{l=1}^{n}\frac{1}{2}P_{kl}[2(ij|kl) - (il|kj)] \quad (2)$$

The core operator $H^{\text{core}}(\mu)$ is the sum of the kinetic energy operator $T(\mu)$ for electron μ and the potential energies of interaction $U_\alpha(\mu)$ for electron μ with each nucleus α and its associated inner and σ-bonding electrons

$$H^{\text{core}}(\mu) = T(\mu) + \sum_{\alpha=1}^{5} U_\alpha(\mu) \quad (3)$$

The elements P_{kl} of the charge and bond-order matrix[18] are defined by the sum over the occupied MO's

$$P_{kl} = 2\sum_{m=1}^{3} c_{mk}c_{ml} \quad (4)$$

A two-electron integral $(ij|kl)$, representing the interaction between a pair of π electrons a distance r_{12} apart, is

$$(ij|kl) = \langle\chi_i(1)\chi_k(2)|e^2r_{12}^{-1}|\chi_j(1)\chi_l(2)\rangle \quad (5)$$

In order to reduce the HF matrix to a workable form, we follow the procedure introduced by Pariser and Parr[19] and neglect all two-electron integrals that depend on overlap between two AO's centered on different nuclei. Thus, if the AO's χ_i, χ_j, χ_k, χ_l are not all situated on the same atom (the sulfur atom in this case), we have

$$(ij|kl) = \delta_{ij}\delta_{kl}(ii|kk) \quad (6)$$

where δ_{ij} is the Kronecker δ function. Equation 6 implies the formal neglect of overlap

$$\langle\chi_i|\chi_j\rangle = \delta_{ij} \quad (7)$$

for AO's not centered on the same atom.

It is convenient at this point to require also the mutual orthogonality of the AO's χ_1, χ_6, χ_7, χ_8. Consequently, we shall not employ the nodeless Slater-type orbitals (STO), which are customarily used in MO calculations because of their mathematical simplicity, but rather the real hydrogen-like AO's[20] with the reduced radial variable equal to Z_ir/a_0, where Z_i is the effective charge for each orbital, r is the nuclear-electronic distance in angstrom units, and a_0 is the Bohr radius. The effective charges suggested by Burns[21] for atomic shielding in hydrogen-like orbitals for neutral atoms are 5.75 for Z_1; 2.80 for Z_2, Z_3, Z_4, Z_5; 3.00 for Z_6 and Z_7; and 1.90 for Z_8. Of the orbitals centered on sulfur, all except the pair χ_1,χ_8 are mutually orthogonal regardless of the values of the effective charges. The AO χ_1 is orthogonal to χ_8 only if the ratio Z_1/Z_8 is unity or $^3/_2 \pm {^3/_4}\sqrt{3}$. Therefore, by slightly modifying Z_8 to the value 2.05, we ensure that $\langle\chi_1|\chi_8\rangle = 0$. Thus, eq 7 now applies to all the AO's in the LCAO basis set.

We also introduce the approximation due to Pople[22] that

$$\langle\chi_i(1)|H^{\text{core}}(1)|\chi_i(1)\rangle = \omega_i + \sum_k{}'\zeta_k(ii|kk) \quad (8)$$

where

$$\omega_i = \langle\chi_i(1)|T(1) + U_\alpha(1)|\chi_i(1)\rangle \quad (9)$$

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(14) D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24**, 89, 111, 426 (1928); V. Fock, *Z. Physik*, **61**, 126 (1930).

(15) M. Born and J. R. Oppenheimer, *Ann. Physik*, **84**, 457 (1927).

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(19) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

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(21) G. Burns, *J. Chem. Phys.*, 41, 1521 (1964).

(22) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

with α being the site of the AO χ_i. The quantity ζ_k is the number of π electrons contributed to the molecular framework by atom k. Here ζ_1 is 2, while ζ_2, ζ_3, ζ_4, ζ_5 are each unity. The prime on the summation sign in eq 8 indicates that the atom on which χ_i is centered is omitted from the sum.

With the simplifications induced by eq 6 and 7 and with the introduction of eq 8 and the definition

$$\beta_{ij} = \langle\chi_i(1)|H^{\text{core}}(1)|\chi_j(1)\rangle \quad i \neq j \tag{10}$$

the elements of the symmetric matrix **H** take the form

$$H_{ii} = \omega_i + \frac{1}{2}P_{ii}(ii|ii) + \sum_k{}'\zeta_k(ii|kk) + \sum_{\substack{j=1\\(\neq i)}}^{n} P_{jj}(ii|jj) + I_{ii}$$

$$H_{ij} = \beta_{ij} - \frac{1}{2}P_{ij}(ii|jj) + I_{ij} \quad i \neq j \tag{11}$$

where, for the eight-orbital model

$$\begin{aligned}
I_{ij} &= 0 \quad i, j = 2, 3, 4, 5\\
I_{11} &= \sum_{j=6,7,8}\frac{1}{2}P_{jj}(1j|1j) + P_{18}(11|18)\\
I_{66} &= I_{77} = \sum_{j=1,7,8}\frac{1}{2}P_{jj}(6j|6j)\\
I_{88} &= \sum_{j=1,6,7}\frac{1}{2}P_{jj}(8j|8j) + P_{18}(88|18) \qquad (12)\\
I_{16} &= I_{17} = \frac{3}{2}P_{16}(16|16) + \frac{1}{2}P_{68}[3(16|86) - (18|66)]\\
I_{68} &= I_{78} = \frac{3}{2}P_{68}(68|68) + \frac{1}{2}P_{16}[3(16|86) - (18|66)]\\
I_{67} &= \frac{3}{2}P(67|67)\\
I_{18} &= \frac{3}{2}P_{18}(18|18) + \sum_{j=1,6,7,8}\frac{1}{2}P_{jj}[2(jj|18) - (1j|8j)]
\end{aligned}$$

Except for the appearance of the terms I_{ij}, eq 11 have the form of the usual Hamiltonian matrix elements used in SCF LCAO MO calculations. These extra terms arise from the consideration of more than one AO on the sulfur atom of thiophene. As the number n of AO's in eq 1 is reduced from 8 to 7 to 5, the various integrals in eq 12 vanish accordingly.

Parameter Values

The basic problem in any SCF MO calculation is the determination of the atomic integrals ω_i, β_{ij}, and $(ij|kl)$. These integrals or parameters depend on the geometry of the molecule. The bond lengths and bond angles for thiophene[23] are given in Table I.

We approximate the one-electron one-center integrals ω_i by setting them equal to the corresponding atomic valence state ionization potentials as determined from the atomic eigenvalue equation proposed by Goeppert-Mayer and Sklar[24]

$$[T(1) + U_\alpha(1)]\chi_i(1) = \omega_i\chi_i(1) \tag{13}$$

Table I. Geometry of Thiophene

Bond[a]	Distance, A[b]	Bond angle[a]	Value[b]
r_{12}	1.7140 ± 0.0014	∠512	92° 10′ ± 6′
r_{23}	1.3696 ± 0.0017	∠123	111° 28′ ± 14′
r_{34}	1.4232 ± 0.0023	∠234	112° 27′ ± 11′

[a] For numbering see Figure 1. [b] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, **7**, 58 (1961).

where α is the site of χ_i. These values for the ω_i are obtained from spectroscopic data[25] and are given in Table II. The valence-state ionization potentials ω_6 and ω_8 are approximated by weighted spectroscopic averages and are valid to within 0.5 ev.

Table II. One-Electron Integrals

Integral	Value, ev	Integral	Value, ev
ω_1	$-22.88^{a,b}$	β_{26}	-2.649^{d}
ω_2	-11.22^{c}	β_{27}	0.000^{d}
ω_6	-9.54^{a}	β_{28}	0.286^{d}
ω_8	-7.70^{a}	$\langle\chi_1|\chi_2\rangle$	0.250
β_{12}	-1.400^{d}	$\langle\chi_2|\chi_6\rangle$	0.473
β_{23}	-2.499^{e}	$\langle\chi_2|\chi_7\rangle$	0.000
β_{34}	-2.163^{e}	$\langle\chi_2|\chi_8\rangle$	−0.051

[a] C. E. Moore, "Atomic Energy Levels," Vol. I, National Bureau of Standards, Washington, D. C., 1949. [b] H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953). [c] R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953). [d] Found from eq 15 with $k = -5.60$ ev. [e] Found from eq 14.

The use of atomic-state ionization potentials for the parameters ω_i is an approximation which has been widely used. In general, this approximation is not a serious one. However, for the parameter ω_6 ($=\omega_7$) the approximation is less valid. Since the 3d atomic orbitals χ_6 and χ_7 are directed toward the adjacent carbon atoms, these positively charged sites distort the distributions of the electrons in χ_6 and χ_7 and thereby render ω_6 and ω_7 different from the atomic-state ionization potential. Many SCF MO calculations treat the ω_i as empirical parameters, and some readers may wish to regard our assignments, especially for ω_6 and ω_7, as empirical. Nevertheless, we prefer here to keep the number of purely empirical parameters at a minimum, and hence we use eq 13 to obtain the ω_i.

The carbon–carbon resonance integrals β_{23} and β_{34} are obtained from the empirical equation of Hoyland and Goodman[26]

$$\log(-\beta_{ij}) = 2.00054 - 1.17030r_{ij} \tag{14}$$

where r_{ij} is the bond distance in angstrom units. The values for β_{12}, β_{26}, β_{27}, and β_{28} are assumed to be directly proportional to the corresponding overlap integrals

$$\beta_{i2} = k\langle\chi_i|\chi_2\rangle \quad i = 1, 6, 7, 8 \tag{15}$$

We treat k as an empirical parameter, so adjusted as to make the predicted lowest $\pi \rightarrow \pi^*$ spectral transitions of the five-orbital model agree with the experimental lowest $\pi \rightarrow \pi^*$ transitions in thiophene. The value of

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(23) B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, **7**, 58 (1961).

(24) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(25) C. E. Moore, "Atomic Energy Levels, Vol. I," National Bureau of Standards, Washington, D. C., 1949.

(26) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 12 (1962).

k so selected is -5.6 ev, although values in the range -5.2 to -6.0 ev give essentially the same results. The integrals β_{16}, β_{18}, β_{67}, and β_{68}, which are also taken to be proportional to the corresponding overlap integrals, are zero by virtue of the mutual orthogonality of the atomic orbitals involved. In accord with the standard semiempirical method of Pariser and Parr,[19] the resonance integrals for nonadjacent atoms are zero. The values for β_{ij} are listed in Table II.

The evaluation of the two-electron integrals $(ij|kl)$ is more elaborate. According to Pariser,[27] one-center integrals of the type $(ii|ii)$ may be equated to the difference between the atomic valence state ionization potential and electron affinity. Thus, we have $(22|22) = (11.22 - 0.69) = 10.53$ ev,[27] and $(11|11) = (22.88 - 10.98) = 11.90$ ev.[25,28] The theoretical value of $(11|11)$ using Z_1 equal to 5.75 is 12.14 ev. Since the semiempirical and the theoretical values of $(11|11)$ are less than 0.25 ev apart, we feel confident in adopting for our calculations the theoretical values for all the two-electron integrals centered on the sulfur atom. These integrals are listed in Table III.

Table III. Two-Electron Integrals

Integral[a]	Distance, A	Value, ev	Integral	Value, ev
$(11\|11)$	0.000	12.14[b]	$(66\|66)$	7.52[j]
$(11\|22)$	1.714	6.67[c]	$(66\|77)$	6.85[k]
$(11\|33)$	2.556	5.09[c]	$(66\|88)$	2.98
$(11\|66)$	0.000	8.52	$(88\|88)$	2.36[l]
$(11\|88)$	0.000	3.22	$(16\|16)$	1.06
$(22\|22)$	0.000	10.53	$(18\|18)$	0.07
$(22\|33)$	1.370	7.32[d]	$(67\|67)$	0.34[m]
$(22\|44)$	2.322	5.57[d]	$(68\|68)$	0.07
$(22\|55)$	2.469	5.33[d]	$(11\|18)$	0.42
$(22\|66)$	1.714	6.29[e]	$(18\|88)$	0.03
$(22\|77)$	1.714	5.91[f]	$(18\|66)$	0.19
$(22\|88)$	1.714	3.45[g]	$(16\|86)$	−0.07
$(33\|33)$	0.000	10.53	$(11\|16)$	0.00
$(33\|44)$	1.423	7.21[d]	$(16\|66)$	0.00
$(33\|66)$	2.556	5.07[h]	$(88\|86)$	0.00
$(33\|77)$	2.556	4.83[i]	$(86\|66)$	0.00
$(33\|88)$	2.556	2.64[g]	$(66\|67)$	0.00

[a] For numbering see Figure 1. [b] $(11|11) = 2.118Z_1$. [c] $(ii|jj) = 11.336 - 3.2833r_{ij} + 0.3287r_{ij}^2$. [d] $(ii|jj) = 10.530 - 2.6451r_{ij} + 0.2189r_{ij}^2$. [e] $(22|66) = 9.026 - 1.7932r_{26} + 0.1139r_{26}^2$. [f] $(22|77) = 9.026 - 2.1128r_{27} + 0.1712r_{27}^2$. [g] $(ii|jj) = 6.442 - 2.2805r_{ij} + 0.3105r_{ij}^2$. [h] $(33|66) = 9.026 - 1.8821r_{36} + 0.1300r_{36}^2$. [i] $(33|77) = 9.026 - 2.0523r_{37} + 0.1605r_{37}^2$. [j] $(66|66) = 2.5075Z_6$. [k] $(66|77) = 2.2831Z_6$. [l] $(88|88) = 1.1459Z_8$. [m] $(67|67) = 0.1122Z_6$.

For the two-center Coulomb integrals of the type $(ii|jj)$, Pariser and Parr[19,29] suggest semiempirical values obtained from the classical electrostatic energy relationships of a tangent-sphere model. Their model, in effect, places a point charge $e/2$ at a distance $4.34a_0/Z$ above and below a site with a $2p_z$ STO and $9.1a_0/Z$ above and below a site with a $3p_z$ STO, where e is the electronic charge and Z is the effective charge of the STO. These distances compare favorably with the most probable values of r of the corresponding STO's, namely $4a_0/Z$ and $9a_0/Z$.

This agreement leads us to propose a point-charge model for the evaluation of two-center integrals of the type $(ii|jj)$ in which either hydrogen-like or Stater-type atomic orbitals may be used. First, the distribution $|\chi_i(1)|^2$ of charge of electron 1 is approximated by point charges positioned at the most probable value of r in each lobe of the AO χ_i. The magnitude of each point charge is determined by the fraction of electron 1 in each lobe. Thus, the radical part of χ_1 in our model of thiophene distributes a charge of $0.1105e/2$ in each of the first lobes above and below the plane of the ring and a charge of $0.8895e/2$ in each of the second lobes, regardless of the value of Z_1. The most probable value of r for each lobe, however, does depend on Z_1. Similarly, each of the first pair of lobes for $|\chi_8|^2$ has a charge $0.0375e/2$, each of the second pair, $0.1281e/2$; and each of the last pair, $0.8344e/2$. Again, the charges in each lobe are independent of Z_8, but the most probable values of r are not. The other hydrogen-like orbitals χ_i are nodeless in the radical function and are identical with the STO's. The magnitudes and positions of the point charges for the hydrogen-like orbitals in our model of thiophene are given in Table IV. For purposes of comparison, Table IV also lists the magnitudes and positions of charges for STO's and for the tangent-sphere model.

For large distances between the sites of χ_i and χ_j, a two-center integral of the type $(ii|jj)$ may now be evaluated as the coulombic energy of the repulsion between electron 1 and electron 2 with their distributions approximated by the point-charge model. The results are as follows.

For $r \geq 2.8$ A

$$(2p_z2p_z|2p_z2p_z) = \frac{e^2}{2r}\left\{1 + \left[1 + \left(\frac{8R_j}{r}\right)^2\right]^{-1/2}\right\}$$

$$(3p_x3p_z|2p_z2p_z) = 0.1105\frac{e^2}{2}\{[r^2 + (3R_i + 4R_j)^2]^{-1/2} + [r^2 + (3R_i - 4R_j)^2]^{-1/2}\} + 0.8895\frac{e^2}{2}\{[r^2 + (12R_i + 4R_j)^2]^{-1/2} + [r^2 + (12R_i - 4R_j)^2]^{-1/2}\}$$

$$(4p_z4p_z|2p_z2p_z) = 0.0375\frac{e^2}{2}\{[r^2 + (2.83R_i + 4R_j)^2]^{-1/2} + [r^2 + (2.83R_i - 4R_j)^2]^{-1/2}\} + 0.1281\frac{e^2}{2} \times \{[r^2 + (9.59R_i + 4R_j)^2]^{-1/2} + [r^2 + (9.59R_i - 4R_j)^2]^{-1/2}\} + 0.8344\frac{e^2}{2}\{[r^2 + (23.58R_i + 4R_j)^2]^{-1/2} + [r^2 + (23.58R_i - 4R_j)^2]^{-1/2}\} \tag{16}$$

For $r \geq 3.9$ A

$$(3d_{xz}3d_{xz}|2p_z2p_z) = (3d_{yz}3d_{yz}|2p_z2p_z) = \frac{e^2}{4}\{[r^2 + 40.5R_i^2 + 36(2^{1/2})rR_i\cos\theta_j + (4.5(2^{1/2})R_i + 4R_j)^2]^{-1/2} + [r^2 + 40.5R_i^2 + 36(2^{1/2})rR_i\cos\theta_j + (4.5(2^{1/2})R_i - 4R_j)^2]^{-1/2} + [r^2 + 40.5R_i^2 - 36(2^{1/2})rR_i\cos\theta_j + (4.5(2^{1/2})R_i + 4R_j)^2]^{-1/2} + [r^2 + 40.5R_i^2 - 36(2^{1/2})rR_i\cos\theta_j + (4.5(2^{1/2})R_i - 4R_j)^2]^{-1/2}\} \tag{17}$$

In eq 16 and 17, R_i is a_0/Z_i and θ_j is the angle which the interatomic distance r $(=r_{ij})$ makes with the x axis. These angles and their values for thiophene are shown in Figure 1.

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(27) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

(28) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

(29) R. G. Parr, *J. Chem. Phys.*, **20**, 1499 (1952).

Table IV. Point-Charge Model for Two-Center Integrals[a]

AO distribution	Charge	Location of charge
$\|2p_z\|^2$	$e/2$	$(4a_0/Z)$ above and below the plane of the ring
$\|3p_z\|^2$ with hydrogen-like AO	$0.1105\,(e/2)$	$(3a_0/Z)$ above and below the plane of the ring
	$0.8895\,(e/2)$	$(12a_0/Z)$ above and below the plane of the ring
$\|4p_z\|^2$ with hydrogen-like AO	$0.0375\,(e/2)$	$(2.83a_0/Z)$ above and below the plane of the ring
	$0.1281\,(e/2)$	$(9.59a_0/Z)$ above and below the plane of the ring
	$0.8344\,(e/2)$	$(23.58a_0/Z)$ above and below the plane of the ring
$\|3d_{xz}\|^2$	$e/4$	At four corners of a square centered in the xz plane of Figure 1 and whose diagonal is $18a_0/Z$
$\|3d_{yz}\|^2$	$e/4$	At four corners of a square centered in the yz plane of Figure 1 and whose diagonal is $18a_0/Z$
$\|3p_z\|^2$ with STO	$e/2$	$(9a_0/Z)$ above and below the plane of the ring
$\|3p_z\|^2$ with STO using tangent-sphere model	$e/2$	$(9.1a_0/Z)$ above and below the plane of the ring
$\|2p_z\|^2$ with STO using tangent-sphere model	$e/2$	$(4.34a_0/Z)$ above and below the plane of the ring

[a] e is the electronic charge, a_0 is the Bohr radius, and Z is the effective charge of the atom under consideration.

Table V. SCF MO's and Eigenvalues for Thiophene

	Energy level, ev
Five-Orbital Model	
$\phi_1 = 0.5061\chi_1 + 0.4231(\chi_2 + \chi_5) + 0.4393(\chi_3 + \chi_4)$	-14.0887
$\phi_2 = 0.8001\chi_1 - 0.0402(\chi_2 + \chi_5) - 0.4222(\chi_3 + \chi_4)$	-11.0972
$\phi_3 = 0.5926(\chi_2 - \chi_5) + 0.3858(\chi_3 - \chi_4)$	-10.8336
$\phi_4 = 0.3219\chi_1 - 0.5652(\chi_2 + \chi_5) + 0.3589(\chi_3 + \chi_4)$	-0.2491
$\phi_5 = 0.3858(\chi_2 - \chi_5) - 0.5926(\chi_3 - \chi_4)$	1.8503
Seven-Orbital Model	
$\phi_1 = 0.4599\chi_1 + 0.4354(\chi_2 + \chi_5) + 0.4455(\chi_3 + \chi_4) + 0.0788\,(\chi_6 + \chi_7)$	-14.3167
$\phi_2 = 0.5943(\chi_2 - \chi_5) + 0.3578(\chi_3 - \chi_4) + 0.1372(\chi_6 - \chi_7)$	-11.3223
$\phi_3 = 0.8125\chi_1 - 0.0072(\chi_2 + \chi_5) - 0.4121(\chi_3 + \chi_4) - 0.0011(\chi_6 + \chi_7)$	-11.0509
$\phi_4 = 0.3541\chi_1 - 0.5174(\chi_2 + \chi_5) + 0.3586(\chi_3 + \chi_4) - 0.2025(\chi_6 + \chi_7)$	-0.9897
$\phi_5 = 0.3185(\chi_2 - \chi_5) - 0.6020(\chi_3 - \chi_4) + 0.1903(\chi_6 - \chi_7)$	1.2507
$\phi_6 = 0.0541\chi_1 - 0.2067(\chi_2 + \chi_5) + 0.0551(\chi_3 + \chi_4) + 0.6729(\chi_6 + \chi_7)$	6.8604
$\phi_7 = 0.2131(\chi_2 - \chi_5) - 0.0982(\chi_3 - \chi_4) - 0.6671(\chi_6 - \chi_7)$	6.9014
Eight-Orbital Model	
$\phi_1 = 0.4663\chi_1 + 0.4347(\chi_2 + \chi_5) + 0.4418(\chi_3 + \chi_4) + 0.0785(\chi_6 + \chi_7) - 0.0433\chi_8$	-14.3666
$\phi_2 = 0.5942(\chi_2 - \chi_5) + 0.3579(\chi_3 - \chi_4) + 0.1372(\chi_6 - \chi_7)$	-11.3489
$\phi_3 = 0.8078\chi_1 - 0.0128(\chi_2 + \chi_5) - 0.4154(\chi_3 + \chi_4) - 0.0026(\chi_6 + \chi_7) - 0.0453\chi_8$	-11.1218
$\phi_4 = 0.2056\chi_1 - 0.2122(\chi_2 + \chi_5) + 0.1580(\chi_3 + \chi_4) - 0.0766(\chi_6 + \chi_7) + 0.8978\chi_8$	-1.3554
$\phi_5 = 0.2915\chi_1 - 0.4722(\chi_2 + \chi_5) + 0.3229(\chi_3 + \chi_4) - 0.1882(\chi_6 + \chi_7) - 0.4357\chi_8$	-0.9451
$\phi_6 = 0.3186(\chi_2 - \chi_5) - 0.6018(\chi_3 - \chi_4) + 0.1905(\chi_6 - \chi_7)$	1.2238
$\phi_7 = 0.0537\chi_1 - 0.2070(\chi_2 + \chi_5) + 0.0552(\chi_3 + \chi_4) + 0.6727(\chi_6 + \chi_7) - 0.0148\chi_8$	6.8330
$\phi_8 = 0.2132(\chi_2 - \chi_5) - 0.0983(\chi_3 - \chi_4) - 0.6670(\chi_6 - \chi_7)$	6.8725

For shorter interatomic distances, the point-charge model is not a good approximation for the electronic distributions. Accordingly, we follow here the procedure of Pariser and Parr,[19] in which the two-center integrals are given by

$$(ii|jj) = \frac{1}{2}[(ii|ii) + (jj|jj)] + ar + br^2 \qquad (18)$$

The parameters a and b are determined for each pair of atomic orbitals χ_i, χ_j by fitting eq 18 to the values of $(ii|jj)$ given by eq 16 for $r = 2.8$ and 3.7 A and by eq 17 for $r = 3.9$ and 4.8 A. Table III gives the results of these approximations for the two-center two-electron integrals which are needed in the SCF MO treatment of thiophene.

The point-charge model proposed here is quite simple in form and can easily be extended to other heterocyclic molecules. It can be applied to situations in which STO's are employed as well as to those in which hydrogen-like orbitals are used. The directional character of d orbitals can be readily included, as is evidenced by eq 17. The model possesses all the essential features of the tangent sphere model, but the simplicity of positioning the charges at the most probable value of r within each lobe gives the model wider applicability to include all types of atomic orbitals.

Results

With the choice of parameters discussed in the preceding section and an initial guess for the elements P_{kl} of the change and bond-order matrix, a starting Hamiltonian matrix **H** may be constructed according to eq 11. The eigenvectors c_{ij} and eigenvalues ϵ_i of **H** are then found. The eight-orbital model yields eight eigenfunctions, the seven-orbital model seven, and the five-orbital model five. Of these, the three eigenfunctions for each model corresponding to the three lowest eigenvalues represent occupied MO's. The coefficients

Table VI. π-Electronic Populations of the Atomic Orbitals in the Ground State of Thiophene

Atomic orbital[a]	5-orbital model	7-orbital model	8-orbital model
χ_1 ($3p_z$ on S)	1.793	1.743	1.740
χ_2 ($2p_z$ on C_α)	1.064	1.086	1.084
χ_3 ($2p_z$ on C_β)	1.040	0.993	0.992
χ_6 ($3d_{xz}$ on S)		0.050	0.050
χ_8 ($4p_z$ on S)			0.008

[a] For numbering see Figure 1.

c_{ij} for the three occupied MO's are then used to construct a charge and bond-order matrix and hence a new Hamiltonian matrix, whose eigenvalues give a new charge and bond-order matrix. The iterative process is continued until two successive charge and bond-order matrices agree to ±0.00001. This routine was performed on an IBM 7040 digital computer.

Table VII. Calculated Charge Densities and Dipole Moments

	5-orbital model	7-orbital model	8-orbital model	Sappenfield[a]	Wachters[b]	Solony[c]	Exptl[d]
Sulfur	1.793	1.843	1.848	1.809	1.860	1.906	...
α-Carbon	1.064	1.086	1.084	1.022	1.060	1.020	...
β-Carbon	1.040	0.993	0.992	1.073	1.010	1.030	...
μ_π, D.	1.67	0.81	0.77	1.99	0.93	0.87	...
μ_σ(est),[a] D.	−1.49	−1.49	−1.49	−1.49	−1.49	−1.49	...
μ_{total}, D.	0.18	−0.68	−0.72	0.50	−0.56	−0.62	−0.55 ± 0.04

[a] D. S. Sappenfield and M. Kreevoy, *Tetrahedron Suppl.*, **2,** 157 (1963). [b] A. J. H. Wachters and D. W. Davies, *Tetrahedron*, **20,** 2841 (1964). [c] N. Solony, F. W. Birss, and J. B. Greenshields, *Can. J. Chem.*, **43,** 1569 (1965). [d] B. Harris, R. J. W. Le Fèvre, and E. P. A. Sullivan, *J. Chem. Soc.*, 1622 (1953).

The SCF molecular orbitals and eigenvalues for thiophene for the five-, seven-, and eight-orbital models are given in Table V. In all three calculations the same parameter values were used. For each model ϕ_1, ϕ_2, and ϕ_3 are occupied in the ground state and the remaining MO's are virtual or unfilled orbitals.

The electronic populations of the atomic orbitals in the ground state are given by the diagonal elements of the final SCF charge and bond-order matrix

$$P_{jj} = 2\sum_{i=1}^{3} c_{ij}^2 \tag{19}$$

These AO populations are presented in Table VI. The sum of the AO populations at site α is called the charge density q_α at α (in units of the electronic charge e). Thus, for thiophene, we have

$$\begin{aligned} q_1 &= P_{11} + P_{66} + P_{77} + P_{88} \\ q_2 &= q_5 = P_{22} \\ q_3 &= q_4 = P_{33} \end{aligned} \tag{20}$$

These charge densities are listed in Table VII and are compared with the results of three other SCF calculations[10-12] on thiophene. These other SCF calculations[10-12] are the only previously published ones on thiophene and all of them employ the five-orbital model.

The π-electronic dipole moment μ_π in Debye units for thiophene may be readily expressed in the form

$$\mu_\pi = 4.8025[2.378(q_2 - 1) + 4.909(q_3 - 1)] \tag{21}$$

A positive value for μ_π indicates that the dipole is directed away from the sulfur atom toward the C_3–C_4 bond. The calculated μ_π for each model and an estimated[10] σ-electronic dipole moment μ_σ are given in Table VII along with values for μ_π from the three other SCF MO calculations[10-12] performed on thiophene. The experimental absolute value of the total dipole moment is 0.55 ± 0.04 D., as determined in the gas phase by Harris, Le Fèvre, and Sullivan.[30] Convincing arguments that μ_{total} is negative, *i.e.*, directed toward the sulfur atom, have been proposed by Wachters and Davies.[11] The work of Keswani and Freiser[31] supports this conclusion.

The electronic spectral transition energies relative to the ground state for the one-electron MO jump $\phi_i \rightarrow \phi_j$ are given in SCF MO theory by[17]

$$\begin{aligned} {}^{1,3}E_{i\rightarrow j} = \epsilon_j - \epsilon_i - \langle \phi_i(1)\phi_k(2) | e^2 r^{-1}{}_{12} | \phi_i(1)\phi_k(2) \rangle + \\ \binom{2}{0} \langle \phi_i(1)\phi_k(2) | e^2 r_{12}{}^{-1} | \phi_k(1)\phi_i(2) \rangle \end{aligned} \tag{22}$$

where the upper and lower figures in

$$\binom{2}{0}$$

refer to the singlet (superscript 1) and triplet (superscript 3) excitations, respectively. The $\pi \rightarrow \pi^*$ electronic transitions for the five-, seven-, and eight-orbital models as calculated from the corresponding SCF MO's are presented in Figure 2. Also shown in Figure 2 are the experimental electronic spectral lines for thiophene as determined by Milazzo[32] (first band), Price and Walsh[33] (second band), and Padbye and Desai[34] (triplet transitions). We recall that the empirical parameter k in eq 15 was adjusted so that the lowest singlet transitions in the five-orbital model would agree with the experimental results. Transitions to the MO ϕ_4 in the eight-orbital model are not shown in Figure 2 for the reasons discussed in the next section. These calculated transitions (in ev) are as follows.

$$\begin{aligned} {}^1E_{2\rightarrow 4} &= 6.32 \quad & {}^3E_{2\rightarrow 4} &= 6.04 \\ {}^1E_{3\rightarrow 4} &= 6.63 \quad & {}^3E_{3\rightarrow 4} &= 5.91 \end{aligned}$$

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(30) B. Harris, R. J. W. Le Fèvre, and E. P. A. Sullivan, *J. Chem. Soc.*, 1622 (1953).

(31) R. Keswani and H. Freiser, *J. Am. Chem. Soc.*, 71, 218 (1949).

(32) G. Milazzo, *Gazz. Chim. Ital.*, 78, 835 (1948).

(33) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A179,** 201 (1941).

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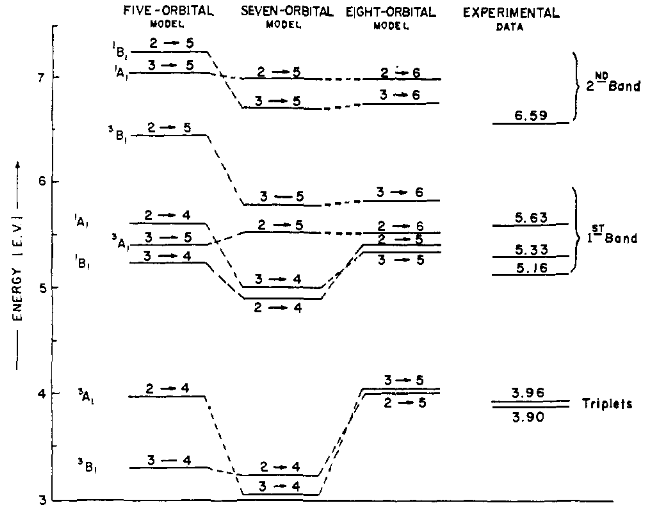

Figure 2. Calculated and experimental $\pi \rightarrow \pi^*$ electronic transitions in thiophene.

Discussion

The π-electronic densities obtained from an MO calculation which includes the zero differential overlap approximation eq 6 and 7 indicate the general disposition of charge in the molecule rather than the exact populations of the AO's. These electronic densities represent the populations of modified atomic orbitals which are not well localized. Thus, the relative values of the AO densities, rather than their precise magnitudes, reflect the general electronic behavior of the molecule.

According to the charge densities given in Table VII, the α-carbon atom in all three models is more susceptible to electrophilic attack than is the β-carbon atom. This prediction is in agreement with experiment, which finds the α-carbon atom highly favored.[35] The effect of adding higher AO's on sulfur is to increase the electronic charges on the sulfur and α-carbon atoms at the expense of the β-carbon atoms. This effect on the calculated dipole moment is quite pronounced in that it changes the direction (sign) of μ_{total} and brings μ_{total} into close agreement with the experimental value.

The $\pi \rightarrow \pi^*$ electronic spectrum predicted by the five-orbital model is in reasonable agreement with experiment, but the inclusion of additional AO's on sulfur does improve the agreement by lowering the $^1A_1$ and $^1B_1$ transitions of the second band to fit more closely the experimental value of 6.59 ev (see Figure 2). Moreover, the $^1A_1$ and $^1B_1$ transitions of the first band are closer together in the seven- and eight-orbital models. This situation is in keeping with the findings of Gronowitz,[36] who reported two maxima at 5.28 and 5.37 ev and stated that the first broad band is composed of two or three overlapping transitions of comparable intensities. The singlet–triplet transitions involving these same MO's are fortuitously close in the eight-orbital model to the experimental values 3.90 and 3.96 ev. The occurrence of these two closely spaced spectral transitions answers the query of Padbye and Desai[34] as to whether one or two transitions are being observed.

As shown in Table V, the MO ϕ_4 in the eight-orbital model is predominantly the AO χ_8. An electronic transition from an MO occupied in the ground state (ϕ_1, ϕ_2, or ϕ_3) to the MO ϕ_4 is in effect a transition from an MO to essentially the localized AO χ_8. Thus, we may regard such a transition as an intramolecular electron transfer. For this reason, transitions in the eight-orbital model to the MO ϕ_4 are not given in Figure 2. This procedure of including several AO's on an atom in the LCAO scheme and obtaining MO's which are essentially pure AO's may prove useful in future work for studying intramolecular electron transfer processes and $n \rightarrow \pi^*$ transitions.

Because we used hydrogen-like AO's instead of STO's for evaluating the two-electron two-center integrals in the SCF MO scheme, an anomaly arises in the eight-orbital model. The redefinition of χ_8 as $-\chi_8$ changes the signs of the integrals $\langle\chi_2,\chi_8\rangle$, β_{28}, $(11|18)$, $(18|18)$, $(18|66)$, and $(16|86)$, but does not change the orthogonality conditions for the AO's. These sign changes affect the final results by changing the signs of c_{18}, c_{38}, c_{48}, c_{58}, and c_{78} in Table V. However, the calculated physical properties depend only on the squares of these coefficients and hence are not affected. In our calculations we chose the sign of χ_8 such that the sign of the largest lobe above the molecular plane has the same sign as the only lobe of χ_2.

In conclusion, we observe that the $3d_{xz}$ and $3d_{yz}$ atomic orbitals on sulfur participate only slightly in the ground state of thiophene. Nevertheless, this small participation does influence the charge densities and the electronic spectrum markedly. The additional inclusion of the $4p_z$ AO influences the results to a small extent. Finally, we remark that a side effect of this investigation is the increased flexibility given to the Pariser–Parr–Pople semiempirical technique by the extension of the SCF LCAO method to include more than one orbital per atomic site.

(35) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, Chapter 5.

(36) S. Gronowitz, *Arkiv Kemi*, 13, 239 (1959).