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A THEORETICAL STUDY OF THE UV SPECTRA OF DITHIENYLS AND THIOPHENE

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Abstract—A calculation by the self-consistent MO method of the UV spectra of thiophene, 2,2′-, 3,3′-, and 2,3′-dithienyl is described. For the dithienyls the local energy method developed by Longuet-Higgins and Murrell is applied. Only the π-electrons are considered explicitly and the zero differential overlap approximation is used. Values are given for the transition energies and oscillator strengths of thiophene, the dithienyls and some cyclopentadithiophenes, and for the angles of twist of the dithienyls in non-polar solution. For thiophene a reasonable charge distribution is obtained and the bond-orders lead to bond lengths in good agreement with experiment.

1. INTRODUCTION

LITTLE theoretical work has been done on compounds consisting of two or more conjugated heterocyclic rings. In a recent paper Sappenfield and Kreevoy[1] mentioned that for a long time the development of a satisfactory theory of conjugated heterocyclic molecules such as furan and thiophene was impeded by a number of difficulties, especially the choice of appropriate integrals and parameters for the hetero atom. Sufficient experimental data are however available for the dithienyls to enable an adequate comparison between theory and experiment to be made. The object of the present work was to discover, if the local energy method developed by Longuet-Higgins and Murrell[2] could be used to give a satisfactory account of the UV spectra of 2,2′-, 3,3′-, and 2,3′-dithienyl. For the application of this method a knowledge of the self-consistent molecular orbitals (SCMO's) and energies[3,4] of thiophene is indispensable and a calculation of the UV spectrum of thiophene and a comparison with experiment is also included.

2. THE SCMO AND LOCAL ENERGY METHOD

In this section the SCMO method, used for the calculation of the SCMO's and orbital energies of thiophene and the local energy method will be discussed.

Full discussions of the SCMO method have been given in the literature. The present work followed in general the basic approximations used by Pople[5] and by McWeeny and Peacock.[6] In this simplification of the method only the π-electrons are considered, and the SCMO's ψ_i may be written as a linear combination of atomic orbitals ϕ_p, thus,

$$\psi_i = \sum_p c_{ip}\,\phi_p\,, \tag{2.1}$$

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[1] D. S. Sappenfield and M. Kreevoy, *Tetrahedron* **19**, 157 (1963).

[2] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* **A68**, 601 (1955).

[3] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* § II.6 and § III.13. W. A. Benjamin, New York (1963).

[4] C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

[5] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).

[6] R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.* **A70**, 41 (1957).

where p refers to the pth atom and for an n-atom system $p,\ i = 1, 2, \ldots, n$. The molecular orbital energies ε_i are obtained from the secular equation,

$$\mathrm{Det}\,|F_{pq} - \delta_{pq}\varepsilon_i| = 0 \tag{2.2}$$

and the coefficients c_{ip} from the corresponding set of simultaneous equations

$$\sum_q c_{iq}(F_{pq} - \delta_{pq}\varepsilon_i) = 0;\ p, q = 1, 2, \ldots, n. \tag{2.3}$$

F_{pq}, the elements of the self-consistent Hamiltonian matrix **F** are given by,

$$F_{pp} = \omega_p + \tfrac{1}{2}P_{pp}\gamma_{pp} + \sum_{r \neq p} (P_{rr} - \zeta_r)\,\gamma_{pr};\ r = 1, 2, \ldots, n. \tag{2.4}$$

$$F_{pq} = \beta_{pq}^{\mathrm{core}} - \tfrac{1}{2}P_{pq}\,\gamma_{pq}\,, \tag{2.5}$$

where ζ_r is the number of π-electrons contributed by the rth atom and,

$$\gamma_{pq} = \iint \phi_p{}^*(1)\phi_p(1)\frac{1}{r_{12}}\,\phi_p{}^*\,(2)\,\phi_p(2)\,dv(1)\,dv(2)$$

the so-called Coulomb electronic repulsion integral. Let $H^{\mathrm{core}}(\mathrm{i})$ be the Hamiltonian of an electron i in the field of the molecule stripped of the π-electrons and $H_p^{\mathrm{core}}(\mathrm{i})$ that in the field of the pth atom, minus the π-electron(s), then ω_p and $\beta_{pq}^{\mathrm{core}}$ are given by,

$$\omega_p = \int \phi_p{}^*(i)\ H_p^{\mathrm{core}}(i)\ \phi_p(i)\,dv(i) \tag{2.7}$$

$$\beta_{pq}^{\mathrm{core}} = \int \phi_p{}^*(i)\ H^{\mathrm{core}}(i)\ \phi_q(i)\,dv(i);\ p \neq q. \tag{2.8}$$

P_{pq}, the elements of the bond order matrix **P** are given by,

$$P_{pq} = 2\sum_i c_{ip}c_{iq}\,, \tag{2.9}$$

where i refers to filled orbitals only. The simple form of these equations results to a great extent from the use of the zero differential overlap approximation,[3,7] in which $\phi_p{}^*(i)\ \phi_p(i)\ dv(i)$ is taken as zero unless $p = q$ in the two-electron integrals. In the SCMO theory[3,4,8] the molecular orbital wave function for the ground state can be written as an antisymmetrized product,

$$\chi_0 = [(2m)!]^{-\frac{1}{2}} \sum_P (-1)^P\mathscr{P}\,\{(\psi_1\alpha)(\psi_1\beta)(\psi_2\alpha)\cdots(\psi_m\beta)\}\,, \tag{2.10}$$

where $\sum\limits_P (-1)^P\mathscr{P}$ is the usual antisymmetrizing summation over all permutations of the electrons. If one electron is excited from a bonding $MO\psi_i$ to an antibonding $MO\psi_k$, the excited state can be written as,

$${}^{1,3}\chi_i{}^k = [2(2m)!]^{-\frac{1}{2}} \sum_P (-1)\,\mathscr{P}^P\,\{(\psi_1\alpha)\cdots(\psi_{i-1}\beta)[(\psi_i\alpha)(\psi_k\beta) \pm (\psi_k\alpha)(\psi_i\beta)]\cdots(\psi_m\beta)\}, \tag{2.11}$$

and the excitation energy as,

$${}^{1,3}\Delta E_i^k = \varepsilon_k - \varepsilon_i - \left(ik\left|\frac{1}{r_{12}}\right|ik\right) + \left(ik\left|\frac{1}{r_{12}}\right|ki\right) \pm \left(ik\left|\frac{1}{r_{12}}\right|ki\right), \tag{2.12}$$

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

[8] J. A. Pople, *Proc. Phys. Soc.* **A68**, 81 (1955).

where

$$\left(ij\left|\frac{1}{r_{12}}\right|kl\right) = \iint \psi_i{}^*(1)\psi_j{}^*(2)\,\frac{1}{r_{12}}\,\psi_k(1)\psi_l(2)\,dv(1)\,dv(2)\,, \tag{2.13}$$

the positive and negative sign being taken for singlet and triplet states respectively.

In the local energy method[2] R–S is in general a system made up of two conjugated subsystems R and S joined by one bond. For the dithienyls R and S are the same, so that the total system is described as R–R'. In future dashes will be used to distinguish between the thienyl rings, e.g. $\chi_i{}^{k'}$ means the state corresponding to the excitation of one electron from a bonding $MO\psi_i$ of one ring to the antibonding $MO\psi_{k'}$ of the other ring. Let the bond between the thienyl rings R and R' be formed between atom μ in R and ν' in R', then it can be shown that the changes in the molecular orbitals are entirely determined by the value of the resonance integral $\beta^{\text{core}}_{\mu\nu'}$, if in Eq. (2.8) ϕ_μ and ϕ_ν are the π-atomic orbital functions of these atoms. Two cases are distinguished: 1, the rings are perpendicular to each other; 2, they lie in the same plane. The latter can be subdivided in two cases *a* and *b*, in which the sulphur atoms of the two thienyl rings are in the *trans*- and in the *cis*-position respectively.

1. In this case Longuet-Higgins and Murrell assume that $\beta^{\text{core}}_{\mu\nu'} = 0$. As the SCMO's of thiophene are non-degenerate, see Table 1, only the singly excited states $\chi_3{}^4$ and $\chi_{3'}{}^{4'}$ have to be considered for the two lowest bands in the UV spectra of the dithienyls. Since the MO's of both rings are self-consistent for the whole molecule as well as for the separated rings, the ground state will not interact with these excited states, so that the interaction matrix becomes,

$$\begin{array}{c} \chi_3{}^4 \\ \chi_{3'}{}^{4'} \end{array} \begin{bmatrix} H^{4,4}_{3,3} & H^{4,4'}_{3,3'} \\ H^{4,4'}_{3,3'} & H^{4',4'}_{3',3'} \end{bmatrix} \tag{2.14}$$

where $H^{k,l}_{i,j}$ is written for $({}^1\chi_i{}^k\,|H|\,{}^1\chi_j{}^l)$. Now $H^{4,4}_{3,3} = H^{4',4'}_{3',3'} = {}^1\Delta E_3{}^4$, see Eq. (2.12), and with the zero differential overlap approximation[8] $H^{4,4'}_{3,3'} = 2(3'4\,|1/r_{12}|\,4'3)$. This integral can be easily reduced to an expression in the Coulomb electronic repulsion integrals. The eigenvectors and eigenvalues of this matrix represent the lowest excited states and transition energies respectively.

2. $\beta^{\text{core}}_{\mu\nu'} \neq 0$. All the interactions between $\chi_3{}^4$, $\chi_{3'}{}^{4'}$, $\chi_3{}^{4'}$, $\chi_{3'}{}^4$ and χ_0 must be considered. As before $H^{4,4}_{3,3} = H^{4',4'}_{3',3'} = {}^1\Delta E_3{}^4$, $H^{4,4'}_{3,3'} = 2(3'4\,|1/r_{12}|\,4'3)$, and $H^{4',4'}_{3\,,3} = H^{4,4}_{3',3'} = \varepsilon_4 - \varepsilon_3 - (34'\,|1/r_{12}|\,34')$.

Also $H^{4,4'}_{3,3} = H^{4',4}_{3',3'} = c_{4\mu}c_{4'\nu'}\beta^{\text{core}}_{\mu\nu'}$, $H^{4,4}_{3,3'} = H^{4',4'}_{3',3} = -c_{3\mu}c_{3'\nu'}\beta^{\text{core}}_{\mu\nu'}$, $H_3{}^{4'}$, $0 = \sqrt{2}c_{3\mu}c_{4'\nu'}\beta^{\text{core}}_{\mu\nu'}$, $H_{3'}{}^4$, $0 = \sqrt{2}\,c_{4\mu}c_{3'\nu'}\beta^{\text{core}}_{\mu\nu'}$, and $H_{0,0} = H^{4',4}_{3\,,3'} = H^4_{3,0} = H^{4'}_{3',0} = 0$, where $H^k_{i,0} = ({}^1\chi_i{}^k\,|H|\,{}^1\chi_0)$. Thus the interaction matrix becomes,

$$\begin{array}{c} \frac{1}{\sqrt{2}}(\chi_3^4-\chi_{3'}^{4'}) \\[1.5ex] \frac{1}{\sqrt{2}}(\chi_3^{4'}-\chi_{3'}^{4}) \\[1.5ex] \frac{1}{\sqrt{2}}(\chi_3^4+\chi_{3'}^{4'}) \\[1.5ex] \frac{1}{\sqrt{2}}(\chi_3^{4'}+\chi_{3'}^{4}) \\[1.5ex] \chi_0 \end{array} \begin{bmatrix} H^{4,4}_{3,3}-H^{4,4'}_{3,3'} & H^{4,4'}_{3,3}-H^{4,4}_{3,3'} & 0 & 0 & 0 \\ H^{4,4'}_{3,3}-H^{4,4}_{3,3'} & H^{4',4'}_{3\,,3} & 0 & 0 & \frac{1}{\sqrt{2}}(H^{4'}_{3\,,0}-H^{4}_{3',0}) \\ 0 & 0 & H^{4,4}_{3,3}+H^{4,4'}_{3,3'} & H^{4,4'}_{3,3}+H^{4,4}_{3,3'} & 0 \\ 0 & 0 & H^{4,4'}_{3,3}+H^{4,4}_{3,3'} & H^{4',4'}_{3\,,3} & \frac{1}{\sqrt{2}}(H^{4'}_{3\,,0}+H^{4}_{3',0}) \\ 0 & \frac{1}{\sqrt{2}}(H^{4'}_{3\,,0}-H^{4}_{3',0}) & 0 & \frac{1}{\sqrt{2}}(H^{4'}_{3\,,0}+H^{4}_{3',0}) & 0 \end{bmatrix} \tag{2.15}$$

The eigenvectors of this matrix represent the excited states as well as the ground state, the energy of which is generally lowered, so that the transition energies can be obtained by subtracting the eigenvalue of the ground state from the eigenvalues of the excited states.

3. CALCULATIONS

Thiophene has the structure[9] shown in Fig. 1.

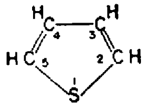

FIG. 1. Structure of thiophene

bond lengths
$r_{12} = 1{\cdot}714$ Å
$r_{23} = 1{\cdot}370$ Å
$r_{34} = 1{\cdot}423$ Å

angles
$C_5S_1C_2 = 92°10'$
$S_1C_2C_3 = 111°28'$
$C_2C_3C_4 = 112°27'$

The bond lengths and angles given above were also used for the thienyl rings, and a length[10] of 1·480 Å was used for the bond between the rings. For instance, 2,2′-dithienyl has the structure shown in Fig. 2. The *MO*'s were written as a linear combination of the $3p\pi$ atomic orbital on the sulphur atom and the four $2p\pi$ atomic orbitals on the carbon atoms. The sulphur atom contributes two π-electrons and the carbon atoms one each, thus $\zeta_S = 2$ and $\zeta_C = 1$.

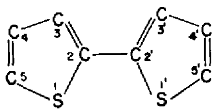

FIG. 2. Structure of 2,2′-dithienyl

The Coulomb electronic repulsion integrals are given below in eV. They were evaluated with the uniformly charged sphere method due to Pariser and Parr.[7]

For thiophene,

$$\gamma_{pq} = \begin{bmatrix} 11{\cdot}90 & 6{\cdot}80 & 5{\cdot}20 & 5{\cdot}20 & 6{\cdot}80 \\ & 10{\cdot}70 & 7{\cdot}40 & 5{\cdot}62 & 5{\cdot}41 \\ & & 10{\cdot}70 & 7{\cdot}28 & 5{\cdot}62 \\ & & & 10{\cdot}70 & 7{\cdot}40 \\ & & & & 10{\cdot}70 \end{bmatrix},$$

for 2,2′-dithienyl, $\gamma_{pq'} =$

$$\overset{1}{\begin{bmatrix} 3{\cdot}54 & 4{\cdot}85 & 3{\cdot}79 & 2{\cdot}88 & 2{\cdot}78 \\ & 7{\cdot}18 & 5{\cdot}35 & 3{\cdot}73 & 3{\cdot}57 \\ & & 4{\cdot}09 & 3{\cdot}04 & 2{\cdot}93 \\ & & & 2{\cdot}40 & 2{\cdot}32 \\ & & & & 2{\cdot}24 \end{bmatrix}}; \quad \overset{2a}{\begin{bmatrix} 3{\cdot}14 & 4{\cdot}80 & 4{\cdot}24 & 3{\cdot}02 & 2{\cdot}70 \\ & 7{\cdot}20 & 5{\cdot}30 & 3{\cdot}73 & 3{\cdot}57 \\ & & 3{\cdot}69 & 2{\cdot}92 & 3{\cdot}00 \\ & & & 2{\cdot}35 & 2{\cdot}34 \\ & & & & 2{\cdot}23 \end{bmatrix}};$$

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[9] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectry.* 7, 58 (1961).
[10] A. Almenningen, O. Bastiansen and P. Svendsäs, *Acta Chem. Scand.* **12**, 1671 (1958).

$$\overset{\text{2b}}{\begin{bmatrix} 4{\cdot}01 & 4{\cdot}80 & 3{\cdot}40 & 2{\cdot}75 & 2{\cdot}85 \\ & 7{\cdot}20 & 5{\cdot}30 & 3{\cdot}73 & 3{\cdot}57 \\ & & 4{\cdot}54 & 3{\cdot}18 & 2{\cdot}86 \\ & & & 2{\cdot}44 & 2{\cdot}29 \\ & & & & 2{\cdot}26 \end{bmatrix}},$$

for 3,3′-dithienyl, $\gamma_{pq'} =$

$$\overset{1}{\begin{bmatrix} 2{\cdot}20 & 2{\cdot}89 & 3{\cdot}48 & 2{\cdot}87 & 2{\cdot}30 \\ & 4{\cdot}12 & 5{\cdot}38 & 4{\cdot}07 & 3{\cdot}07 \\ & & 7{\cdot}14 & 5{\cdot}28 & 3{\cdot}75 \\ & & & 4{\cdot}02 & 3{\cdot}04 \\ & & & & 2{\cdot}42 \end{bmatrix}}; \quad \overset{\text{2a}}{\begin{bmatrix} 2{\cdot}17 & 2{\cdot}79 & 3{\cdot}48 & 2{\cdot}97 & 2{\cdot}34 \\ & 3{\cdot}71 & 5{\cdot}31 & 4{\cdot}54 & 3{\cdot}22 \\ & & 7{\cdot}16 & 5{\cdot}22 & 3{\cdot}74 \\ & & & 3{\cdot}61 & 2{\cdot}90 \\ & & & & 2{\cdot}36 \end{bmatrix}};$$

$$\overset{\text{2b}}{\begin{bmatrix} 2{\cdot}23 & 3{\cdot}00 & 3{\cdot}48 & 2{\cdot}76 & 2{\cdot}26 \\ & 4{\cdot}59 & 5{\cdot}31 & 3{\cdot}66 & 3{\cdot}01 \\ & & 7{\cdot}16 & 5{\cdot}22 & 3{\cdot}74 \\ & & & 4{\cdot}48 & 3{\cdot}19 \\ & & & & 2{\cdot}47 \end{bmatrix}}$$

and for 2,3′-dithienyl, $\gamma_{pq'} =$

$$\overset{1}{\begin{bmatrix} 2{\cdot}74 & 3{\cdot}80 & 4{\cdot}84 & 3{\cdot}76 & 2{\cdot}89 \\ 3{\cdot}49 & 5{\cdot}38 & 7{\cdot}16 & 5{\cdot}43 & 3{\cdot}76 \\ 2{\cdot}89 & 4{\cdot}11 & 5{\cdot}35 & 4{\cdot}05 & 3{\cdot}06 \\ 2{\cdot}29 & 3{\cdot}05 & 3{\cdot}73 & 3{\cdot}03 & 2{\cdot}41 \\ 2{\cdot}22 & 2{\cdot}94 & 3{\cdot}56 & 2{\cdot}91 & 2{\cdot}33 \end{bmatrix}}; \quad \overset{2}{\begin{bmatrix} 2{\cdot}63 & 3{\cdot}40 & 4{\cdot}78 & 4{\cdot}22 & 3{\cdot}05 \\ 3{\cdot}49 & 5{\cdot}33 & 7{\cdot}18 & 5{\cdot}24 & 3{\cdot}75 \\ 2{\cdot}99 & 4{\cdot}56 & 5{\cdot}28 & 3{\cdot}65 & 2{\cdot}92 \\ 2{\cdot}33 & 3{\cdot}19 & 3{\cdot}72 & 2{\cdot}89 & 2{\cdot}35 \\ 2{\cdot}20 & 2{\cdot}86 & 3{\cdot}56 & 2{\cdot}92 & 2{\cdot}35 \end{bmatrix}}$$

The resonance integrals β_{pq}^{core} were evaluated with a relation suggested by Carra and Polezzo,[11]

$$\beta_{pq}^{\text{core}} = \frac{2{\cdot}39}{2{\cdot}873} S_{pq}\cdot \tfrac{1}{2}(W_p + W_q)\,, \qquad (3{\cdot}1)$$

where S_{pq} is the overlap integral[12] and W_p, W_q are the ionization potentials of the pth and qth atoms respectively. The values $W_s{}^+ = -22{\cdot}9$ eV and $W_C = -11{\cdot}54$ eV can be found from the ionization potentials given by Skinner and Pritchard,[13] and by Moore.[14] Thus the resonance integrals are, $\beta_{12}^{\text{core}} = -2{\cdot}51$ eV, $\beta_{23}^{\text{core}} = -2{\cdot}47$ eV, $\beta_{34}^{\text{core}} = -2{\cdot}26$ eV and $\beta_{\mu\nu'}^{\text{core}} = -2{\cdot}05$ eV.

ω_p which can be called the Coulomb parameter for the pth atom, was treated as an empirical parameter.[6] To form the **F** matrix defined in the Eqs. (2.4) and (2.5) it is necessary to guess a preliminary set of values for **P**. This matrix was obtained by a Hückel method with $(H_{11} - H_{33})/\beta_{CC} = 1{\cdot}5$, $(H_{22} - H_{33})/\beta_{CC} = 0{\cdot}15$ and $\beta_{CS}/\beta_{CC} = 0{\cdot}48$, where the β's and H's are the resonance and Coulomb integrals of Hückel theory. A value for the π-electron moment was obtained from the experimental

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[11] S. Carra and S. Polezzo, *Gazz. Chim. Ital.* **88**, 1103 (1958).

[12] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

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

[14] C. E. Moore, *Atomic Energy Levels.* Nat. Bur. Stand., Washington (1949).

total dipole moment[15,16] and an estimated σ-electron moment. The Hückel parameters were then chosen such that the calculation gave this value for the π-electron moment. Eq. (2.3) can be solved by finding the eigenvalues and eigenvectors of **F**, forming a new **P** and thus a new **F**, and repeating until the commutator of the **F** matrix and the density matrix $\frac{1}{2}\mathbf{P}$ is sufficiently small. In these calculations the value was chosen such that the Hamiltonian matrix was self-consistent to about four places of decimals. The calculations were carried out on the X-1 computer of the Central Computing Institute of Leiden University. The Coulomb parameters finally obtained, which also satisfied the dipole moment criterion, were, $\omega_1 = -18$ eV, $\omega_2 = \omega_5 = -0{\cdot}5$ eV and $\omega_3 = \omega_4 = 0$.

4. RESULTS

By the method outlined in section 3 the SCMO's and energies for thiophene, shown in Table 1, were obtained.

TABLE 1. SCMO'S AND ENERGIES (eV) OF THIOPHENE

SCMO	Form	Energy
$\psi_1 =$	$0{\cdot}9047\phi_1 + 0{\cdot}2786(\phi_2 + \phi_5) + 0{\cdot}1147(\phi_3 + \phi_4)$	$-13{\cdot}432$
$\psi_2 =$	$0{\cdot}3340\phi_1 - 0{\cdot}2967(\phi_2 + \phi_5) - 0{\cdot}5968(\phi_3 + \phi_4)$	$-6{\cdot}840$
$\psi_3 =$	$0{\cdot}6035(\phi_2 - \phi_5) + 0{\cdot}3685(\phi_3 - \phi_4)$	$-5{\cdot}254$
$\psi_4 =$	$0{\cdot}2645\phi_1 - 0{\cdot}5783(\phi_2 + \phi_5) + 0{\cdot}3615(\phi_3 + \phi_4)$	$5{\cdot}517$
$\psi_5 =$	$0{\cdot}3685(\phi_2 - \phi_5) - 0{\cdot}6035(\phi_3 - \phi_4)$	$7{\cdot}645$

ψ_1, ψ_2, and ψ_4 belong to the representation a_1, and ψ_3 and ψ_5 to the representation b_1 of the symmetry group C_{2v}. From these orbitals the charge distribution and bond orders for thiophene can be obtained. These are given in Fig. 3.

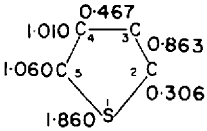

FIG. 3. Charge distribution and bond orders for thiophene

With Eq. (2.12) four singlet-singlet (s.s) and four singlet-triplet (s.t) transition energies for thiophene were calculated. They are given in Table 2 together with the experimental values. The oscillator strengths f were evaluated with the following formula,

$$f_{ik} = 8{\cdot}7495 \times 10^{-2} \Delta E_i^{\,k} \,|\mathbf{Q}_{ik}|^2 , \tag{4.1}$$

where ΔE_{ik} is the transition energy in eV and $\mathbf{Q}_{ik}$ is the transition moment divided by e, the absolute charge of the electron, thus,

$$\mathbf{Q}_{ik} = ({}^1\chi_0 \,|\sum_j \mathbf{r}(j)|\, {}^1\chi_i^{\,k}) = \sqrt{2}\,(\psi_i \,|\mathbf{r}|\, \psi_k) = \sqrt{2} \sum_p c_{ip} c_{kp} (\mathbf{x}_p + \mathbf{y}_p + \mathbf{z}_p), \tag{4.2}$$

where $\mathbf{r}(j)$ is the position vector of the jth electron in Å.

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[15] R. Keswani and H. Freiser, *J. Amer. Chem. Soc.* **71**, 218 and 1789 (1949).

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

TABLE 2. TRANSITION ENERGIES (eV) AND OSCILLATOR STRENGTHS OF THIOPHENE

	B_1		A_1		A_1		B_1	
Theory	$\Delta E_3{}^4$	f_{34}	$\Delta E_2{}^4$	f_{24}	$\Delta E_3{}^5$	f_{35}	$\Delta E_2{}^5$	f_{25}
s. s Transition	5·50	0·44	6·85	0·51	7·19	0·40	8·18	0·08
s. t Transition	3·34	0	5·24	0	5·59	0	6·71	0
Experiment								
s. s Transition	5·17–5·90[a]	0·1[b]			6·59–7·25[a]			
s. t Transition	3·90; 3·96[c]	$0·5 \times 10^{-6}$[c]						

[a] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* **A179,** 201 (1941).

[b] A. Trombetti and C. Zauli, *Ann. di Chim.* **53,** 702 and 805 (1963).

[c] M. R. Padhye and S. R. Desai, *Proc. Phys. Soc.* **A65,** 298 (1952).

With the integrals given in section 3 the matrix elements of the Eqs. (2.14) and (2.15) are evaluated for 2,2′-, 3,3′-, and 2,3′-dithienyl. From the eigenvalues and eigenvectors of these matrices the transition energies and transition moments were obtained. The oscillator strengths *f* were again evaluated with Eq. (4.1). The transition energies and oscillator strengths for 2,2′-, 3,3′-, and 2,3′-dithienyl are given in Table 3 together with the experimental values for 2,2′-dithienyl, cyclopenta[2,1-b;

TABLE 3. TRANSITION ENERGIES (eV) AND OSCILLATOR STRENGTHS OF DITHIENYLS

Theory	B_1		A_1		A_1		B_1	
2,2′-dithienyl	*E*	*f*	*E*	*f*	*E*	*f*	*E*	*f*
perpendicular	5·12	0·79	5·88	0·22				
planar (*trans*)	4·60	0·08	6·18	0·77	7·52	3·3	8·01	2·7
planar (*cis*)	4·60	0·07	6·18	0·05	7·51	3·3	8·00	2·6
Experiment[a]								
2,2′-dithienyl	4·11	0·26	5·02	0·18				
cyclopenta[2,1-b; 3,4-b′]dithiophene	4·30	0·30	5·02	0·20				

Theory	B_1		A_1		A_1		B_1	
3,3′-dithienyl	*E*	*f*	*E*	*f*	*E*	*f*	*E*	*f*
perpendicular	5·49	0·57	5·51	0·30				
planar (*trans*)	5·44	0·68	5·47	$2·8 \times 10^{-5}$	7·23	0·60	7·36	0·55
planar (*cis*)	5·29	0·13	5·63	0·61	7·19	0·61	7·31	0·48
Experiment[a]								
3,3′-dithienyl	4·77	0·24	5·85	0·70				
cyclopenta[1,2-b; 4,3-b′]dithiophene	4·16	0·02	5·64	0·88				

Theory	A'		A'		A'		A'	
2,3′-dithienyl	*E*	*f*	*E*	*f*	*E*	*f*	*E*	*f*
perpendicular	5·37	0·66	5·63	0·20				
planar (*trans*)	5·29	0·17	5·52	0·55	7·29	1·5	7·59	0·76
Experiment[a]								
2,3′-dithienyl	4·38	0·23	5·28	0·16				

[a] H. Wynberg and A. Bantjes, *J. Org. Chem.* **24,** 1421 (1959); H. Wynberg and A. Kraak, *Ibid.* 1964 (in the press).

3,4-b′]dithiophene, 3,3′-dithienyl, cyclopenta[1,2-b;4,3-b′]dithiophene and 2,3′-dithienyl.

5. DISCUSSION

The charge distribution of thiophene (Fig. 3) gives a π-electron moment of 0·93 D, directed from the sulphur atom to the ring. With the value of the σ-electron moment $-1{\cdot}49$ D, given by Sappenfield and Kreevoy,[1] the value obtained for the dipole moment of thiophene is 0·56 D, which is in good agreement with the experimental values, $\mu = 0{\cdot}53$ D[15] (in benzene) and $\mu = 0{\cdot}55 \pm 0{\cdot}04$ D[16] (in gas phase). The dipole moment obtained is directed from the ring to the sulphur atom. Sappenfield and Kreevoy obtained, however, such a large value for the π-electron moment, that they also got a dipole moment of thiophene in agreement with experiment, but with the opposite direction. The dipole moment of thiophene derivatives, shown in columns I and II of Table 4 can be obtained from the C—Cl and C—CH_3 bond dipole moments for substituted benzenes, which are 1·58 D and 0·34 D respectively.[15]

TABLE 4. CALCULATED AND OBSERVED DIPOLE MOMENTS (D) OF SUSTITUTED THIOPHENES

Molecule	Theory I	Theory II	Expt.
2-Chlorothiophene	1·77	1·56	1·60
2,5-Dichlorothiophene	1·18	0·12	1·12
2-Methylthiophene	0·57	0·69	0·67
3-Methylthiophene	0·77	0·44	0·82

The dipole moments given in column I can be obtained on the assumption that the dipole moment of thiophene is directed from the ring to the sulphur atom, and the dipole moments given in II can be obtained on the assumption that the dipole moment of thiophene is in opposite direction. Table 4 supports the view that the dipole moment of thiophene is directed from the ring to the sulphur atom. Thus, the calculated dipole moment of thiophene agrees with experiment in magnitude as well as direction. The charge distribution obtained here also gives a good explanation for the larger electrophilic reactivity of the α-carbon atom compared to the β-carbon atom, and the calculated bond orders P_{23} and P_{34} yield distances $r_{23} = 1{\cdot}36$ Å and $r_{34} = 1{\cdot}43$ Å, which are in good agreement with the experimental values, given in Fig. 1.

Table 2 shows that the calculated transition energies of thiophene are satisfactory. Price and Walsh[17] correlated their measured spectral band with the N–V_1 and N–V_2 transitions in butadiene and this assignment is confirmed in these calculations. The only oscillator strength, for which there is an experimental value, f_{34} is less satisfactory. The reason may be that in the derivation of Eq. (4.1) the assumption is made that the wave functions are exact solutions of the Hamiltonian.

For the dithienyls there is less satisfactory agreement between theory and experiment; it is possible that a fully self-consistent calculation on the dithienyls would yield better results than the method used here. When the inverse distance approximation $\gamma_{pq'} = R_{pq'}^{-1}$ is used for pairs of different rings, the results are slightly modified; but the same qualitative picture is obtained. The oscillator strengths suggest that the

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[17] cf. Ref. [a], beneath Table 2.

angle of twist θ for 3,3′-dithienyl is about 0°, if $\theta = 0$ for *cis*-position. The angles of twist were also evaluated by comparing the dipole moments of the dithienyls[18] and that of thiophene.[16] Relations between the dipole moments of the dithienyls and the angles of twist can be obtained from the structure of the dithienyls,[9,10] if the assumption is made, that moments of the rings are independent. They are

for 2,2′-dithienyl $\mu = 0{\cdot}979\,\mu_{\mathrm{th}}\,(2 + 2\cos\theta)^{\frac{1}{2}}$,
for 3,3′-dithienyl $\mu = 0{\cdot}556\,\mu_{\mathrm{th}}\,(2 + 2\cos\theta)^{\frac{1}{2}}$
and for 2,3′-dithienyl $\mu = \mu_{\mathrm{th}}\,(2{\cdot}340 + 1{\cdot}088\cos\theta)^{\frac{1}{2}}$,

where μ_{th} is the dipole moment of thiophene. The angles of twist thus obtained are from 79°–97° and from 0°–29° for 2,2′-, and 2,3′-dithienyl respectively, and for 3,3′-dithienyl the angle is 0°. These are consistent with the values obtained from the oscillator strengths.

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[18] H. Wynberg, *Angew. Chem.* **75**, 453 (1963).