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## A Theoretical Calculation of the Bond Orders and Bond Lengths in Thiophthen

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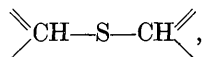
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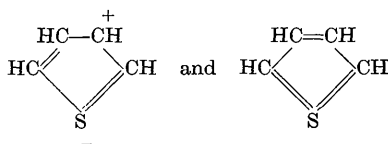
Using a molecular-orbital method, which involves the  $d$  orbitals of the sulphur atom, as developed by Longuet-Higgins for thiophen, we have calculated the bond orders in thiophthen and related them to bond lengths. The calculated bond lengths are compared with the observed values reported by Cox, Gillot & Jeffrey; taking into account the approximate character of the calculations, the agreement is very satisfactory. The value calculated for the central bond in the molecule is in greatest error. This 'central-bond discrepancy' has also appeared in molecular-orbital calculations not involving  $d$  orbitals on molecules not containing heterocentres, and appears to be a more general feature which requires further investigation.

### Introduction

It has been suggested of late (Schomaker & Pauling, 1939; Longuet-Higgins, 1949) that in the treatment of molecules containing the group



we have to consider the possibility of the  $d$  atomic orbitals in the valence shell of the sulphur atom being available for bonding. This idea was first put forward by Schomaker & Pauling (1939) to account for bond lengths, resonance energy and dipole moment in thiophen. Adopting a valence-bond approach these authors introduced canonical structures of the type



each of which was supposed to contribute about 10% to the total electronic structure. These two canonical

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forms must involve the sulphur  $d$  orbitals because sulphur here has a 'decet' of electrons in its valence shell.

Longuet-Higgins (1949), although admitting the qualitative value of the above arguments, has drawn attention to the fact that, as in many other cases, the valence-bond approach gives rise to difficulties if we consider larger molecules of a similar type. He therefore developed a molecular-orbital treatment for the thiophen problem by introducing hybrid atomic orbitals compounded of the sulphur  $3p$  and  $3d$  orbitals with the appropriate geometrical disposition to participate, together with the carbon  $2p$  orbitals, in the formation of molecular  $\pi$  orbitals. For details we refer to the original paper. As a result Longuet-Higgins could account for the close resemblance between thiophen and benzene derivatives, and for the magnitude of the resonance energy, *bond lengths* and dipole moment in thiophen. It was also possible to explain some aspects of the chemical reactivity of this molecule.

To quote Longuet-Higgins (1949), 'the method of molecular orbitals is particularly suitable for the investigation of large molecules because it provides

a definite and manageable technique for determining electronic structures once the values of certain parameters have been fixed'. In his approach to molecules containing the group  $\begin{array}{c} \diagup \\ \text{CH-S-CH} \\ \diagdown \end{array}$  only one such parameter is involved. The fact that bond lengths in thiophthen are now available provides us with the first case where we are able to test the validity of this method by extrapolating it to a more complicated molecule without changing this parameter.

### Method and results

As in thiophen, we form hybrid atomic orbitals compounded out of the sulphur  $3p_z$ ,  $3d_{yz}$  and  $3d_{zx}$  atomic orbitals. The  $z$  axis is taken to be perpendicular to the molecular plane, which is a plane of antisymmetry for all the above orbitals and also for the carbon  $2p_z$  orbitals. The approximate form of those atomic orbitals in thiophthen which can participate in the formation of molecular  $\pi$  orbitals is shown in Fig. 1.

Following Longuet-Higgins we assume that the orbitals  $\phi_h$  and  $\phi_{h'}$  are too high in energy to be occupied in the ground state. So the ten aromatic electrons in thiophthen will occupy molecular orbitals compounded out of six atomic  $2p_z$  orbitals (from the six  $sp^2$ -hybridized carbon atoms) and the four hybrid orbitals  $\phi_f$ ,  $\phi_g$ ,  $\phi_{f'}$  and  $\phi_{g'}$  of the sulphur atoms. This implies immediately a close correspondence in  $\pi$ -electronic structure of thiophthen and naphthalene (Fig. 2); the following orbitals may be considered as equivalent:

In thiophthen (Fig. 1)	In naphthalene (Fig. 2)
$\phi_f$	$\phi_6$
$\phi_g$	$\phi_5$
$\phi_{f'}$	$\phi_2$
$\phi_{g'}$	$\phi_1$

So the secular equations of the two molecules should be identical apart from (i) the extra solutions in the thiophthen case corresponding to the unoccupied, localized, non-bonding orbitals  $\phi_h$  and  $\phi_{h'}$ ; (ii) possible changes in some of the coulombic and resonance integrals involved.

As to this second point, a detailed analysis by Longuet-Higgins (1949) showed that the only resonance integrals to be changed are those between  $\phi_f$ ,  $\phi_g$ ,  $\phi_{f'}$  and  $\phi_{g'}$  on the one hand and the adjacent carbon  $2p_z$  orbitals on the other hand.\* These must be given values 20% lower than the corresponding integrals in naphthalene. Therefore we should obtain the bond orders in thiophthen by calculating the corresponding bond orders in a hypothetical naphthalene molecule which is distorted so as to reduce the resonance integrals of bonds 1-9, 2-3, 6-7 and 5-10 by an amount  $\frac{1}{5}$ .

Here we can easily apply a first-order perturbation calculus according to Coulson & Longuet-Higgins (1948). If in a conjugated system we change the resonance integral between centres  $t$  and  $u$ ,  $\beta_{tu}$ , by an amount  $\delta\beta_{tu}$ , then as a result the mobile bond-orders between

all centres will change. The change in bond order between centres  $r$  and  $s$ ,  $\delta p_{rs}$ , caused by this change in  $\beta_{tu}$ , can be written

$$\delta p_{rs} = \pi_{rs,tu} \delta \beta_{tu},$$

where  $\pi_{rs,tu}$  is called the 'mutual polarizability' between the bonds  $rs$  and  $tu$  (Coulson & Longuet-Higgins, 1947). Or

$$\delta p_{rs} = \beta \cdot \pi_{rs,tu} \delta \beta_{tu} / \beta,$$

where  $\beta$  is the resonance integral in the unperturbed naphthalene molecule. Numerical values for  $\beta \cdot \pi_{rs,tu}$  are given by Coulson & Longuet-Higgins (1948). From the discussion above it follows that we have to put

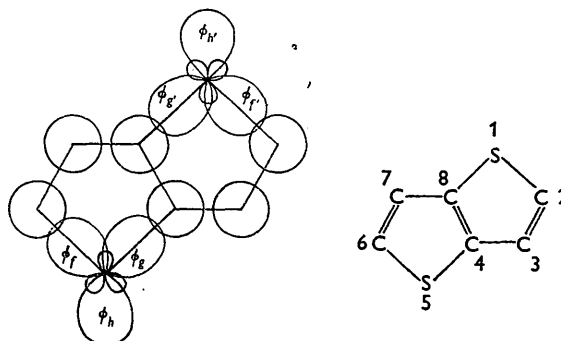


Fig. 1. Thiophthen.

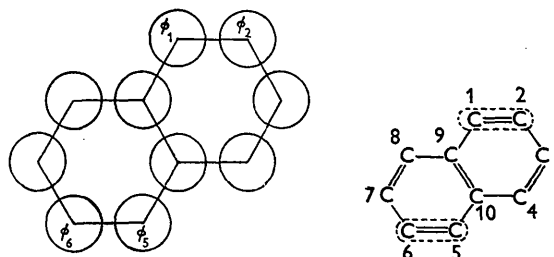


Fig. 2. Naphthalene.

$\delta\beta_{tu}/\beta = -\frac{1}{5}$  for the bonds 1-9, 2-3, 6-7 and 5-10. Thus we obtain the bond orders in thiophthen as

$$(p_{rs})_{\text{thiophthen}} = (p_{rs})_{\text{corresponding bond in naphthalene}} - \frac{1}{5} \sum_{\substack{tu=1-9 \\ 2-3 \\ 6-7 \\ 5-10}} (\beta \cdot \pi_{rs,tu})_{\text{naphthalene}}$$

To illustrate the procedure we will write down in detail the calculation of the bond order of the  $C_2-C_3$  bond (Fig. 1). The corresponding bond in naphthalene is the one between  $C_3$  and  $C_4$  (Fig. 2). The following quantities can be directly obtained from the literature cited:

$$\begin{aligned} \text{Naphthalene: } p_{34} &= 0.725, \\ \beta \cdot \pi_{34,19} &= -0.074, \\ \beta \cdot \pi_{34,23} &= -0.209, \\ \beta \cdot \pi_{34,67} &= 0.032, \\ \beta \cdot \pi_{34,5-10} &= 0.059. \end{aligned}$$

Hence

$$\begin{aligned} (p_{23})_{\text{thiophthen}} &= 0.725 - \frac{1}{5} \{ -0.074 - 0.209 \\ &\quad + 0.032 + 0.059 \} \\ &= 0.725 + 0.038 = 0.76. \end{aligned}$$

\* All coulombic integrals remaining constant.

For all the C=C bonds we can immediately read off the bond lengths concerned from the well-known curve connecting bond order and bond length. In our example we find for the C<sub>2</sub>-C<sub>3</sub> bond length 1.37 Å. For the C=S bonds a relatively large uncertainty arises since a similar curve cannot be drawn with any accuracy. The values which we indicate in Table 1 below were obtained by using a straight line between C-S, bond order  $p=0$ , bond length  $l=1.79$  Å. and C=S,  $p=1$ ,  $l=1.60$  Å.

Table 1. *Bond orders and bond lengths in thiophthen*

(For numbering see Fig. 1)

Bond	Mobile order calculated	Length calculated (Å.)	Length determined* (Å.)
S-C <sub>2</sub>	0.54	1.69 ± 0.02	1.72
S-C <sub>3</sub>	0.49	1.70 ± 0.02	1.74
C <sub>2</sub> -C <sub>3</sub>	0.76	1.37	1.36
C <sub>3</sub> -C <sub>4</sub>	0.56	1.41	1.41
C <sub>4</sub> -C <sub>8</sub>	0.58	1.41	1.36

### Discussion

Remembering the uncertainty in the C-S order/length relation the agreement between theory and experiment is very satisfactory except for the C<sub>4</sub>-C<sub>8</sub> bond. It is striking that such a 'central bond discrepancy' has also been found in other molecules; compare, for example, the theoretical (Moffit & Coulson, 1948) and experimental (Robertson & White, 1945, 1947) results on coronene and pyrene. Expressed qualitatively one feels that such a discrepancy might be caused by the fact that our theory does not take into account that the central C atoms are tertiary and all the others secondary. However, it then remains surprising that (i) no discrepancy at all is encountered for bonds which involve one tertiary atom; (ii) the discrepancy is negative

\* Cox, Gillot & Jeffrey (1949).

(theoretical lengths too low) in the case of coronene and pyrene and positive in thiophthen. It is to be hoped that the measuring of more central bond lengths in other molecules, together with further theoretical developments, may elucidate this point.

One can ask how far a change of the parameter used,  $-\frac{1}{5}$ , changes the results. We find that a very large increase is necessary to get a noticeable improvement in the results. But such an increase is not in accordance with the work of Longuet-Higgins (1949) on thiophen, and in addition such a large perturbation-parameter would make the value of a first-order perturbation calculus, as used, extremely doubtful. We shall have to wait for more information about related heterocyclic molecules in order to examine further the validity of the parameter  $-\frac{1}{5}$ . For the time being our investigation lends considerable support to the treatment of conjugated  $\begin{array}{c} \diagup \text{CH} \\ | \\ \text{S} \\ | \\ \text{CH} \diagdown \end{array}$  systems put forward by Longuet-Higgins.

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