

The Molecular Structure of Thiophthen from X-ray Crystal Analysis

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The molecular structure of thiophthen, $C_4H_4S_2$, has been determined by X-ray analysis, using Fourier three-dimensional syntheses and differential syntheses. Corrections have been made for 'termination of the series' errors, which were found to be important in this structure. The bond lengths in the centro-symmetrical molecule are $C_1-C_2 = 1.36 \text{ \AA}$, $C_2-C_3 = 1.41 \text{ \AA}$, $C_3-C'_3 = 1.36 \text{ \AA}$, $C_1-S = 1.72 \text{ \AA}$, $C'_3-S = 1.74 \text{ \AA}$. A statistical analysis of the accuracy of these values has been attempted from information given by the differential syntheses.

The results are discussed in relation to molecular orbital calculations on thiophen and to similar preliminary calculations on thiophthen itself. While the general agreement is good, there appear to be significant discrepancies between theory and experiment in the lengths of the C-S bonds and of the central C-C bond of the molecule.

It is suggested that only for the latter must reconciliation necessarily be sought in a refinement of the theoretical treatment; while the C-S discrepancy may be accounted for in the same way, it is also possible that it will be partially or wholly removed by revision of the C-S bond-order/length relationship, knowledge of which is at present inadequate.

Introduction

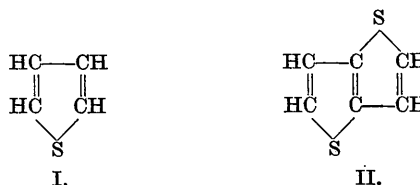
The quantum-mechanical calculations which form the basis of the theoretical description of the electron distribution in aromatic homocyclic carbon compounds can be applied to their heterocyclic analogues. The actual results obtained, usually expressed in terms of the mobile electron density on the atoms and the order of the bonding between them, depend upon certain adjustable parameters describing the distribution and interaction of the so-called π or mobile electrons which are contributed by the various atoms in the molecule. These parameters cannot at present be calculated theoretically with any degree of certainty, and they are normally estimated indirectly from a diversity of experimental data, some of the most important of which are the bond lengths in appropriate structures. In the case of heterocyclic molecules containing sulphur, this structural information is at present very inadequate; apart from isoprene sulphone (Cox & Jeffrey, 1942), the theoretical interpretation of which is as yet uncertain, it is limited entirely to the results of the electron-diffraction study of thiophen (I) (Pauling & Schomaker, 1939). In this investigation the molecular dimensions which were found to give a calculated diffraction curve compatible with the experimental pattern were

$$C-S = 1.74 \text{ \AA}, \quad C-C = 1.44 \text{ \AA}, \quad C=C = 1.35 \text{ \AA},$$

$$C-H = 1.09 \text{ \AA}, \quad \angle C-S-C = 91^\circ.$$

From the theoretical calculation of the electronic structure of the molecule (Longuet-Higgins, 1949) and from the chemistry of thiophen it might be expected that the C-C bonds should be more nearly equal in length and benzenoid in character. However, as is

clear from the description of the analysis, the electron diffraction pattern is sensitive only to the C-S distance, and the other bond lengths were assumed values, inferred from the results on furan and pyrrole, which in

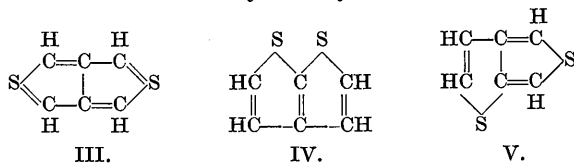


themselves are not definite on account of the relatively large number of parameters. In fact, if it were not for its low melting point, which gives rise to experimental difficulties, thiophen is a molecule which would undoubtedly be regarded as more suited to the X-ray method of structure analysis. Pending the development of the special apparatus required for the detailed analysis of crystals at low temperatures, we have studied thiophthen (II) in the expectation that it would have the same relationship to thiophen as naphthalene has to benzene, and would so provide a valuable contribution to the structural knowledge of organic sulphur compounds.

The X-ray structure analysis

The solid thiophthen, $C_6H_4S_2$, with m.p. 54° C ., is reported by Challenger & Harrison (1935) to possess a centro-symmetrical molecule on the evidence of a zero dipole moment and X-ray measurements by J. D. Bernal of which details are not published. It therefore possesses one of the configurations II or III, but the latter is considered to be very unlikely from the mode of formation and reactions. An isomer which is

liquid at room temperature is also known, and is presumably IV or a mixture of IV and V (Challenger, Clapham & Emmott, 1948). The well-defined solid compound which is the subject of this investigation crystallizes well from ligroin (40–60°) in colourless bipyramids of the orthorhombic system. The form {111} is always present and generally predominates, with occasionally {100}, {010} or {001}, but seldom more than one of them on any one crystal.



The unit-cell dimensions measured from photographs with the film in the Straumanis position were

$$a = 10.050, \quad b = 9.806, \quad c = 6.127 \text{ \AA.},$$

all $\pm 0.005 \text{ \AA.}$ This gave a calculated density of 1.53 g.cm.^{-3} with four molecules in the unit cell; the density found by flotation was 1.55 g.cm.^{-3} . The systematic extinctions of ($hk0$) absent for h odd, ($0kl$) for k odd and ($h0l$) for l odd, uniquely characterize the space group as $Pbca$ with four centro-symmetrical molecules. The complete structure analysis therefore requires the determination of twelve independent parameters, excluding those of the hydrogen atoms.

For the analysis, the X-ray intensities of all spectra within the range of $\text{Cu K}\alpha$ radiation were recorded on single-crystal oscillation and Weissenberg photographs. A multiple-film technique was used to encompass the necessary range of intensities, and the relative intensities were estimated visually. It was not found necessary to make absolute intensity measurements, and the interpretation was based on the relative structure amplitudes of 480 planes.

In order to assign atomic co-ordinates with the highest degree of accuracy possible with contemporary methods, calculations were made in the following sequence:

(i) Patterson F^2 line and sectional syntheses to locate the sulphur atoms.

(ii) Fourier F projections and 'trial and error' calculations using Bragg-Lipson charts to find the orientation of the molecules.

(iii) Fourier F sections and lines evaluated at $\frac{1}{60}$ ths of cell edges using Beevers and Lipson strips, to define the approximate atomic positions more exactly.

(iv) Fourier F sections in $\frac{1}{120}$ ths of cell edges using a Hollerith punched-card method, for further refinement of the co-ordinates.

(v) Differential syntheses for locating the maxima with high accuracy and correcting for the 'termination of the series' errors; a Hollerith method was also used for these computations.

These five steps are described in detail below:

(i) Combination of the equivalent positions for the

space group $Pbca$ gives the general co-ordinates of all the S-S vector peaks. Of these, the type $(\frac{1}{2}, 0, \frac{1}{2} - 2z)$, $(0, \frac{1}{2} - 2y, \frac{1}{2})$, $(\frac{1}{2} - 2x, \frac{1}{2}, 0)$ offered the simplest means of determining the three sulphur parameters by F^2 syntheses along the appropriate lines. Sections were also computed to reveal peaks of the type $(\frac{1}{2}, \frac{1}{2} + 2y, 2z)$, $(2x, \frac{1}{2}, \frac{1}{2} + 2z)$, $(\frac{1}{2} + 2x, 2y, \frac{1}{2})$, and the best mean sulphur co-ordinates, from the consideration of all the vector peaks observed, were (0.103, 0.104, 0.25). These x and y co-ordinates were actually within 0.01 \AA. of the final values, but the z value was inevitably less certain because of the extra plane of symmetry at $z = \frac{1}{4}$ in the F^2 syntheses.

(ii) As a consequence of the space-group relationships and the proximity of the S atoms to the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes, the sulphur atoms contribute largely to the structure factors of planes of the h -even types and only slightly to those of the h -odd type, a fact which is apparent from the weak odd layer lines of the [100] and [102] rotation photographs. With the assumption that the sulphur contributions dominated the phase angles of the h -even structure factors, Fourier F projections on the principal faces were computed. As was expected from the positions of the sulphur atoms, the resolution of the carbon atoms was poor, but the [001] projection revealed the molecules sufficiently clearly to confirm the configuration as II rather than III and indicated their approximate orientation in the unit cell.

The orientation of the S-S axis in the molecule was fairly accurately known from the vector syntheses and, with the assumption of a planar molecule with dimensions from the electron diffraction data on thiophen, it was possible to improve on the information from the projections by trial and error calculations. The paths traced by each carbon atom as the model was rotated about the fixed S-S axis were projected on to Bragg-Lipson charts for the purpose of rapid calculations; in this way a position of the molecules was found, close to that suggested by the Fourier projections, which gave calculated structure factors in good agreement with those observed for many of the planes in the principal zones. All the structure factors were then recalculated and some small improvement in the resolution of the peaks was effected by the inclusion of more terms in the revised projections.

(iii) Since the plane of the molecule is inclined at an appreciable angle in all three projections, the only satisfactory method of locating the carbon atoms with any accuracy was by means of three-dimensional Fourier sectional and line syntheses. These were computed in the first instance at $\frac{1}{60}$ ths of the cell edge in the vicinity of maxima and $\frac{1}{30}$ ths elsewhere with the aid of Beevers and Lipson strips. Two sectional syntheses at $z = 0.250$ and 0.050 gave the x and y co-ordinates of the sulphur and the three carbon atoms; their z co-ordinates were obtained from appropriate line syntheses. These co-ordinates were then used for recalculating the structure factors and gave a $\Sigma |\Delta F/F|$ agreement

index of 0.25. The recalculations led to a number of sign changes which were introduced into the sections and lines by means of correcting syntheses.

(iv) A more detailed examination of the electron density in the regions of the peak maxima was now necessary. The following sectional syntheses were computed in order to determine the twelve parameters and provide a number of cross checks on the computations:

- at $z=0.230$ for the x and y co-ordinates of S and C_1 ,
- at $x=0.104$ for the y and z co-ordinates of S and C_2 ,
- at $y=0.060$ for the x and z co-ordinates of C_1 and C_3
- at $z=0.033$ for the x and y co-ordinates of C_3 ,
- at $z=0.069$ for the x and y co-ordinates of C_2 .

The electron densities were evaluated by means of the Hollerith punched-card method of Cox, Gross & Jeffrey (1947), at $\frac{1}{120}$ ths of the cell edges near the peak maxima and at $\frac{1}{60}$ ths on the outlying parts of the atoms. The sign changes resulting from the new set of co-ordinates were introduced by means of correcting syntheses (also at $\frac{1}{120}$ ths) for which the Robertson strips (Robertson, 1948) were found to be most convenient. The final co-ordinates from the Fourier syntheses are shown in column *A* of Table 1, and the corresponding bond lengths are in column *A* of Table 2. This shows the structure as determined by the hitherto standard method of successive Fourier refinement without correction for termination of the series.

Up to this stage, the structure factors had been calculated using the atomic scattering factor curves of the *International Tables* with a temperature factor of $B=2.0 \text{ \AA}^2$. It was found possible, however, to derive experimental f curves for this particular structure from the calculations on some 90 planes where almost the whole of the structure factor was due to the sulphur scattering, and a similar number where the structure factors were due mainly to the carbon atoms alone. The data for these curves are given in Table 3; their use resulted in a small improvement in the agreement between the observed and calculated structure factors ($\Sigma |\Delta F/F| = 0.167$), but there were no sign changes.

(v) Because of the comparatively heavy sulphur atoms in the structure, it was considered particularly important in this case to examine the influence of the 'termination of the series' effects on the atomic parameters, and this was done by the method proposed by Booth (1945).

The co-ordinates from the final experimental synthesis are used to calculate a set of structure factors; these structure factors are used as coefficients in a synthesis from which a new set of co-ordinates is derived. Provided that the two syntheses are terminated in the same way, and that the agreement between experimental and calculated structure factors is reasonably good, we can assume that the differences between the two sets of co-ordinates represent the effect of the finite termination of the experimental

synthesis. Thus these differences can be applied in the opposite sense as corrections to obtain the final co-ordinates.

Absorption errors should also be taken into account. Since in practice the only feasible corrections for variation of path length with glancing angle are those for the case of cylindrical or spherical specimens the crystals used were cut so as to approximate to cylinders or spheres of 0.03 cm. in diameter; a table of corrected F_{obs} values were calculated on this basis. Since these absorption corrections change smoothly with glancing angle (cf. the 'artificial' temperature correction), their application to the Fourier coefficients should not alter the positions of the maxima but should merely change the height and shape of the atom peaks. It is possible, however, that this is strictly true only for an infinite Fourier series, and it was considered worth while, in order to be sure on this point, to compute syntheses both with corrected and uncorrected values of F_{obs} .

(The scattering factor values given in Table 3 were calculated from the uncorrected structure factors in keeping with the usual practice of ignoring crystal absorption. The absorption has an effect in the opposite sense to that of thermal motion; the true f_c and f_s curves will fall off more rapidly with increase of $(\sin \theta)/\lambda$.)

The technique used for the calculations was to locate the maxima in the electron density by the Booth differential method, using as coefficients (i) F_{obs} , (ii) F_{obs} with absorption corrections, (iii) F_{calc} . The differential series were computed at points whose co-ordinates (rounded off to three figures) were taken from the final F_{obs} electron-density maps, i.e. the same co-ordinates as used for obtaining the calculated structure factors. The errors were then calculated by means of the simplified expressions to which the general formulae are reduced by the assumption of spherical symmetry about the peak maxima. These are of the form (Booth, 1948, p. 46)

$$\epsilon_x = -A_h/A_{h^2},$$

$$\text{where } A_h = -\frac{2\pi}{aV} \sum_3 h F_{hkl} \sin 2\pi(hx + ky + lz),$$

$$\text{and } A_{h^2} = -\frac{4\pi^2}{a^2V} \sum_3 h^2 F_{hkl} \cos 2\pi(hx + ky + lz).$$

Detailed study of the differential method may indicate better criteria for examining departures from spherical symmetry, but for the present we believe that it is a useful guide to compare the values of the second differential coefficients A_{h^2} , A_{k^2} and A_{l^2} for each atom. The results in this particular structure are shown in Table 4; the use of the mean in place of the individual values for any atom would in no case change the correction by more than 0.003 Å.

The computation of these differential series was carried out by means of a Hollerith punched-card method, the general features of which are described in a separate paper, except that the data were arranged

rather differently on the cards to meet the requirements of this particular problem, and the disposition is shown in Fig. 1. Since, with the method used, it was not possible to accommodate more than the trigonometric functions relating to the three carbon atoms and the three structure factors on one card the investigation was not extended to the sulphur atom, for which in any case the 'termination of the series' errors are negligible in comparison with those affecting the carbon atoms.

Discussion of the results of the analysis

It might be expected that the uncorrected Fourier and differential syntheses, calculated from exactly the same data, should give precisely the same atomic co-ordinates. Comparison of columns *A* and *B* (Table 1), however, shows that this is not exactly so although the differences are small, the greatest being 0.022 Å. and the mean 0.011 Å. These figures presumably represent the differences between the true positions of the maxima and

$\phi = hx + ky + lz$

Class	h	k	l	ϕ_{C_1}	ϕ_{C_2}	ϕ_{C_3}	$(2\pi\phi_{C_1})$		$(2\pi\phi_{C_2})$		$(2\pi\phi_{C_3})$		+	F	F	F	
							cos	sin	cos	sin	cos	sin					obs.
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
4	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
5	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68
6	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85
7	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102

Fig. 1. Arrangement of data on cards.

The results of these calculations are shown in Table 1, where the various sets of parameters are given in Ångström units for the half of the molecule whose centre of symmetry is at the point $(\frac{1}{2}, \frac{1}{2}, 0)$ of the unit cell.

Table 1. Co-ordinates (in Å.) from $(0, 0, 0)$ for half the molecule at $(\frac{1}{2}, \frac{1}{2}, 0)$

		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
C_1	<i>x</i>	3.263	3.276	3.280	3.271	3.275
	<i>y</i>	4.375	4.362	4.365	4.370	4.373
	<i>z</i>	1.387	1.385	1.378	1.362	1.355
C_2	<i>x</i>	3.920	3.898	3.898	3.884	3.884
	<i>y</i>	3.576	3.585	3.587	3.583	3.585
	<i>z</i>	0.438	0.443	0.443	0.439	0.438
C_3	<i>x</i>	5.127	5.147	5.149	5.116	5.118
	<i>y</i>	5.559	5.552	5.545	5.544	5.537
	<i>z</i>	0.202	0.213	0.211	0.210	0.208
<i>S</i>	<i>x</i>	3.979				
	<i>y</i>	5.931				
	<i>z</i>	1.471				

A refers to co-ordinates from the Fourier syntheses at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ ths; *B*, *C*, *D* and *E* are from the differential syntheses: *B*, uncorrected; *C*, corrected for absorption; *D*, corrected for termination-of-series errors; *E*, corrected for absorption and termination-of-series errors.

Table 2. Bond lengths and distances (in Å.)

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
C_1-C_2	1.404	1.370	1.365	1.359	1.353
C_2-C_3	1.366	1.374	1.374	1.409	1.408
C_3-C_1	1.388	1.387	1.375	1.362	1.349
C_1-S	1.715	1.721	1.717	1.718	1.715
C_3-S	1.751	1.758	1.762	1.741	1.745
p_1	0.011	0.025	0.029	0.002	0.002
p_2	0.057	0.034	0.040	0.011	0.033

p_1 = distance from origin to the plane $C_1C_2C_3$.
 p_2 = distance from S atom to the plane $C_1C_2C_3$.

Table 3. Sulphur and carbon atomic scattering factors

$(\sin \theta)/\lambda$	0.1	0.2	0.3	0.4	0.5	0.6
<i>S</i>	16.0	12.5	8.8	6.0	4.0	2.5
<i>C</i>	6.0	4.5	2.6	1.5	1.0	0.6

Table 4. Curvatures of electron-density peaks

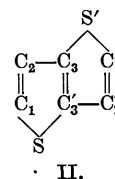
	$-A_{h^2}$	$-A_{k^2}$	$-A_{l^2}$
C_1	31.6	31.2	28.0
C_2	37.4	32.2	30.8
C_3	33.0	34.6	29.4

those obtained by interpolation from electron-density values on a $\frac{1}{120}$ th network. (The three-point parabola method was used for the interpolation (Booth, 1948, p. 62).) Discrepancies of this kind have also been found in other structures and are being investigated in detail.

The changes effected by introducing the absorption corrections are, as anticipated, very small indeed. Comparison of columns *B* and *C*, or *D* and *E*, shows a maximum shift of 0.007 Å. and a mean of only 0.003 Å., although the corrections reduced the actual peak heights by a factor of 0.6.

The bond lengths obtained from these various co-ordinates are given in Table 2, in which the columns *A-E* correspond exactly with those in Table 1. In discussing the accuracy of the bond lengths it is necessary not only to give due weight to the physical considerations which have led to the corrections but also to have regard to the consistency of the molecular structure as a whole in relation to existing theoretical knowledge. Thus each of the columns *A-E* of Table 2 represent in summary form a molecular structure whose validity can be examined from the points of view of (i) diffraction theory, and (ii) chemical plausibility.

The general theory of molecular structure enables us to predict that the thiophthen molecule has a structure intermediate between two extremes; one that corresponds to the formal representation II in which the electrons are completely localized in the double bonds, and the other which corresponds to complete delocalization of the π 'unsaturation' electrons as in the molecule of benzene. In the former the bond lengths would be $C_2-C_3 = 1.54$ Å. and $C_1-C_2 = C_3-C_1 = 1.34$ Å.; if the π electrons were completely delocalized all three



bonds would be equal at some intermediate length. From the chemical properties of thiophthen and the quantum-mechanical calculation on this and related compounds it is certain, however, that the true structure is between these two extremes. For this reason the structures *B* and *C*, in which the C-C bonds are all equal within 0.02 Å., must be regarded as most unlikely. Furthermore, the structure *A*, derived directly from the contour map of the Fourier syntheses, can be entirely rejected, for the electronic arrangement could in no circumstances be such as to make C₂-C₃ shorter than C₁-C₂ and C₃-C₃'.

Diffraction theory indicates the desirability of applying corrections for 'termination of series' errors, and their values in this case (0.01, 0.03 and 0.03 Å. on the three C-C bond lengths) confirm their importance; indeed, it is only when these corrections are applied that the bond lengths fulfil the criteria.

$$1.54 \text{ \AA.} > C_2-C_3 > C_1-C_2 \text{ (or } C_3-C_3') > 1.34 \text{ \AA.}$$

Although fortuitous, it is none the less fortunate that in this first example of a detailed treatment of three-dimensional syntheses the application of the 'series termination' corrections should tip the balance from the chemically unacceptable to the chemically plausible.

As an internal check on the co-ordinates, they were used to calculate the perpendicular distance from the point ($\frac{1}{2}, \frac{1}{2}, 0$), i.e. the centre of symmetry at the midpoint of C₃-C₃', to the plane through C₁C₂C₃. As shown in Table 2, this quantity becomes very small indeed for the co-ordinates *D* and *E*. The sulphur atom would also be expected to lie in this plane; its displacement from it (last row of Table 2) appears to be more than that of the carbon atoms, but since the sulphur atom is farther from the centre of symmetry the comparison is over-emphasized, and this displacement for *D* in fact corresponds to an angle of only $\frac{1}{2}^\circ$ between the C₁SC₃ and C₂C₁C₃' planes.

The final results of the analysis are represented by structures *D* and *E*, both of which contain corrections for 'series termination' errors, *E* also being corrected for absorption errors within the limits described above. The only significant difference between the two results is in the central C₃-C₃' bond. Taking account of the facts that in the computation of the 'series termination' corrections we used the scattering factors shown in Table 3, for which the absorption corrections were omitted, and that the structure *D* deviates less from exact planarity, we are inclined to place more weight on the structure *D*. Accordingly we consider that the data in Table 5 give the most reliable dimensions for the thiophthen molecule.

Table 5. *Dimensions of the thiophthen molecule*

C ₁ -C ₂	1.36 Å.	C ₁ -S-C ₃ '	91.2°
C ₂ -C ₃	1.41 Å.	S-C ₁ -C ₂	116.5°
C ₃ -C ₃ '	1.36 Å.	C ₁ -C ₂ -C ₃	111.7°
C ₁ -S	1.72 Å.	C ₂ -C ₃ -C ₃ '	114.3°
C ₃ -S	1.74 Å.	C ₃ -C ₃ '-S	110.2°
		C ₂ -C ₃ '-S	135.5°

The intermolecular arrangement

The orientation of the molecules in the unit cell is shown in Figs. 2 and 3. The angles between the normal to the plane of the molecule and the principal crystallographic axes are 50° to [100], $71\frac{1}{2}^\circ$ to [010] and $45\frac{1}{2}^\circ$ to [001]. The closest approaches between atoms in adjacent molecules are S...S 4.20, S₂...C 3.86, C...C 3.82 Å. These distances are indicated in Fig. 2 by the broken lines.

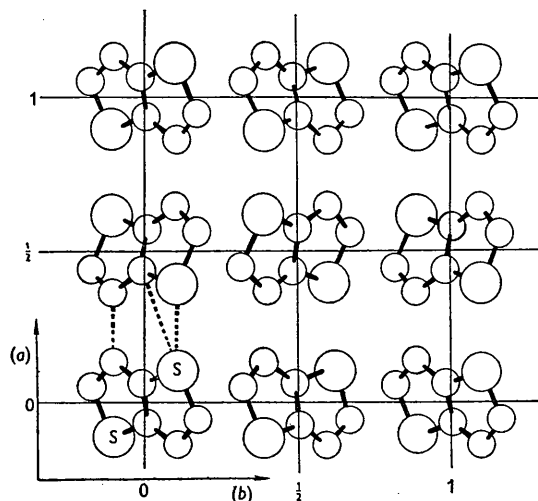


Fig. 2. Thiophthen: projection on (001).

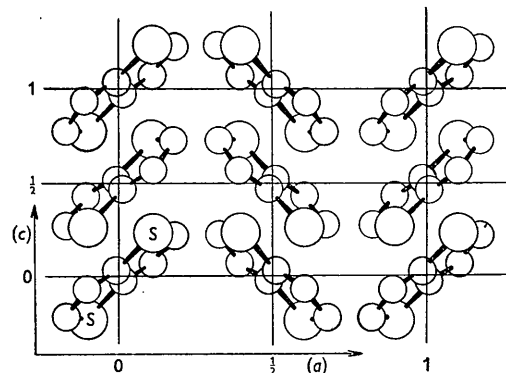


Fig. 3. Thiophthen: projection on (010).

The accuracy of the analysis

In assessing the accuracy of our results we have attempted a more quantitative approach than has been customary in the past. In most structure analyses limits of error (not defined in any recognized statistical sense) have been assigned after inspection of the results, having regard to such factors as their internal consistency, the convergence of the results of successive Fourier syntheses, and, in the case of two-dimensional projections, the degree of resolution of the peaks. In this structure analysis, where attempt has been made to eliminate systematic errors, it is particularly desirable to use a statistical method to obtain a quantitative measure of the effects of random errors, and we have followed a method suggested by Cox & Cruickshank (1948) (for

a detailed treatment see Cruickshank (1949)). In this method the estimate of accuracy is based on two factors, the agreement between observed and calculated intensities and the shape of the Fourier peaks. The standard deviations σ_x , σ_y and σ_z of the peak positions are given by expressions of the type

$$\sigma_x = \sigma(A_x)/A_{h^2},$$

$$\text{where } \sigma(A_x) = \frac{2\pi}{aV} \left[\sum_3 m h^2 \Delta \overline{F^2} \right]^{\frac{1}{2}}.$$

In this expression $\Delta F = |F_{\text{calc.}}| - |F_{\text{obs.}}|$ and m is a multiplicity factor.

With the mean values of the second differentials A_{h^2} , etc. given in Table 4, the standard deviations of the carbon peak positions are

$$\sigma_x = 0.012, \quad \sigma_y = 0.012, \quad \sigma_z = 0.016 \text{ \AA}.$$

Owing to the large amount of data which it was necessary to put on the Hollerith cards, the sulphur atoms were not included in the differential analysis, but an estimate of the curvature of the peak on the Fourier contour map gave a mean standard deviation of about 0.003 \AA., which is negligible compared with that of the carbon atoms.

The standard deviation of the C₁-C₂ and C₂-C₃ bonds is approximately $\frac{1}{3}\sqrt{2(\sigma_x + \sigma_y + \sigma_z)}$, i.e. 0.018 \AA.; for the C₃-C_{3'}, since the two atoms are related by a centre of symmetry, it is simply twice the mean standard deviation of the peak positions, i.e. 0.026 \AA. The standard deviation of the C-S bonds is for all practical purposes that of the carbon atoms, i.e. 0.013 \AA.

The standard deviations can be used to determine the significance of the difference Δ between a bond length and any *standard* bond length, by means of the relation

$$P = \frac{1}{2} - \frac{1}{2} \text{erf}(\Delta/\sigma),$$

where P is the probability that the difference Δ is due to random errors. Values of Δ corresponding to chances 1 in 100 and 1 in 20 are given in Table 6 for the various bonds derived from this analysis. A full statistical analysis for problems of this type has not yet been made, and in consequence we can by no means be certain that Table 6 can be interpreted rigorously; it would be unwise to assert, for example, that in a hundred repetitions of this structure analysis one could expect that on one occasion the measured C₃-C_{3'} bond length would be 1.40 \AA., i.e. 1.36 + 0.04 \AA. Nevertheless, we believe that this analysis of errors is a considerable advance on any type of *ad hoc* assessment.

Table 6. Values of Δ (in \AA.)

	$P = 0.01$	$P = 0.05$
C ₁ -C ₂	0.030	0.021
C ₂ -C ₃	0.043	0.030
C ₃ -C _{3'}	0.021	0.015

Discussion of the molecular structure of thiophthen

The electronic structure of the parent compound, thiophen, has been discussed theoretically by Longuet-Higgins (1949) who used the method of molecular

orbitals. From consideration of the ionization potentials of hydrogen sulphide and ethylene, and of the experimental resonance energy of thiophen, the values of certain parameters appropriate to the structure were estimated. The bond lengths derived by Longuet-Higgins from these results did not agree well with the electron-diffraction data. However, the latter, as mentioned above, are subject to some uncertainty, more particularly in the C-C values. The comparison of theory and experiment is given in Table 7. These theoretical calculations on thiophen have been extended to thiophthen by Evans & de Heer (1949), whose preliminary results serve as the basis for comparison with our experimental results. Before making this comparison we must consider the experimental data relating to C-C and C-S bonds in other molecules, since it is essential to set up a bond-order/bond-length curve before bond lengths can be interpreted in terms of electron distribution. In the case of C-C bonds there is sufficient reliable information upon which to attempt a detailed analysis (e.g. Coulson, 1948), but for C-S bonds, as indeed for any combination of atoms other than carbon, we can at present hope to establish only the broad trend of the order/length relationship.

Table 7. Comparison of theory and experiment for thiophen

	Theoretical order	Theoretical length (Å.)	Experimental length (Å.)
C-S	1.59	1.68	1.74
C ₁ -C ₂	1.73	1.38	(1.35)
C ₂ -C ₃	1.61	1.40	(1.44)

For the C-S single bond, available experimental values are 1.78 ± 0.04 \AA. from the electron diffraction of (CH₃)₂S₂ by Stevenson & Beach (1938); 1.78 ± 0.04 \AA. on (CH₃)₂S₃ by Donohue & Schomaker (1948); 1.79 \AA. from the X-ray study of 2-2' diiododiethyltrisulphide by Dawson & Robertson (1948), this being apparently a preliminary value for which no great reliability was claimed. The same analysis, however, gave a S-S distance of 2.04 \AA. which is more accurate and is in agreement with electron-diffraction values with the exception of that for S₈ where the value obtained was 2.07 \AA. (Lu & Donohue, 1944). A covalent radius of 1.02 \AA. for sulphur gives a C-S single bond length of 1.79 \AA., which we propose to take as the point on the curve for unity bond-order.

There is no recent work giving a direct experimental value for the length of the C-S double bond; in fact, the only measurement reported is 1.64 \AA. from the early X-ray analysis of thiourea by Wyckoff & Corey (1932). Spectroscopic data from related compounds are C-S in CS₂, 1.554 \AA.; C-O in CO₂, 1.163 \AA.; C-O in H₂CO, 1.225 \AA., so that assuming that the electronic structures of CS₂ and CO₂ are analogous, a value of about 1.61 \AA. can be inferred for the C-S double bond in thioformaldehyde. From consideration of the S-O distances in other sulphur compounds, Cox, Jeffrey & Stadler

(1949) deduced a double-bond covalent radius for sulphur of 0.90 Å. and hence a C-S double-bond length of 1.57 Å. It would clearly be of great value to repeat the analysis of thiourea by modern methods. In the absence of more definite information we use 1.60 Å. for the length corresponding to the bond order of 2.0. A third point on the curve is necessary to determine its curvature, but the information is completely lacking. By analogy with other bond-order/length/energy curves (cf. Skinner, 1945), a straight line or a curve slightly convex toward the axes (Fig. 4) may be expected, and we make the simplest assumption of a straight line. We have

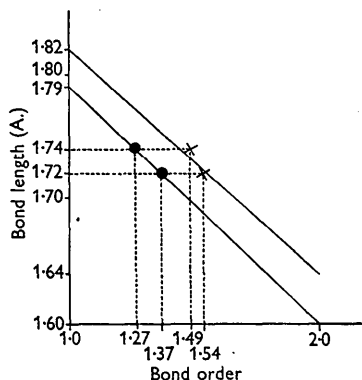


Fig. 4. C-S bond length as a function of bond order.

used the curve thus obtained, together with the usual curve for C-C bonds, to derive 'experimental' bond orders from our measured bond lengths; these are given in Table 8, which also contains the theoretical bond orders of Evans & de Heer, and the bond lengths derived from them by means of the same curves. For the peripheral C-C bonds the agreement is very satisfactory, and the only difference that we must consider for significance is in the central bond of the molecule. As pointed out above, this is subject to a greater experimental error because of the centre of symmetry and may also, for a similar reason, be especially sensitive to the parameters in the theoretical calculations. If we were to take the theoretical value as a standard, we should find by the application of the significance test described above that there is a 1 in 300 chance that the difference of 0.05 Å. could be ascribed to random experimental errors. This suggests strongly that the difference is real and that a reconciliation of the two values is likely to be brought about by a refinement of the theoretical treatment.

Table 8. Bond orders

Bond	Theoretical		Experimental	
	Order	Length (Å.)	Length (Å.)	Order
C ₁ -C ₂	1.76	1.37	1.36	1.85
C ₂ -C ₃	1.56	1.41	1.41	1.58
C ₃ -C _{3'}	1.58	1.41	1.36	1.85
C ₁ -S	1.54	1.69	1.72	1.37
C ₃ -S	1.49	1.70	1.74	1.27

In regard to the C-S bonds, it is noteworthy that there is agreement in that C₁-S should be shorter than C₃-S by an amount of the order of 0.01 Å., and this encourages us to suggest that the observed difference in length of these two bonds is real, although our statistical comparison gives no ground for stating that either can be distinguished from the mean of 1.73 Å. The experimental values are, however, 0.03 and 0.04 Å. longer than the theoretical, and these correspond to *P* values of 0.0006 and less, indicating that the differences are beyond experimental error (cf. the corresponding difference between theory and experiment in thiophen). Some part, if not all, of this discrepancy may well lie in the C-S bond-order/length curve, for which much more experimental information is required. Points corresponding to order/length 1.54/1.72 Å. and 1.49/1.74 Å. could be made to fit on the curve Fig. 4 either (i) by adopting a curve concave to the axes in contradiction to observations from other pairs of atoms, or (ii) by increasing the single and double C-S bond lengths to at least 1.82 and 1.64 Å. respectively. Although on the available evidence we arrived at values 0.03 Å. shorter, a case could be made for accepting the longer bond lengths. The sum of the Pauling (1938) covalent radii gives a single-bond C-S distance of 1.81 Å., and values of 1.80 and 1.84 Å., have been obtained by Toussaint (1945) for some organic sulphur compounds, while the 1.64 Å. is the actual length obtained for the C-S double bond in the early work on thiourea. Since there is this latitude in the choice of proper values for the single and double C-S bonds, the results of the theoretical molecular orbital treatment can for the present therefore be considered to agree satisfactorily with the experimental measurements. The only difference which it is difficult to reconcile is in the central C-C bond of the molecule where the experimental measurements indicate a bond 0.05 Å. shorter than predicted theoretically.

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

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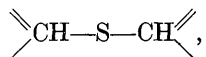
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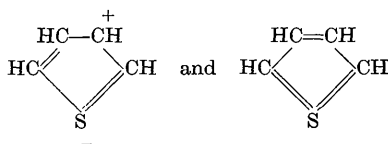
Using a molecular-orbital method, which involves the d orbitals of the sulphur atom, as developed by Longuet-Higgins for thiophen, we have calculated the bond orders in thiophthen and related them to bond lengths. The calculated bond lengths are compared with the observed values reported by Cox, Gillot & 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

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 π 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

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