$$a = 8{,}4 \text{ (Nadelachse)}, \quad b = 12{,}8, \quad c = 15{,}0 \text{ Å}.$$

Bedingungen für mögliche Reflexe:

$(h0l)$ nur mit $l = 2n$, $(hk0)$ nur mit $h+k = 2n$.

Raumgruppe: D_{2h}^{16}–$Pmcn$ oder C_{2v}^{9}–$P2_1cn$.

Beobachtete Dichte: 2,62 g.cm.$^{-3}$.

Berechnete Dichte: 2,53 g.cm.$^{-3}$.

$$Z = 8.$$

Die (hkl) mit $h+k = 2n+1$ sind systematisch schwach im Vergleich zu denen mit $h+k = 2n$. Die Patterson-Projektionen $P(u, v)$, $P(u, w)$, $P(v, w)$ $P_1(v, w)$ bestätigen die Annahme, dass die Ba-Lagen einer C-zentrierten Zelle entsprechen. Aus den Patterson-Projektionen ergeben sich die Koordinaten der Ba-Atome

	Ba$^{\text{I}}$	Ba$^{\text{II}}$
x	1/4	3/4
y	7/60	14/60
z	1/4	1/4

wobei für die Raumgruppe $P2_1cm$ eine x-Koordinate willkürlich gleich 1/4 gesetzt wurde.

Für die weitere Strukturanalyse wurden Intensitäten auf folgende Weise erhalten: zur Vermeidung von Absorptionsfehlern wurden die Kristalle zu Kugeln mit 0,012–0,013 cm. Durchmesser geschliffen und diese durch einen Fettfilm gegen Lufteinwirkung geschützt. Die Strukturanalyse wird fortgesetzt.

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The crystal structure of thianthrene.

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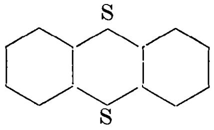
Introduction

A preliminary report on the results of a study of the crystal structure of thianthrene

$C_{12}H_8S_2$,



was published by the present authors (Rowe & Post, 1956). While the final results were being prepared for publication, Lynton & Cox (1956) published the results of an independent structure determination, refined by the method of successive differential syntheses. The refinement described in the present paper was based primarily on the method of least squares. In view of the importance of the structure and the differences in refinement procedures, a description of our work and results and a comparison with those of Lynton & Cox are given here.

Experimental

Needle-like crystals of thianthrene were grown from trichlorethylene solution. The crystals used for X-ray study were cleaved to dimensions of about 0·2 × 0·4 × 0·04 mm. No absorption corrections were considered necessary.

X-ray diffraction data were obtained, using the equi-inclination Weissenberg camera (multiple-film technique with Cu radiation) and the precession camera (with Mo radiation). The unit cell is monoclinic and contains four molecules; the space group is $P2_1/a$ and the dimensions of the unit cell are:

	Present work	Lynton & Cox
a	$14{\cdot}46 \pm 0{\cdot}01_5$ Å	$14{\cdot}48_4 \pm 0{\cdot}002$ Å
b	$6{\cdot}09_5 \pm 0{\cdot}01$	$6{\cdot}147 \pm 0{\cdot}002$
c	$11{\cdot}90 \pm 0{\cdot}02$	$11{\cdot}932 \pm 0{\cdot}002$
β	$110{\cdot}15 \pm 0{\cdot}02°$	$109°\ 51{\cdot}6' \pm 1{\cdot}5'$

The differences, though small, are well beyond the limits of error in both cases. Our results are based on measurements of precession and Weissenberg films, supplemented by careful measurements of powder patterns obtained with a Geiger-counter diffractometer.

A total of approximately 2100 reflections are accessible when Cu radiation is used. Almost 90% of these (i.e. about 1820) are contained within the region of reciprocal space explored during the present investigation; of these, 1384 were sufficiently intense to be measured and used in the structure determination.

Structure determination

Approximate x and z parameters of each of the two sulfur atoms in the asymmetric unit of structure were determined from a Patterson–Harker section at $(U, \frac{1}{2}, W)$. An $(h0l)$ electron-density map was plotted, using the signs of Fourier coefficients computed from these parameters. Extensive use was made of X-RAC for computation of Patterson sections and electron-density projections. After the usual iterative refinement process, the discrepancy factor for this projection was reduced to 18%.

Approximate y parameters of the sulfur atoms were deduced from a series of Patterson sections computed at intervals of $b/8$. These were used to compute signs of Fourier coefficients for an $(hk0)$ electron-density map. Because of overlap in this projection, refinement was not satisfactory and $R(hk0)$ did not drop below 40%, even after a large number of trials.

Use was then made of a least-squares refinement program written for the IBM 704 computer by Dr David Sayre. At this stage of the refinement process, $R(hkl)$ was slightly greater than 40%. In the initial stages of the least-squares refinement process, only 500 reflections, at relatively low Bragg angles, were used. Additional reflections were included in the calculations as the refinement progressed. The refinement of atomic posi-

Table 1. *Coordinates and temperature factors*

Atom	x	y	z	B (Å^2)
S_1	0·2334	0·1321	0·0807	5·302
S_2	0·3498	0·5792	0·0442	4·739
C_1	0·2987	0·3177	0·1780	5·172
C_2	0·3026	0·2580	0·2736	5·587
C_3	0·3574	0·3949	0·3501	6·212
C_4	0·4074	0·5928	0·3335	6·182
C_5	0·3995	0·6506	0·2401	5·281
C_6	0·3480	0·5138	0·1633	4·429
C_7	0·1505	0·3162	0·9874	4·794
C_8	0·0347	0·2627	0·9300	5·517
C_9	0·9712	0·4072	0·8568	5·517
C_{10}	0·0179	0·6012	0·8431	5·831
C_{11}	0·1334	0·6549	0·9000	5·394
C_{12}	0·2005	0·5097	0·9714	4·749

tional coordinates was speeded considerably by interrupting the least-squares machine calculations after a few cycles in order to adjust the coordinates on the basis of a compromise between computed and 'chemically reasonable' values. The entire procedure was repeated three times, by which time $R(hkl)$ had dropped from the initial 40% to 18% for all 1384 observed reflections.

An effort was then made to improve these results by weighting the observations in accordance with the procedure recommended by Abrahams (1955). In addition, reflections too weak to be measured (other than absences due to space-group extinctions) were assigned intensity values equal to one-half the minimum observed value in the region of reciprocal space in which they were found.

The atomic coordinates and the isotropic temperature factors of the atoms finally obtained from the least-squares refinement process, after inclusion of the weighting terms and the corrections mentioned above, are listed in Table 1. Intramolecular distances and angles are shown in Table 2. The corresponding values reported by Lynton & Cox are listed in the last column. The average lengths of chemically-equivalent bonds and their mean standard deviations are given in Table 3. The application of the criteria described by Cruickshank (1949) indicated that in no instance is there any statistical significance in the deviation of an individual bond length from the mean length of the appropriate set of chemically-equivalent bonds. The value of $R(hkl)$ for all 1820 reflections used in the final least-squares calculation is 18·2%; $R(h0l)$ = 11%; $R(hk0)$ = 14·5%; $R(0kl)$ = 12%. For the 1100 reflections used in their determination, Lynton & Cox reported R = 12%; our value for these 1100 reflections is 15%. In assessing the relative merits of the two determinations, it must be borne in mind that the least-squares refinement process which we used minimizes $R' = \Sigma w(F_o-F_c)^2$ and not $R = \Sigma||F_c|-|F_o|| \div \Sigma|F_c|$.

The structure consists of puckered and interleaved layers of thianthrene molecules. These layers are approximately parallel to the $(21\bar{2})$ planes. The atoms of each molecule lie in two planes which intersect in the S–S axis to form a dihedral angle of 128·1°. A value of 140° had been reported earlier on the basis of dipole-moment measurements (Wood & Crackston, 1941). The maximum distances of individual atoms from the two planes are 0·039 and 0·024 Å respectively.

The orientation of the molecule is in good agreement with that deduced by Wood & Crackston (1941) from optical and magnetic data. The long direction of the molecule is close to the [101] direction, which is also close to the direction of the largest index of refraction. No unusual types of intermolecular contacts are present

Table 2. *Intramolecular distances and angles*

	Present work		
	Length (Å)	Standard deviation (Å)	Lynton & Cox Length (Å)
S_1–S_2	3·183	0·004	—
S_1–C_1	1·766	0·011	1·744
S_1–C_7	1·773	0·010	1·756
S_2–C_6	1·774	0·009	1·755
S_2–C_{12}	1·778	0·010	1·778
C_1–C_2	1·414	0·015	1·386
C_2–C_3	1·361	0·017	1·391
C_3–C_4	1·402	0·017	1·394
C_4–C_5	1·368	0·016	1·375
C_5–C_6	1·357	0·015	1·399
C_6–C_1	1·381	0·015	1·427
C_7–C_8	1·383	0·015	1·425
C_8–C_9	1·386	0·016	1·380
C_9–C_{10}	1·351	0·016	1·369
C_{10}–C_{11}	1·378	0·016	1·419
C_{11}–C_{12}	1·387	0·015	1·360
C_{12}–C_7	1·376	0·015	1·407

	Present work	Lynton & Cox
Valence angle at S_1	100° 18′; σ = 29′	100° 10′
Valence angle at S_2	100° 24′; σ = 26′	100° 10′
Average valence angle	100° 21′; σ = 19′	100° 10′; σ=30′
Dihedral angle	128° 8′	128°

Table 3. *Average values of chemically-equivalent bond lengths*

	Present work		
	Length (Å)	Average standard deviation (Å)	Lynton & Cox Length (Å)
S_1–C_1	$1{\cdot}773^{+0{\cdot}005}_{-0{\cdot}007}$	0·005	$1{\cdot}759^{+0{\cdot}019}_{-0{\cdot}015}$
C_1–C_6	1·379±0·002	0·011	1·417±0·010
C_3–C_4	1·376±0·025	0·012	1·382±0·012
C_1–C_2	1·385±0·028	0·007	1·393±0·033
C_2–C_3	1·374±0·012	0·008	$1{\cdot}391^{+0{\cdot}028}_{\pm0{\cdot}016}$
All C–C	$1{\cdot}379^{+0{\cdot}035}_{-0{\cdot}028}$	0·005	1·394±0·034

Table 4. *Comparison of results*

	Present work	Lynton & Cox
Maximum distance of any atom from molecular plane	0·0394 Å	0·0438 Å
B, sulfur (average)	5·2 Å^2	3·5 Å^2
B, carbon (average)	5·73	3·73
Closest intermolecular approach		
C–C	3·61 Å	3·47 Å
C–S	3·83	3·92
S–S	3·77	3·78
Distance between intermolecular planes	3·77 Å	3·78 Å

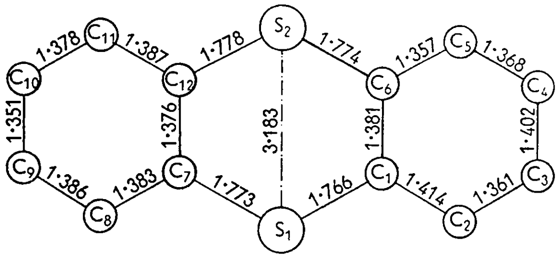


Fig. 1. Thianthrene bond lengths in Ångström units.

in the crystal. The closest approach between molecules occurs between two carbon atoms separated by 3·61 Å. The shortest distance between sulfur atoms in adjacent molecules is 3·77 Å; the shortest intermolecular S–C contact is 3·83 Å.

A comparison of additional results obtained in this work with those of Lynton & Cox is given in Table 4. In general the results of the two determinations agree very well; the most significant difference between the two concerns the C–C bond length. Lynton & Cox report apparently significant variations among C–C bonds. No significant variations among these bonds are indicated by our results. Pending further work, this aspect of the molecular structure of thianthrene must be considered unresolved. A schematic diagram of thianthrene, giving bond lengths determined in this investigation, is shown in Fig. 1.

The authors wish to thank Prof. Ray Pepinsky for the use of his X-RAC calculator. They acknowledge with thanks the help of Dr David Sayre in providing the least-squares refinement program and for illuminating discussions of the computing problem. Thanks also go to the International Business Machines Corporation for a grant, which provided for the use of their Type 704 computer, and to Dr A. Tulinsky, who helped with some of the calculations.

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Scale-factor adjustment for optimum comparison of observed and calculated structure factors.*

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In most of the structures reported to date, the observed structure factors have been scaled to the calculated ones by using the ratio of the sums as a scaling factor. This procedure is justified only if the differences between the observed and calculated structure factors are random over a large body of data. With the accuracy and sensitivity of modern techniques for collecting data, and assuming a 'correct' structure has been proposed, this is usually the case. Thus a more accurate method for deriving the scale factor, as is proposed here, will be of little general value. Nevertheless, if a structure is based on only a few reflections and the discrepancies are large, it is quite possible to give a marked improvement in the reported accuracy of a structure determination by adjusting this scale factor. The derived atomic coordinates are unaffected by this adjustment; but absolute electron-density measurements could be improved.

The optimum scale factor can be directly derived by including the scale factor as a variable in the expression for the residual being used as a measure of the structure determination accuracy, and setting the partial derivative of the residual with respect to the scale factor equal to zero.

In the following examples we shall define x as the scale factor, k the index (hkl), F_k cal. and F_k obs. given calculated and observed structure factors, and R the residual. In the case of the general least-squares approach (Hughes, 1941; Booth, 1947), where

$$R_1 = \sum_k W_k(|F_k \text{ cal.}| - |xF_k \text{ obs.}|)^2$$

the scale factor for minimum R becomes

$$x_m = \frac{\sum_k W_k|F_k \text{ obs.}||F_k \text{ cal.}|}{\sum_k W_k|F_k \text{ obs.}|^2}\,.$$

In the case of the least-squares method used by Shoemaker *et al.* (1950), where

$$R_2 = \sum_k W_k^{\frac{1}{2}}(|F_k \text{ cal.}|^2 - |xF_k \text{ obs.}|^2)^2\,,$$

the scale factor for minimum R_2 becomes

$$x_m = \left[\frac{\sum_k W_k^{\frac{1}{2}}|F_k \text{ cal.}|^2|F_k \text{ obs.}|^2}{\sum_k W_k^{\frac{1}{2}}|F_k \text{ obs.}|^4}\right]^{\frac{1}{2}}\,.$$

In the case of the iterative Fourier technique, where the residual usually employed is the 'reliability index', which for the moment may be defined as

$$R_3 = \frac{\sum_k \big||F_k \text{ cal.}| - |xF_k \text{ obs.}|\big|}{\sum |F_k \text{ cal.}|}\,,$$

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