954. *The Crystal and Molecular Structure of Thianthren.*

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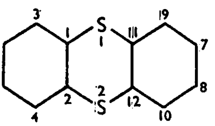
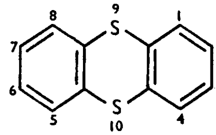
A detailed *X*-ray structure analysis of thianthren, $C_{12}H_8S_2$, has been made. The molecule is folded on the S–S line, so that the two benzene rings lie in two planes at an angle of 128°. The sulphur valency angle is 100° and the C–S bond length is $1{\cdot}76 \pm 0{\cdot}01_5$ Å.

THIANTHREN (diphenylene disulphide), $C_{12}H_8S_2$ (I), has long been considered (although on circumstantial rather than direct evidence) to be an example of a folded molecule in which the folding enables the central sulphur atoms to retain their " natural " valency angles even though they form part of a ring system. The folded configuration was first suggested by Bergmann and Tschudnowsky [1] to account for the dipole moment of thianthren (about 1½ D). Attempts to substantiate this suggestion by the methods of classical stereochemistry (for a summary see Turner and Harris [2]) were not successful, but this was attributed to the flexibility of the molecule permitting the folding to be reversed easily. *X*-Ray measurements on crystalline thianthren were first made by Prasad, Shanker, and Peermohamed [3] and by Cox; [4] Wood and Crackston [5] showed that the *X*-ray intensities and optical properties were consistent with a structure built up of layers of non-planar molecules, and they estimated the angle of fold to be about 140°.



Numbering used in this paper.

(I)



Chemical numbering.

The present work was undertaken to obtain accurate values of the sulphur valency angle and the C–S bond length; the latter is of interest since, as Sutton [6] has pointed out, the sulphur atoms could use $d\pi$ as well as $p\pi$ orbitals and conjugation could therefore occur even though the molecule is not flat.

EXPERIMENTAL

Suitable crystals were grown by evaporation from acetone solution in the form of radiating clusters of prisms, elongated along the *b*-axis and exhibiting the forms $\{001\}$, $\{\bar{1}01\}$, $\{\bar{2}01\}$, $\{011\}$, $\{021\}$, $\{110\}$, and $\{\bar{1}11\}$.

The unit-cell dimensions, measured from Straumanis photographs, are $a = 14{\cdot}484 \pm 0{\cdot}002$, $b = 6{\cdot}147 \pm 0{\cdot}002$, $c = 11{\cdot}932 \pm 0{\cdot}002$ Å, and $\beta = 109° 51{\cdot}6' \pm 1{\cdot}5'$. These results, which agree with those of Wood and Crackston, are also in accord, when suitably transformed, with the axial ratios given by Friedel and Crafts.[7] It should be noted that in Friedel and Crafts's description of the crystals, as transcribed by Groth,[8] two planes are wrongly indexed as (101) and (111); on Groth's orientation and axial ratios they should be (201) and (221) respectively.

The density determined by flotation is 1·44 g. cm.$^{-3}$ (calc. 1·44, by assuming four molecules in the unit cell). The systematic absences of ($h0l$) reflections for h odd and ($0k0$) for k odd indicate unambiguously that the space group is $P2_1/a - C_{2h}^5$.

An optical examination in sodium light gave the following values for the principal refractive indices and the optic axial angle, in good agreement with those of Wood and Crackston : [5] $\alpha = 1{\cdot}65$, $\beta = 1{\cdot}76$ (parallel to [*b*]), $\gamma = 1{\cdot}95$ (inclined at 69° to [*c*] in the obtuse angle β), and $2V = 82°$.

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[1] Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 457.

[2] Turner and Harris, " Organic Chemistry," Longmans, Green and Co., London, 1952, pp. 783—784.

[3] Prasad, Shanker, and Peermohamed, *J. Indian Chem. Soc.*, 1937, **14**, 177.

[4] Cox, *Ann. Reports*, 1937, **34**, 189.

[5] Wood and Crackston, *Phil. Mag.*, 1941, **31**, 62.

[6] Sutton, in " Determination of Organic Structures by Physical Methods," ed. Braude and Nachod, Academic Press, Inc., New York, 1955, p. 402.

[7] Friedel and Crafts, *Ann. Chim. Phys.*, 1888, **14**, 438.

[8] Groth, " Chemische Krystallographie," 1919, Vol. V, p. 34.

X-Ray intensity measurements were made with Cu-$K\alpha$ radiation on multiple-film Weissenberg photographs about the three principal axes. The crystals employed were approximately square sections about 0·25 mm. across cut from larger crystals, and no correction for absorption effects was made (μ = 43 cm.$^{-1}$). 1100 independent reflections were observed and their relative intensities were estimated visually by comparison with a standard chart.

STRUCTURE DETERMINATION

The $h0l$ and $hk0$ intensities were put on the absolute scale by Wilson's method.[9] A Patterson $h0l$ synthesis gave the x and y co-ordinates of the two sulphur atoms, which were then used to determine the phases of a number of terms for the first Fourier synthesis. The resultant electron-density map satisfactorily indicated the positions of the two benzene nuclei and the projection was refined by computing three further Fourier syntheses and one difference synthesis; the R factor (agreement index) was then 0·18.

The y co-ordinates of the sulphur atoms were found from the $hk0$ Patterson projection. After five successive Fourier syntheses and one difference synthesis the R factor was 0·23. In the calculation for these $h0l$ and $hk0$ syntheses Hartree scattering factors multiplied by temperature factors with B = 3·8 Å^2 and 2·5 Å^2 respectively were used. The atomic co-ordinates derived from the two-dimensional analysis are given in Table 1.

TABLE 1. *Atomic co-ordinates from the two-dimensional analysis.*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S_1	0·421	0·134	0·267	C_4	0·601	0·647	0·364	C_9	0·225	0·280	0·195
S_2	0·457	0·570	0·150	C_5	0·654	0·357	0·542	C_{10}	0·256	0·683	0·100
C_1	0·513	0·322	0·340	C_6	0·660	0·547	0·488	C_{11}	0·325	0·336	0·200
C_2	0·524	0·508	0·292	C_7	0·148	0·433	0·143	C_{12}	0·344	0·526	0·152
C_3	0·568	0·270	0·466	C_8	0·163	0·625	0·093				

A set of hkl structure factors, with a mean temperature factor of B = 3·5 Å^2 was calculated on the University of Manchester's electronic digital computer and used to place the observed structure amplitudes on the absolute scale.[10] Differential syntheses for both observed and calculated structure factors were then computed at the atomic peak positions so as to obtain new co-ordinates corrected for termination-of-series errors. This was repeated four times, the individual scale and temperature factors found to give most satisfactory agreement in the final stage being those listed in Table 2. The significance of the scale factors introduced here may be understood from the following considerations. Ideally the two peaks, representing a particular atom in the "observed" and "calculated" electron-density syntheses respectively, should have the same heights and the same curvatures. Perfect agreement cannot be attained with the assumptions of spherically symmetrical atoms and isotropic thermal motion, but the "calculated" synthesis can be brought into approximate agreement with the "observed" by introducing two parameters for each atom, (i) a temperature factor and (ii) a scale factor. This scale factor must not be confused with the scale factor used to put the observed structure amplitudes on the absolute scale (although the two are interrelated if the absolute scaling has been brought about by making $\Sigma F_{\text{obs.}} = \Sigma F_{\text{calc.}}$); it represents a deviation from the assumption that the structure factor for zero scattering angle is equal to the atomic number, *i.e.*, it represents a loss or gain of electrons by the atom in question according as it is less or greater than unity. With the assumptions mentioned above it is doubtful if the individual scale factors have much physical significance but they can be subjected to the collective test that over a whole molecule the net loss and gain of electrons should be zero; in the present case, with the factors of Table 2 there is a net gain of about 0·4 *e*, *i.e.*, less than ½%, which is within the experimental error.

TABLE 2. *Individual scale and temperature factors used in final differential synthesis.*

Atom	S_1, S_2	C_1, C_2, C_{11}, C_{12}	C_3, C_4, C_9, C_{10}	C_5, C_6, C_7, C_8
Scale factor	1·05	0·94	1·02	0·99
Temperature factor (B)	3·5	3·2	3·8	4·2

If the four groups of atoms in Table 2 are put in ascending order of their temperature factors they are also in ascending order of their distances from the centre of gravity of the molecule. This effect is normally interpreted (cf., *e.g.*, acridine [11]) as evidence of rigid-body oscillation

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[9] Wilson, *Nature*, 1942, **150**, 152.

[10] Wheatley, *Acta Cryst.*, 1954, **7**, 68.

[11] Phillips, *ibid.*, 1956, **9**, 237.

(libration) of the molecule, and can be partly so interpreted in this case. In addition, however, it can readily be shown that a "flapping" motion of the molecule about the S–S "hinge" would produce rather similar effects and the overall thermal motion is presumably a combination of the two (together with translational motions) although in what proportions the present work is not sufficiently detailed to decide.

TABLE 3.

(Densities in e.Å^{-3} and curvatures in e.Å^{-5}.)

Atom	ρ_o	ρ_c	ρ_o/ρ_c	Curv$_o$	Curv$_c$	$\frac{\text{Curv}_o}{\text{Curv}_c}$
S_1	25·6	26·9	0·967	214·8	229·6	0·955
S_2	26·3	26·8		225·3	231·4	
C_1	6·6	6·4	1·047	56·2	56·5	1·013
C_2	7·1	6·7		65·0	62·1	
C_{11}	6·9	6·7		60·5	61·4	
C_{12}	7·7	7·2		65·1	63·6	

Atom	ρ_o	ρ_c	ρ_o/ρ_c	Curv$_o$	Curv$_c$	$\frac{\text{Curv}_o}{\text{Curv}_c}$
C_3	6·3	6·4	0·963	52·4	54·8	0·946
C_4	7·1	7·4		61·4	65·3	
C_9	6·0	6·4		50·3	54·4	
C_{10}	7·2	7·3		57·6	59·9	
C_5	6·2	6·4	0·966	54·0	57·1	0·944
C_6	6·2	6·4		51·3	53·2	
C_7	6·0	6·3		43·3	47·3	
C_8	6·3	6·5		49·0	51·5	

TABLE 4. *Final atomic co-ordinates.*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S_1	0·4196	0·1330	0·2665	C_4	0·6011	0·6562	0·3662	C_9	0·2271	0·2601	0·1977
S_2	0·4553	0·5779	0·1504	C_5	0·6431	0·4092	0·5316	C_{10}	0·2591	0·6516	0·1018
C_1	0·5122	0·3159	0·3509	C_6	0·6581	0·5995	0·4808	C_{11}	0·3225	0·3155	0·2044
C_2	0·5257	0·5124	0·2981	C_7	0·1503	0·3976	0·1420	C_{12}	0·3382	0·5138	0·1513
C_3	0·5696	0·2627	0·4638	C_8	0·1638	0·5959	0·0931				

TABLE 5.

Molecular dimensions.

Bond	Length (Å)		Bond	Length (Å)	
S_1–C_1	1·778	1·759	C_3–C_5	1·419	1·391
S_1–C_{11}	1·755		C_4–C_6	1·380	
S_2–C_2	1·756		C_7–C_9	1·375	
S_2–C_{12}	1·744		C_8–C_{10}	1·391	
C_1–C_3	1·360	1·393	C_1–C_2	1·407	1·417
C_2–C_4	1·425		C_{11}–C_{12}	1·427	
C_9–C_{11}	1·399		C_5–C_6	1·369	1·382
C_{10}–C_{12}	1·386		C_7–C_8	1·394	

Angle.

C_1–S_1–C_{11}	100° 10′	C_2–S_2–C_{12}	100° 10′

The last set of structure factors gave an R factor of 0·12 for all observed planes. The final peak electron densities and mean peak curvatures are given in Table 3, and the final atomic co-ordinates and molecular dimensions in Tables 4 and 5. The complete list of observed and calculated structure factors is given in Table 8.

TABLE 6. *Perpendicular distances of atoms from the best planes through the molecule.*

Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
S_1	+0·0008	S_1	+0·0105	C_3	−0·0145	C_9	−0·0043
S_2	−0·0165	S_2	+0·0383	C_4	+0·0078	C_{10}	−0·0435
C_1	+0·0104	C_7	+0·0409	C_5	+0·0034	C_{11}	−0·0438
C_2	+0·0188	C_8	+0·0192	C_6	−0·0101	C_{12}	−0·0172

TABLE 7. *Mean bond lengths of chemically equivalent bonds.*

Bond type	S_1–C_1	C_1–C_3	C_3–C_5	C_1–C_2	C_5–C_6	all C–C
Mean bond length (Å)	$1{\cdot}75_9$	$1{\cdot}39_3$	$1{\cdot}39_1$	$1{\cdot}41_7$	$1{\cdot}38_2$	$1{\cdot}39_4$

TABLE 8. *Observed and calculated structure factors for thianthren.*

hkl	$F_{obs.}$	$F_{calc.}$
0.0.2	53·5	−70·1
3	73·6	−101·3
4	25·6	−20·7
5	46·4	−44·3
6	31·9	+24·9
7	22·5	+26·9
8	20·3	+23·9
9	21·5	−21·2
10	19·7	−20·9
11	11·6	+13·5
14	7·3	+6·5
2.0.0	33·8	+47·5
1	5·2	+6·4
2	13·8	−8·6
3	20·6	−21·1
4	23·3	−16·3
5	6·8	−2·8
6	5·3	−2·7
7	27·8	+25·3
8	38·0	+41·2
9	8·5	−7·9
10	28·0	−28·9
11	11·5	−10·2
4.0.0	20·6	−20·2
1	64·1	+77·6
2	27·9	+29·4
3	10·7	−8·7
4	20·5	−21·6
5	9·6	+5·0
6	15·3	−12·8
7	20·1	−15·5
8	13·0	+17·1
9	19·7	+19·1
11	14·2	−15·8
6.0.1	26·0	+29·3
2	52·9	+65·8
4	31·5	−32·6
5	19·5	−22·6
6	18·9	+15·9
7	15·2	−15·1
9	14·0	+18·3
11	11·7	−17·3
8.0.0	25·9	−27·1
1	10·3	−11·0
2	32·4	+36·7
3	31·0	+34·4
4	37·4	−42·6
5	22·1	−24·4
6	12·6	+10·4
9	10·4	+11·3
10.0.0	28·0	−30·1
1	40·3	−45·1
3	53·7	+64·1
6	14·8	−15·0
8	8·4	−7·3
12.0.0	17·9	+17·3
1	12·8	−15·1
14.0.1	14·2	−13·4
16.0.0	10·5	−9·4
1.1.0	59·8	+68·4
1	20·0	+19·5
2	77·9	+79·5
3	9·0	+2·6
1.1.4	58·3	−56·5
5	24·4	−21·7
6	35·6	+35·7
7	14·9	+13·6
11	12·3	−12·1
13	9·3	+10·7
3.1.0	19·6	+20·9
1	23·7	+17·9
2	16·0	+12·0
3	39·0	+36·4
4	59·0	−61·9
5	38·4	−40·0
7	29·3	+33·0
11	8·6	−7·9
12	9·4	−10·2
5.1.0	41·0	+38·1
1	18·2	−13·4
2	14·9	−10·5
3	15·5	+14·9
5	25·4	−31·4
7	16·9	+18·1
7.1.0	20·0	+19·1
1	5·8	+5·9
2	21·6	+18·4
3	13·8	+14·3
4	10·8	+11·2
5	22·2	−24·7
6	6·8	−11·2
8	12·2	+14·1
9.1.0	13·8	−13·6
1	18·3	+18·8
2	16·4	+15·8
3	21·3	+22·6
6	21·1	−22·8
7	11·7	−13·3
11.1.0	22·2	−23·7
1	12·7	−11·3
5	13·9	+15·0
13.1.0	15·7	−16·9
1	15·2	−15·2
2	13·4	+16·7
15.1.0	10·1	−9·9
1	10·0	−13·3
0.2.1	26·8	+27·1
3	19·9	−14·5
4	22·4	−21·3
5	22·7	−21·6
6	15·9	+14·7
7	33·0	+32·2
8	10·3	+4·7
9	15·1	−13·3
10	10·0	−8·5
11	13·2	−11·5
13	10·5	+10·1
2.2.0	22·7	+22·1
1	39·1	+39·7
2	24·1	−25·5
4	21·7	−22·0
5	9·2	−7·2
7	18·5	+17·7
9	8·9	+6·5
11	9·8	−7·8
2.2.12	7·3	−5·9
4.2.0	12·0	−11·0
1	5·4	+5·2
3	30·4	+26·2
4	7·6	−8·9
5	8·2	−10·1
7	12·6	+12·5
6.2.0	35·2	+29·9
1	9·5	+8·5
2	22·6	+21·1
3	8·4	−5·7
4	14·3	−11·4
5	19·8	−19·6
7	9·7	+9·3
8.2.0	7·7	−4·9
1	12·7	−10·0
2	16·4	+14·6
3	6·0	+8·0
4	6·9	+9·5
5	9·4	−10·9
6	8·3	−9·5
9	11·6	+8·8
10.2.0	22·6	−19·1
2	8·6	+9·1
8	13·6	−4·6
12.2.0	10·2	−10·2
14.2.0	7·3	−6·2
16.2.0	6·2	−5·7
1.3.0	21·4	+18·5
1	22·4	+19·9
2	44·2	−45·5
3	12·4	−11·4
4	25·6	+22·2
5	17·7	−16·4
6	19·1	−18·3
7	22·1	+23·2
8	16·2	+14·4
3.3.0	5·9	+4·4
1	30·4	+30·7
2	7·9	−7·8
3	10·1	−7·7
4	20·6	+20·1
5	8·5	+8·0
6	11·9	−9·2
7	15·0	−13·8
5.3.0	17·1	−14·0
1	6·9	+7·6
2	10·5	+9·9
3	16·7	−13·4
4	16·3	−15·6
5	11·0	+10·6
6	12·0	+10·8
7.3.0	13·8	−12·1
1	4·6	−2·7
2	24·2	+24·5
3	5·0	+4·9
4	15·1	−16·9
9.3.0	12·4	−11·5
1	15·2	−18·3
9.3.5	5·0	−6·3
11.3.5	9·9	−11·6
13.3.0	6·2	+6·8
0.4.0	36·9	−39·0
2	14·8	+11·7
4	6·5	−2·9
5	15·9	+16·9
6	14·9	+13·4
7	8·3	−7·8
8	17·9	−19·5
9	9·6	+8·5
10	8·3	+8·0
11	8·2	−7·1
2.4.0	13·6	−10·3
1	26·0	−22·9
2	28·1	+29·9
3	27·7	+26·2
4	8·2	−4·7
5	29·1	−30·1
6	7·9	+9·1
8	9·8	−11·0
9	7·1	+4·7
10	11·8	+13·0
4.4.0	20·5	+20·0
1	41·4	−40·0
2	15·4	−16·8
3	16·3	+13·3
4	12·2	+10·2
5	12·0	−11·3
6	14·5	+17·1
8	10·5	−10·2
9	10·9	−12·7
6.4.0	20·4	+14·3
1	13·5	−14·3
2	25·8	−32·1
3	10·9	+12·9
4	9·6	+8·5
8.4.0	10·8	+7·7
1	17·2	+16·1
5	7·5	+7·1
10.4.1	7·6	+7·0
5	5·3	+6·0
12.4.0	8·1	−8·3
1.5.0	11·0	+7·3
2	12·8	−14·7
3	8·0	+6·6
4	7·9	+6·0
3.5.0	8·5	−8·5
1	24·6	−26·6
3	5·7	+4·6
4	19·6	+22·9
5	8·6	+7·2
5.5.1	8·3	−7·1
5	12·7	+12·8
7.5.4	12·0	−16·8
5	6·8	+7·5
9.5.1	16·6	−17·2

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$
11.5.0	13·4	+14·1
13.5.0	7·2	+8·0
0.6.2	12·1	−9·5
3	19·2	+22·4
6	5·7	−8·8
2.6.1	7·0	−7·5
3	11·2	+10·6
4	8·2	+8·0
4.6.1	15·3	−14·7
4	5·8	+7·5
5	5·8	+6·1
6.6.1	7·1	−6·7
2	9·7	−11·8
5	10·0	+13·5
10.6.0	10·8	+11·5
1.7.0	13·4	−12·3
1	8·3	−8·0
2	11·1	+6·7
3	10·5	+10·9
3.7.0	6·6	−6·5
1	17·0	−19·1
3	7·7	+8·2
5.7.0	6·5	+6·3
1	8·9	−9·7
2	7·8	−9·4
7.7.0	6·3	+7·5
$\bar{2}$.0.1	70·4	−91·3
2	58·1	−81·8
3	82·2	+110·7
4	23·3	+17·4
5	31·9	−31·4
6	39·5	+37·5
7	44·7	+46·5
8	21·6	−19·9
9	32·1	−35·6
10	22·7	−22·7
11	9·6	+14·1
13	6·2	+4·8
14	6·7	+10·8
$\bar{4}$.0.1	13·2	−15·2
2	67·7	−90·2
3	40·7	+40·5
4	30·9	−36·7
5	14·5	+13·7
6	38·0	+44·7
7	22·5	+23·0
8	49·0	−56·2
9	8·9	−10·8
10	15·1	+18·5
11	14·1	+11·8
14	13·8	+6·7
$\bar{6}$.0.1	27·7	−21·7
2	23·3	−18·1
3	48·4	−44·2
4	15·6	−16·9
5	44·3	+43·3
6	46·2	+48·0
8	39·7	−41·6
$\bar{6}$.0.9	12·7	−6·6
12	10·3	+13·1
13	10·4	+13·1
15	8·1	−11·1
$\bar{8}$.0.1	8·5	−5·4
2	4·2	−2·0
3	13·7	+4·5
4	39·6	+34·3
5	36·5	+21·7
6	20·6	−18·1
7	45·0	−54·2
8	13·0	−9·8
9	5·9	+10·4
10	11·1	+6·3
11	9·2	+4·3
12	11·2	+12·1
14	7·2	−10·6
15	8·5	−5·1
$\overline{10}$.0.1	12·8	+10·6
2	27·5	−25·2
3	13·5	+8·8
4	28·1	+32·3
5	20·5	+24·4
6	13·3	−14·1
7	28·8	−31·6
8	11·5	+13·5
10	7·9	+1·7
11	12·3	+10·9
13	18·0	−21·6
14	8·0	−11·7
$\overline{12}$.0.2	16·0	−18·0
3	13·5	+14·0
4	33·4	+36·1
5	18·2	−20·5
6	24·9	−30·5
7	18·8	−15·4
8	13·1	+15·6
9	11·7	+8·0
11	10·0	+12·0
13	9·7	−14·3
$\overline{14}$.0.1	4·9	−6·7
2	8·6	+5·9
3	12·4	+16·4
4	14·8	+13·9
5	21·4	−24·6
6	10·4	−7·5
7	8·4	+12·2
$\overline{16}$.0.2	11·6	+15·4
3	10·9	+13·9
5	12·3	−17·1
6	9·5	−6·2
9	8·7	+8·6
10	7·4	+10·5
$\overline{18}$.0.4	6·6	−13·9
$\bar{1}$.1.1	42·8	−42·8
2	65·2	−65·2
3	77·3	−80·5
4	19·2	−19·7
5	34·6	+30·5
6	60·0	+61·2
7	7·1	+4·2
9	8·4	−3·3
10	13·9	−15·1
11	10·4	−9·6
$\bar{1}$.1.13	11·9	+13·9
$\bar{3}$.1.1	63·6	+69·9
2	70·9	−77·9
3	17·4	−19·5
5	26·5	+28·3
6	5·5	+5·5
8	12·6	−7·3
9	11·5	−9·1
10	14·5	−15·8
12	16·6	+19·3
13	7·1	+6·4
$\bar{5}$.1.1	24·1	+21·7
2	52·9	−57·5
3	21·0	−19·0
4	37·9	+38·6
5	13·2	+14·0
6	5·9	−8·6
7	14·3	+10·9
9	18·4	−18·0
10	10·3	−10·7
11	7·5	+8·8
12	9·3	+11·3
$\bar{7}$.1.1	58·2	−62·0
2	43·5	−48·5
4	61·7	+63·0
5	17·7	+15·1
8	20·8	−17·3
9	28·7	−27·9
11	22·8	+25·5
12	7·3	+5·1
$\bar{9}$.1.1	29·1	−32·6
2	19·4	−17·7
3	29·8	+30·5
4	17·7	+13·4
6	11·4	−5·2
7	11·8	−5·4
8	14·7	−15·5
9	10·7	−10·6
10	21·4	+20·7
11	20·9	+21·4
13	10·4	−10·3
$\overline{11}$.1.2	15·0	+16·6
3	24·9	+28·4
6	9·1	−3·1
7	19·1	−17·1
8	8·4	−10·8
9	8·4	+6·7
10	15·0	+15·7
13	9·6	−7·4
$\overline{13}$.1.2	12·7	+12·6
4	7·8	+2·6
6	8·4	−5·1
7	13·7	−12·5
9	17·5	+18·9
$\overline{15}$.1.1	9·8	+11·1
2	7·6	+9·0
6	7·7	−12·7
7	9·8	−9·6
9	11·4	+11·2
$\overline{17}$.1.1	11·3	+13·1
$\bar{2}$.2.1	20·2	+18·3
2	35·6	−38·1
$\bar{2}$.2.3	37·1	−36·7
4	18·4	+16·9
5	22·4	+20·6
6	15·7	+14·7
8	15·5	−11·9
9	20·3	−17·7
10	10·8	+9·8
$\bar{4}$.2.1	16·2	−13·4
2	19·6	−17·4
3	9·0	−6·7
4	24·6	+21·1
7	10·6	+6·7
8	4·9	+4·8
9	16·2	−16·8
$\bar{6}$.2.1	12·3	−14·7
2	16·6	−26·4
3	29·1	−25·4
4	26·2	+22·9
6	5·4	+3·4
7	5·9	+1·6
8	6·4	−2·5
9	17·7	−13·6
11	10·1	+10·3
$\bar{8}$.2.1	14·3	−13·7
2	9·9	−6·5
3	11·9	−6·5
4	29·0	+25·7
5	15·9	+12·1
8	17·8	−17·3
9	16·0	−12·0
11	17·0	+16·3
$\overline{10}$.2.1	9·4	−11·2
3	16·3	+15·7
4	24·4	+20·2
5	8·2	+4·4
6	31·7	−26·8
7	8·3	−7·1
$\overline{12}$.2.2	6·5	+8·1
6	12·9	−8·8
$\overline{14}$.2.6	15·6	−12·5
$\overline{16}$.2.8	10·7	+9·5
$\bar{1}$.3.1	11·2	+9·0
2	14·5	−10·8
3	10·4	+6·9
4	19·1	+19·1
5	23·4	−19·7
6	9·8	−9·0
7	29·6	+29·0
8	9·3	−8·7
9	25·8	−26·7
$\bar{3}$.3.1	46·8	−45·2
3	9·8	+9·4
4	13·2	+9·7
5	13·3	−10·6
7	17·8	+14·6
8	6·7	−8·2
9	7·9	−12·1
10	18·4	+20·9
12	7·5	−15·0
$\bar{5}$.3.1	9·3	−11·1
2	28·8	+24·1

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$
$\bar{5}$.3.3	10·5	+12·9
4	16·9	−15·4
5	8·3	− 6·1
6	8·0	+ 9·3
7	5·6	+ 2·5
8	5·9	− 8·8
9	6·6	− 4·6
12	6·5	− 8·4
13	8·4	+ 9·7
$\bar{7}$.3.1	21·4	+19·0
3	29·7	−26·1
4	16·1	−14·5
5	16·7	+12·9
6	17·5	+13·9
$\bar{9}$.3.1	15·7	+15·0
3	17·4	−15·5
4	28·5	+27·4
5	20·7	+19·3
6	18·5	−17·4
7	14·1	−16·1
$\overline{11}$.3.1	8·9	+ 8·2
3	13·3	−11·5
4	10·5	+11·3
6	22·8	−24·2
7	10·2	+10·1
8	12·3	+18·3
$\overline{13}$.$\bar{3}$.4	6·8	+ 6·1
5	7·9	+ 4·0
9	12·8	−16·3
$\overline{15}$.3.1	5·6	−8·1
$\bar{2}$.4.1	14·6	+ 9·7
2	13·9	+13·6
3	21·2	−20·0
5	12·2	+11·4
6	16·0	−12·9
7	12·4	−10·5
9	14·6	+12·6
$\bar{4}$.4.1	23·4	+21·1
2	5·8	− 3·5
3	6·5	− 5·1
4	17·7	+17·8
5	6·0	+ 5·1
6	26·8	−29·9
8	16·1	+16·8
9	7·4	+ 8·3
10	7·0	− 7·7
$\bar{6}$.4.1	26·4	+24·0
2	23·4	−19·4
3	13·2	+16·8
5	17·6	−15·9
6	18·0	−20·3
7	19·9	+18·5
8	18·2	+16·6
9	8·8	− 9·3
0	8·3	− 8·5
$\bar{8}$.4.1	7·8	− 9·8
2	24·8	−24·8
3	11·6	+11·6
4	7·9	+ 8·5
5	11·2	−13·5
$\overline{10}$.4.2	17·9	+16·6
$\overline{10}$.4.4	8·0	−10·8
5	16·3	−19·3
$\overline{12}$.4.2	7·7	+ 9·5
3	10·0	− 8·9
4	6·7	− 8·1
5	5·9	+ 4·9
$\bar{1}$.5.1	13·1	− 7·8
2	11·4	− 9·0
3	28·4	+29·5
4	14·3	+10·5
5	10·8	−10·5
6	15·1	−14·9
$\bar{3}$.5.1	17·3	−17·9
2	15·3	+17·7
3	27·8	+28·5
5	20·4	−20·7
$\bar{5}$.5.1	11·1	+ 8·6
2	12·0	+ 9·5
3	6·5	+ 4·6
4	18·5	−16·2
5	16·0	−13·7
7	5·2	+ 4·4
8	7·9	+ 1·8
10	6·4	+ 4·4
$\bar{7}$.5.1	21·3	+22·7
4	14·4	−15·0
$\bar{9}$.5.1	12·5	+11·6
3	7·4	− 5·4
$\overline{11}$.5.1	7·0	+ 8·4
3	10·5	−13·1
$\bar{2}$.6.1	13·5	−11·5
3	20·9	+17·9
4	9·2	+ 9·1
5	10·1	− 8·4
$\bar{4}$.6.1	7·5	+ 9·4
2	15·3	+22·6
3	11·0	+ 9·6
5	21·2	−25·8
$\bar{6}$.6.1	8·5	+ 7·4
2	6·4	+ 5·2
$\bar{8}$.6.1	8·3	+ 8·6
$\overline{10}$.6.3	5·4	− 6·3
$\bar{1}$.7.5	5·2	+ 3·3
$\bar{3}$.7.1	9·3	+ 8·0
4	7·2	+10·1
6	7·8	−10·0
$\bar{5}$.7.1	9·3	+ 9·9
4	4·9	+ 4·5
5	8·2	−10·0
6	8·0	− 9·5
$\bar{7}$.7.5	7·1	− 8·2
0.1.1	44·2	−49·1
2	24·7	+26·5
3	64·3	+74·1
0.1.4	19·5	+11·6
5	29·7	−33·1
6	9·6	− 9·9
12	11·2	−12·0
14	9·9	+10·9
2.1.0	20·0	+21·9
1	3·5	− 3·7
3	20·9	+20·8
4	16·0	−11·4
5	25·5	−29·0
6	5·5	− 6·3
7	6·2	+ 5·7
8	16·3	+18·7
9	12·8	−13·1
10	11·8	+10·9
11	7·8	+ 9·1
13	9·6	−12·5
4.1.0	6·7	− 5·7
3	27·7	+21·3
4	18·7	+20·1
6	33·3	−37·0
7	6·6	− 4·1
8	19·9	+21·0
6.1.0	32·5	−29·7
3	11·3	− 8·7
4	11·5	+13·6
5	25·7	+27·0
6	25·1	−26·6
8.1.0	19·6	−19·5
1	13·3	+11·6
2	11·7	+ 9·5
3	15·9	−15·3
5	21·7	+21·9
7	12·4	−15·8
8	11·5	−12·4
10.1.0	25·4	−30·9
1	19·0	−19·1
2	11·5	+11·3
6	10·0	+ 9·9
12.1.0	15·5	+11·4
1	13·2	−15·2
14.1.0	7·6	+ 6·8
1	11·1	−11·5
1.2.0	27·9	−28·9
1	48·7	+47·2
2	26·8	+22·9
3	20·5	−16·2
4	17·5	−14·1
5	21·6	+22·2
6	11·8	−12·0
7	16·8	−19·0
8	21·9	+24·1
9	23·8	+27·0
10	10·8	− 9·3
11	15·3	−16·1
12	8·9	− 7·8
3.2.0	41·5	−47·1
1	9·8	+ 8·2
2	70·0	+74·0
4	30·9	−27·5
6	10·5	+ 5·2
7	26·6	−30·1
3.2.9	9·7	+ 8·5
10	14·8	+15·5
5.2.0	55·0	−62·4
1	56·1	−52·1
2	44·0	+45·3
3	41·5	+41·7
6	9·4	− 9·3
7	7·6	− 6·6
8	11·8	−13·5
10	13·1	+16·8
7.2.0	7·8	− 8·0
1	40·3	−39·8
2	4·2	− 4·3
3	22·3	+23·8
4	13·4	+12·1
5	8·5	− 9·8
6	11·3	−11·3
7	8·7	+ 8·7
8	9·4	− 9·8
9.2.1	16·5	−16·2
2	20·1	−23·6
3	10·4	+11·7
4	27·0	+25·4
8	9·7	− 4·7
11.2.0	11·8	+12·2
2	20·0	−25·3
3	9·6	− 8·8
4	13·6	+14·9
5	5·6	+ 7·7
13.2.5	9·7	+14·5
0.3.1	25·1	+31·5
2	27·6	+30·5
3	37·5	+39·1
4	35·8	−34·7
5	23·6	−22·7
6	10·1	− 9·7
7	25·1	+25·8
8	10·1	− 9·8
9	4·8	+ 6·4
12	10·4	−10·3
2.3.0	5·7	+ 5·7
1	15·5	−14·5
2	10·2	+10·7
3	36·2	+38·1
4	17·0	+16·0
5	36·9	−38·3
6	31·0	−30·5
8	14·1	+13·6
9	10·0	+10·8
10	8·3	+ 9·7
4.3.2	10·2	+11·9
3	11·2	+11·2
4	24·3	+23·8
5	16·7	−18·1
6	18·2	−18·0
8	12·6	+13·4
6.3.0	10·6	−10·1
4	26·6	+27·1
5	10·9	+12·2
6	14·2	−14·1
7	14·7	−15·7

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$
8.3.0	28·3	−30·9
1	10·4	−10·7
4	10·1	+12·6
5	5·1	+6·8
10.3.0	16·7	−16·0
1	11·3	−11·9
5	8·6	+10·6
12.3.1	8·5	−10·7
14.3.0	11·0	+13·0
1.4.0	12·5	−11·0
1	15·8	+18·1
2	20·6	+22·7
3	19·8	+17·2
4	9·5	−11·5
5	28·0	−28·5
6	14·2	−15·2
7	13·1	+14·3
8	8·6	+9·0
9	8·1	+9·6
3.4.0	10·1	−13·7
3	18·6	+19·5
4	23·7	+24·5
5	13·9	−14·6
6	9·8	−10·9
5.4.0	5·2	−4·8
1	6·8	+4·2
3	9·2	+11·6
4	9·7	+11·4
5	8·4	−9·0
6	7·5	−8·8
7.4.0	20·3	−17·5
1	12·2	−12·0
3	13·5	+16·1
4	9·3	+9·6
9.4.1	11·9	−14·1
4	9·9	+9·0
5	5·3	+7·5
15.4.0	12·0	+8·0
0.5.1	25·6	+21·8
2	6·7	+6·9
3	20·9	−16·3
6	13·1	−12·3
8	17·2	+17·1
9	8·6	+8·3
10	3·0	−3·2
11	6·8	−7·8
2.5.0	29·1	−29·4
1	25·5	+23·4
2	22·6	+23·7
4	7·9	−3·7
7	11·0	−9·1
4.5.0	23·7	−21·9
3	6·5	+8·3
4	5·3	−2·8
5	6·2	−1·7
6	6·4	+5·3
8	6·0	−6·5
9	6·8	+8·6
6.5.0	9·5	−9·5
1	9·0	−8·7
2	6·9	+6·7
3	23·8	+24·9
5	10·5	−10·4
8.5.0	9·6	+5·9
1	18·2	−19·7
10.5.0	9·8	+9·5
1.6.0	10·8	+5·7
1	12·0	−8·3
3	13·1	+10·3
5	10·5	−9·8
3.6.0	9·1	+4·6
2	12·0	−8·9
3	5·7	+5·4
4	9·4	−8·3
5.6.0	8·4	+6·1
1	10·7	+8·5
2	6·8	−6·9
3	5·8	−4·9
7.6.1	7·1	+5·7
5	6·3	+8·2
9.6.0	10·6	−7·9
2.7.5	8·2	+9·9
$\bar{2}$.1.1	5·5	−6·5
2	66·1	−80·9
3	63·8	+59·5
4	65·1	+65·1
5	25·5	+25·9
6	47·0	−48·7
7	30·6	−25·7
8	9·2	−2·0
11	10·2	+10·3
12	9·9	+11·0
$\bar{4}$.1.2	70·2	−77·2
3	50·5	+49·7
4	12·9	+12·7
5	10·9	−12·8
7	23·3	+23·9
8	11·2	−9·0
9	9·2	−12·1
11	12·2	+14·1
13	9·0	−12·0
$\bar{6}$.1.1	11·9	−13·3
2	10·9	+9·0
3	34·1	+37·3
4	29·4	+24·1
5	50·6	−52·1
6	15·7	+12·5
8	11·1	−12·0
10	22·3	+22·9
13	9·4	−9·3
$\bar{8}$.1.1	9·8	−6·3
2	24·1	+27·6
3	8·6	−3·7
4	12·7	+6·5
5	24·7	−24·1
7	17·2	−14·4
8	10·1	−12·9
$\bar{8}$.1.9	15·7	+14·3
10	28·7	+31·5
11	12·7	−10·7
$\overline{10}$.1.2	33·4	+37·1
4	7·9	−7·8
6	10·1	−5·0
9	9·7	+10·7
11	12·3	−12·7
13	10·8	+13·7
$\overline{12}$.1.1	19·2	+20·3
3	22·9	−26·7
4	9·3	−7·5
8	9·7	+10·1
9	12·3	+15·1
12	8·8	−5·3
$\overline{14}$.1.1	10·1	+11·6
4	7·5	+8·2
5	10·7	−7·7
6	9·5	−12·2
8	11·2	+11·5
10	9·2	−10·9
$\overline{16}$.1.1	5·9	+5·7
2	10·1	−10·9
$\bar{1}$.2.1	84·1	−91·0
2	13·1	−14·5
3	12·6	+14·2
4	15·9	+12·8
5	31·1	+28·6
6	60·6	+56·6
7	8·3	−8·3
8	37·4	−38·2
9	23·9	−24·0
10	15·8	+18·4
$\bar{3}$.2.1	15·5	−12·3
2	3·1	+6·7
3	28·5	+28·5
4	35·5	−34·9
5	13·1	+15·4
7	24·1	−25·1
8	21·0	−24·0
9	29·5	+31·7
10	14·9	+15·4
$\bar{5}$.2.1	26·0	+22·1
2	15·5	+9·0
3	11·5	+9·1
4	28·2	+25·8
5	19·1	+23·4
6	12·7	−9·9
7	37·3	−41·9
8	16·9	−17·1
9	22·6	+26·1
10	5·3	+3·3
12	5·0	+9·3
$\bar{7}$.2.1	27·5	+25·6
3	17·5	−15·6
4	61·9	+58·1
6	22·8	−25·2
7	33·6	−30·0
8	11·5	+12·6
9	9·2	+9·1
10	11·9	+5·3
11	6·4	−5·1
12	6·1	+11·4
$\bar{7}$.2.13	8·8	−9·5
14	4·8	−9·1
$\bar{9}$.2.1	7·2	+4·3
2	10·4	−11·1
3	15·3	+12·7
4	19·7	+21·0
5	25·5	−22·9
6	40·1	−38·2
7	27·0	+22·7
8	26·4	+26·5
9	9·7	+5·5
11	7·4	−3·9
12	10·5	−7·5
$\overline{11}$.2.1	10·4	+7·7
2	15·9	+13·4
3	26·1	+26·7
4	13·5	−11·1
5	29·2	−33·4
6	28·7	−22·8
7	22·4	+20·3
12	7·8	−10·7
$\overline{13}$.2.1	7·3	−9·3
2	7·4	+8·7
5	14·3	−15·1
6	19·0	+17·5
11	9·1	−8·3
12	7·1	−11·8
$\overline{15}$.2.1	8·3	+9·0
2	7·4	+9·1
3	7·5	−6·4
4	15·0	−17·6
5	7·6	−8·0
6	10·6	+12·0
7	7·3	+6·9
$\overline{17}$.2.1	9·8	+12·4
3	7·2	−11·9
4	7·6	−8·9
$\bar{2}$.3.1	23·8	−23·8
2	12·7	−12·5
3	7·9	+5·1
4	42·0	+41·7
5	19·2	+17·5
6	14·0	−11·0
7	24·9	−23·8
8	14·3	−11·6
9	14·1	−14·1
11	21·1	+21·1
12	11·5	+11·9
$\bar{4}$.3.1	49·2	−51·6
2	26·3	−25·2
3	37·1	+37·8
4	36·2	+34·9
5	15·4	+11·8
6	20·6	−19·7
8	14·8	−14·8
11	14·8	+17·1
12	4·5	−6·1
$\bar{6}$.3.1	32·2	−30·7
2	15·7	+14·1
3	28·7	+25·7
4	9·8	+9·3
5	20·6	−18·9
6	9·2	−5·1

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$
$\bar{6}$.3.7	6·6	− 5·9
8	7·0	− 7·6
9	7·0	+ 6·0
10	18·1	+19·3
11	7·1	+ 8·7
12	10·8	−11·3
13	9·0	−10·1
$\bar{8}$.3.1	5·9	− 6·4
2	35·9	+36·9
3	34·3	+35·6
4	7·3	− 8·4
5	21·5	−22·1
6	21·4	−17·3
7	12·1	−12·8
9	15·3	+16·3
10	18·6	+19·4
$\overline{10}$.3.1	18·2	+18·3
2	12·8	+13·2
3	12·5	+11·3
4	19·0	−16·9
5	11·9	+11·1
6	8·0	− 9·8
9	14·9	+16·4
$\overline{12}$.3.1	15·0	+16·9
2	9·8	+ 9·8
3	6·2	− 7·7
4	14·2	−14·1
5	12·0	−10·2
8	21·6	+23·2
$\overline{14}$.3.1	11·1	+11·8
3	9·5	− 8·5
5	9·9	−10·9
8	12·8	+15·1
$\bar{1}$.4.1	28·6	−26·0
$\bar{1}$.4.2	11·6	−13·0
4	21·7	+21·8
5	11·9	+12·5
7	11·0	−11·8
9	10·8	−10·2
12	9·0	+ 8·9
$\bar{3}$.4.1	24·5	−21·7
2	7·5	− 7·7
3	5·8	+ 5·4
4	15·7	+13·3
5	18·0	+17·6
8	10·0	−10·7
11	7·8	+10·6
$\bar{5}$.4.1	26·5	−25·9
2	8·8	+ 8·9
3	22·0	+21·3
4	14·9	+14·1
6	20·0	−21·4
7	16·8	−16·7
8	6·6	− 5·9
9	6·5	+ 4·6
10	12·5	+12·5
11	9·5	+11·3
$\bar{7}$.4.1	26·7	−24·1
2	18·8	+16·9
3	26·7	+24·9
4	5·6	+ 7·0
6	8·3	− 4·9
7	13·4	−12·5
$\bar{9}$.4.1	10·2	+10·4
2	13·8	+14·7
3	11·7	+12·9
4	16·3	−16·3
$\overline{11}$.4.1	6·9	+ 7·9
$\overline{11}$.4.2	6·3	+ 6·5
3	9·2	+7·1
4	6·0	− 6·8
5	8·7	− 6·5
$\overline{13}$.4.2	9·9	+ 9·5
5	8·3	− 8·3
$\overline{15}$.4.3	7·5	− 6·5
$\bar{2}$.5.1	20·6	−18·6
2	5·8	+ 2·1
3	8·2	+10·3
4	10·7	− 7·3
5	6·5	+ 6·7
6	12·0	+ 7·6
8	14·1	−13·7
10	8·8	+ 9·1
$\bar{4}$.5.2	15·6	+14·6
3	5·8	− 3·7
5	19·0	+20·1
7	16·1	−17·2
8	11·1	−11·3
$\bar{6}$.5.4	10·7	+ 8·5
5	11·2	+ 8·2
6	12·0	−12·4
7	14·8	−15·9
8	11·7	+13·5
9	4·8	+ 7·1
$\bar{8}$.5.3	7·0	+ 8·7
4	12·6	+12·1
$\overline{10}$.5.3	10·3	+ 8·6
5	16·2	−17·9
$\overline{12}$.5.3	6·6	+ 6·9
$\overline{12}$.5.5	9·2	− 9·7
$\bar{1}$.6.1	16·4	+12·2
2	17·1	−14·3
3	8·6	− 5·5
4	10·5	+ 8·9
5	8·6	+ 6·7
6	9·7	− 9·4
$\bar{3}$.6.2	12·1	−12·9
3	6·5	+ 7·8
4	15·7	+16·0
5	6·2	− 5·5
6	6·4	− 7·5
7	5·0	+ 4·0
$\bar{5}$.6.1	11·6	− 9·1
2	5·1	− 4·7
3	11·2	+8·7
5	11·3	−11·4
7	8·0	+ 9·0
$\bar{7}$.6.1	9·4	− 8·1
2	4·8	+ 3·7
3	10·9	+10·1
6	6·8	+ 5·2
$\overline{11}$.6.3	7·0	− 9·2
$\bar{2}$.7.5	4·0	− 3·2
$\bar{4}$.7.5	3·9	− 7·9
$\bar{6}$.7.1	7·9	+ 7·7
2	3·6	− 4·2
3	6·2	− 4·6
5	5·5	+ 5·6

DISCUSSION

The Shape and Arrangement of the Molecules.—All the atoms of the thianthren molecule lie very nearly in two planes which intersect in the sulphur atoms at an angle of 128°. Table 6 gives the perpendicular distances of the atoms from the best planes through the two halves of the molecule.

The arrangement of the molecules (see Figure) is essentially the same as that proposed by Wood and Crackston [5] for thianthren and by Wood and Williams [12] for selenanthren. The S_1–S_2 axis of the molecule is inclined to the *b*-axis at an angle of 31° and its projection on (010) makes an angle of 20° with *c* in the acute angle β. The longest direction of the molecule, at 90° to the S_1–S_2 axis, is roughly parallel to [101] and coincides approximately with the vibration direction of the slowest ray (γ) and of minimum susceptibility indicated by magnetic measurements.[13] Molecules related by a centre of symmetry interleave thus  with the planes of the overlapping benzene rings 3·53 Å apart, and the structure can thus be regarded as made of puckered layers parallel to the (10$\bar{1}$) planes.

The closest-approach distances between adjacent molecules are S–C 3·92 Å, S–S 3·78 Å, and C–C 3·47 Å.

Accuracy of the Results.—A statistical calculation of the effects of random errors in the analysis was made by Cruickshank's method [14] and the mean standard deviations of the

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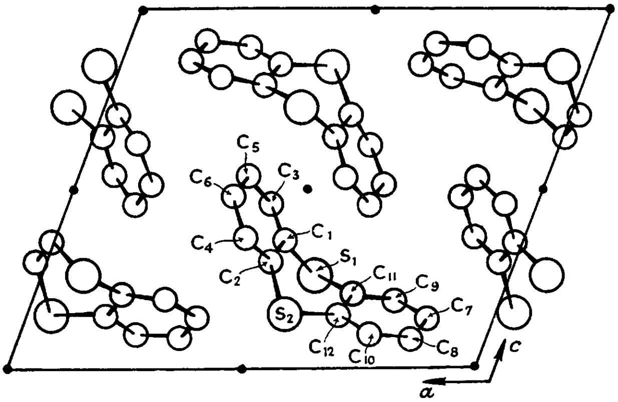
[12] Wood and Williams, *Nature*, 1942, **150**, 321.
[13] Banerjee, *Z. Krist.*, 1939, **100**, 316.
[14] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

bond lengths found to be (range of individual values in parentheses): S–C, 0·008 (0·0071—0·0088) Å; C–C, 0·012 (0·0107—0·0147) Å. The standard deviation of the ∠CSC bond angles was 0·5° and of the electron density 0·16 e.Å^{-3}.

If the lengths of chemically equivalent bonds in the molecule are compared on the basis of these standard deviations significant differences appear, but it seems unlikely that these can be entirely real, *i.e.*, distortions due to intermolecular forces in the crystal (but see Wheatley [15]), and it is much more probable that they are systematic errors due to (*a*) the omission of hydrogen atoms from the calculations and (*b*) the assumption of isotropic thermal motion of the atoms. The scale factors and isotropic temperature factors of Table 2 were introduced in an attempt to bring the ratios of observed and calculated electron densities and mean peak curvatures to unity, but as Table 3 shows this was only moderately successful and considerable improvement could probably be made by the use of anisotropic temperature factors. Independent justification for such factors can be found in the chemical evidence referred to in the introduction, suggesting that the thianthren molecule may be flexible about the line of fold; in the crystal the thermal motion of the molecule may be considerably greater in the directions normal to the planes of the benzene nuclei than in other directions. Further refinement, account being taken of these systematic factors, would be necessary to determine the molecular dimensions with greater precision, but it is doubtful whether the importance of thianthren justifies this. Accordingly we take as the best values of the bond lengths the means of the figures for the various groups of chemically equivalent bonds shown in Table 7. It is difficult to estimate the effect of the systematic errors on the accuracy but experience with similar cases suggests that it would be appropriate to take the " standard deviations " of the figures in Table 7 as approximately double those due to random errors, say $0{\cdot}01_5$ Å for C–S and $0{\cdot}02_5$ Å for C–C.



Thianthren: the structure projected on (010).

The C–S–C bond angle of 100° is the same as that found in 1 : 4-dithiadiene [16] and agrees fairly well with C–S–C angles in various non-cyclic compounds, so that the experimental evidence supports the view that folding of the molecule enables the sulphur atom to retain its " natural " valency angle. Possibly this tendency is assisted by a certain amount of *dπ* conjugation as suggested by Sutton [6] since the C–S bond length (which is in good agreement with other values in aromatic substances, *e.g.*, 1·76 ± 0·02 Å in dibenzenesulphonyl sulphide [17]) appears to be significantly less than the usually accepted single-bond value of about 1·81 Å. The mean length of the C–C bonds in the two benzene nuclei is in good agreement with recent values for benzene itself.[18]

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[15] Wheatley, *Acta. Cryst.*, 1953, **6**, 369.

[16] Howell, Curtis, and Lipscomb, *ibid.*, 1954, **7**, 498.

[17] Mathieson and Robertson, *J.*, 1949, 724.

[18] Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339; Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

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