The Anisotropic Structure Refinement of
4-Methyl-1,2-Dithia-4-Cyclopentene-3-Thione on an IBM Type 650 Computer

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An anisotropic refinement of the structure of 4-methyl-1, 2-dithia-4-cyclopentene-3-thione, $S_3C_4H_4$, has been carried out on an IBM 650 computer using the differential Fourier synthesis technique. Although the shifts in atomic coordinates were small, the thermal anisotropy was appreciable and the convergence of the refinement was slow in that six cycles of refinement were required.

The difference in molecular dimensions as compared with the results from isotropic analysis reported previously were less than 0·05 Å, but the standard deviations, as calculated by Cruickshank's method, were halved with a corresponding reduction in the agreement index.

The methyl carbon atom has thermal parameters about 40% greater than those of the carbon atoms in the five-membered ring. This is believed to be a real effect due, at least in part, to a statistical displacement of the methyl group out of the plane of the ring, by about 0·1 Å, as a consequence of a close intramolecular $CH_3 \cdots S$ distance of 3·23 Å.

Introduction

The purpose of this work was twofold. Firstly to test and record the experience with an anisotropic refinement program which has been developed by Shiono (1958) for the IBM 650 computer; secondly to explore further the refinement of a structure for which the application of a least squares and a Fourier refinement had given somewhat different results at the isotropic stage (Kehl & Jeffrey, 1958).

The structure of 4-methyl-1,2-dithia-4-cyclopentene-3-thione, I, was well suited for testing an anisotropic refinement procedure, since there was evidence, from the isotropic analysis results, that the molecule was vibrating as a rigid body with an amplitude normal to the plane of the molecule significantly greater than that in the plane. There was also the observation that the methyl carbon atom, C(6), had an apparent average mean square amplitude of vibration 40% greater than that of the other atoms in the molecule, which required further clarification.

The structure contains light and heavy atoms in close proximity; C(3), for example, is in a position very susceptible to overlapping or series-termination effects from the adjacent S(2) and S(3) atoms, and it was of interest to determine whether this could lead to any difficulties in the refinement, in view of certain simplifying approximations used in the theory.

I.
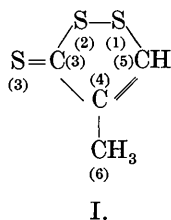
The anisotropic refinement technique

To proceed from the verified approximate structure, i.e. the solved phase problem, to the final stage of the analysis we prefer to use, as far as is possible, refinement methods which can be carried out entirely within the computing machine, as is generally true for the least-squares methods but not necessarily so for the Fourier methods. For this reason, we have developed programs for the IBM type 650 computer using the differential Fourier synthesis technique rather than the difference Fourier, as recently described by Leung, Marsh & Schomaker (1957), for example.

The refinement technique that we favor with an IBM 650 is to apply the isotropic differential synthesis refinement cycle programs, i.e. synthesis and structure factor computations, (Shiono, 1957) until the atomic parameter shifts are small; then calculate the individual atomic anisotropic components, B_{ij}^n, in the expression for the form factors

$$f_{hkl}^{n(t)} = f_{hkl}^{n(0)} \exp -\tfrac{1}{4}\{B_{11}^n h^2 a^{*2} + B_{22}^n k^2 b^{*2} + B_{33}^n l^2 c^{*2} \\ + B_{23}^n 2klb^* c^* + B_{31}^n 2lhc^* a^* + B_{12}^n 2hka^* b^*\}$$

from the curvatures of the atomic peaks in the observed and calculated Fourier syntheses, and finally to reiterate the calculation of both anisotropic and position parameter shifts until both are negligible.

The quantities B_{ij} are then directly comparable with the usual form of the isotropic temperature factor

$$f_{hkl}^{n(t)} = f_{hkl}^{n(0)} \exp -\{B^n \sin^2 \theta / \lambda^2\}.$$

In calculating the anisotropic parameters from the curvatures of the atomic peaks we have used the theory of Cruickshank (1956a) and made use of the approximations which he recommends. In particular

Table 1. *Anisotropic refinement parameters in Å and Å²*

4-methyl-1,2-dithia-4-cyclopentene-3-thione

	Initial parameters Least squares Isotropic	Isotropic	Parameter shifts from differential synthesis refinement Anisotropic				Final parameters	Standard deviations
S_1	I	II	III	IV	V	VI	VII	s.d.
x	1·866	0·001	−0·001	0·000	0·000	0·000	1·866	0·005
y	5·490	0·003	0·003	0·002	0·001	−0·000	5·499	0·005
z	2·054	−0·006	0·005	0·003	0·002	0·001	2·059	0·005
B_{11}	4·63	−1·02	0·37	0·24	0·20	−0·01	4·22	0·28
B_{22}	4·63	1·63	−1·09	0·41	0·21	−0·03	5·55	0·26
B_{33}	4·63	3·46	−1·54	0·62	0·39	−0·06	7·15	0·38
B_{23}	—	−0·29	−0·19	−0·09	−0·06	−0·04	−0·69	0·30
B_{31}	—	0·40	0·06	0·07	−0·02	0·01	0·40	0·24
B_{12}	—	−0·36	−0·10	−0·05	−0·02	−0·02	−0·574	0·26
S_2	I	II	III	IV	V	VI	VII	s.d.
x	0·134	0·004	0·003	−0·001	−0·001	−0·000	0·138	0·004
y	4·848	0·001	−0·000	0·000	−0·000	−0·000	4·848	0·005
z	1·183	−0·019	0·011	0·001	0·000	0·000	1·176	0·005
B_{11}	4·47	−1·35	0·08	0·04	0·04	−0·09	3·10	0·24
B_{22}	4·47	1·55	−1·06	0·26	0·13	−0·04	5·15	0·26
B_{33}	4·47	4·19	−1·76	0·45	0·29	−0·08	7·23	0·38
B_{23}	—	−0·03	0·03	−0·03	−0·02	−0·02	−0·08	0·30
B_{31}	—	0·03	0·04	−0·02	0·02	−0·01	−0·05	0·22
B_{12}	—	−0·01	0·02	0·04	0·02	−0·01	0·04	0·24
S_3	I	II	III	IV	V	VI	VII	s.d.
x	−0·386	−0·000	0·004	−0·000	−0·001	−0·000	−0·384	0·005
y	2·220	−0·006	0·008	0·002	0·000	0·000	2·224	0·006
z	0·029	0·061	−0·001	−0·001	−0·000	0·000	0·034	0·006
B_{11}	5·10	−1·16	0·35	0·18	0·14	−0·03	4·48	0·30
B_{22}	5·10	1·46	−0·77	0·45	0·20	−0·03	6·25	0·30
B_{33}	5·10	2·89	−1·39	0·55	0·32	−0·08	7·08	0·38
B_{23}	—	0·22	0·01	−0·02	−0·02	−0·02	0·18	0·32
B_{31}	—	−0·49	−0·13	−0·15	−0·09	−0·07	−0·96	0·26
B_{12}	—	−1·24	−0·02	−0·02	−0·02	−0·01	−1·31	0·28
C_6	I	II	III	IV	V	VI	VII	s.d.
x	2·658	−0·027	−0·030	0·035	0·007	0·001	2·645	0·028
y	1·566	0·080	−0·018	0·012	−0·004	−0·006	1·631	0·027
z	1·073	−0·025	0·011	−0·001	0·007	0·003	1·069	0·035
B_{11}	7·03	−0·41	−0·48	0·73	0·25	0·09	7·13	1·82
B_{22}	7·03	1·15	−2·05	0·05	0·08	0·10	6·20	1·50
B_{33}	7·03	6·71	−1·74	0·93	0·66	0·01	12·98	3·28
B_{23}	—	3·37	−2·22	0·32	0·27	0·07	1·47	2·08
B_{31}	—	−1·81	−0·29	−0·36	−0·26	−0·08	−2·69	1·84
B_{12}	—	0·24	0·45	0·18	−0·04	0·08	1·09	1·48
C_3	I	II	III	IV	V	VI	VII	s.d.
x	0·692	−0·029	0·011	−0·012	0·001	0·001	0·664	0·017
y	3·259	−0·002	−0·016	−0·007	0·001	0·001	3·236	0·016
z	0·727	0·057	−0·035	0·002	0·005	0·003	0·759	0·018
B_{11}	4·12	−1·08	0·65	0·34	0·22	0·13	4·38	1·02
B_{22}	4·12	1·93	−1·15	0·17	0·03	−0·06	4·91	0·98
B_{33}	4·12	3·89	−2·25	0·35	0·27	−0·03	6·09	1·26
B_{23}	—	0·38	0·13	−0·22	−0·14	−0·01	0·23	1·04
B_{31}	—	−0·17	0·28	−0·25	−0·19	−0·06	−0·35	0·84
B_{12}	—	−0·47	−0·10	−0·45	−0·21	−0·02	−1·23	0·92
C_4	I	II	III	IV	V	VI	VII	s.d.
x	1·998	−0·021	0·000	0·001	0·004	0·000	1·982	0·017
y	2·969	0·005	−0·031	0·006	−0·001	−0·001	2·947	0·017
z	1·204	0·040	−0·008	0·003	0·000	0·000	1·240	0·016
B_{11}	4·98	−0·87	−0·56	−0·02	−0·02	−0·10	3·35	1·00
B_{22}	4·98	1·79	−1·72	0·09	0·03	−0·11	4·88	0·98
B_{33}	4·98	2·90	−2·47	0·50	0·34	−0·12	5·73	1·18
B_{23}	—	1·33	−0·44	−0·26	−0·10	−0·08	0·39	1·00
B_{31}	—	−0·32	0·48	0·30	0·24	0·08	0·73	0·80
B_{12}	—	−0·46	0·33	−0·01	0·06	0·04	−0·05	0·90

Table 1 (cont.)

C$_5$	Initial parameters Least squares Isotropic I	Isotropic II	Parameter shifts from differential synthesis refinement Anisotropic III	IV	V	VI	Final parameters VII	Standard deviations s.d.
x	2·681	−0·055	0·018	0·006	0·009	0·002	2·649	0·016
y	4·030	−0·015	−0·013	−0·013	0·000	−0·001	3·989	0·018
z	1·897	−0·017	−0·010	−0·005	−0·003	−0·001	1·861	0·023
B_{11}	4·96	−1·06	−0·06	−0·14	0·07	−0·03	3·56	1·02
B_{22}	4·96	0·96	−0·81	0·51	0·14	0·01	5·69	0·98
B_{33}	4·96	5·14	−2·26	0·67	0·33	0·01	8·53	1·26
B_{23}	—	0·73	−0·36	−0·02	0·02	−0·03	0·23	1·04
B_{31}	—	−1·06	−0·04	0·27	0·27	0·10	−0·44	0·84
B_{12}	—	−0·09	−0·34	0·04	0·03	0·08	−0·25	0·92

we have used the approximation formulae given in Cruickshank's paper in equations (3·7) to (3·10),

(with $b_{11} = B_{11}(a^{*2}/4)$, $b_{12} = B_{12}(a^*b^*/2)$, etc.).

Since the structure is non-centrosymmetrical, space group $P2_12_12_1$, Cruickshank's equation (3·12) was used to compute the anisotropic parameter corrections, this being equivalent to the 'n-shift rule' for a non-centrosymmetrical coordinate parameter refinement.

Cruickshank (1956a) discussed in some detail the slow convergence of the anisotropic refinements when he applied them to several structures. In our results we found a similar tendency for the calculated thermal parameter shifts to overshoot, although our results appear to be more consistent than his. We concluded that, in this analysis at least, an optimum speed of refinement would have been obtained by taking a uniform 50% of all calculated anisotropic thermal parameter shifts, at each refinement stage.

The results of the anisotropic refinement

Experiences with structure refinement on large computers during the past few years has not proved, in all cases, to run the fully automatic and smooth course that was perhaps envisaged at one time. While this may be due solely to starting the automatic refinement too soon, it still seems to be a wise precaution to watch carefully the way in which the position and anisotropic temperature parameters change at each step in the refinement. Since this is the first time that use has been made of this particular computing program we have reproduced the details of the refinement shifts at each stage in Table 1.

As with the differential synthesis isotropic analysis (Kehl & Jeffrey, 1958), the starting point of the refinement was a set of coordinates and isotropic temperature factors obtained by the least-squares minimization procedures described by Friedlander, Love & Sayre (1955) and computed through five cycles using an IBM type 704. The observed and calculated differential syntheses were computed from which the coordinate shifts in Å and anisotropic temperature factor shifts in Å^2, given in Table 1 column II, were obtained from the

slopes and curvatures of the atomic peaks. For the coordinate shifts, the values obtained from the differential synthesis equations were multiplied by 1·5 for the n-shift rule. For the thermal parameters a factor of 2 is introduced into the computation in the non-centrosymmetrical case and to apply an equivalent n-shift the values were multiplied by 0·75.

The second cycle of refinement gave shifts based on the comparison of the observed Fourier peaks with those computed from the calculated synthesis with the anisotropic structure factors. In the majority of cases it was found that the anisotropic shifts had been considerably overestimated. Consequently the computed values were subsequently multiplied by 0·5; i.e. the anisotropic factors were given an n-shift of unity, (as for the centrosymmetrical case). The coordinate shifts were multiplied by 1·5 as before. These shifts appear in column III. Three more cycles (columns IV, V, VI) were applied at the end of which the largest coordinate shift was 0·005 Å (C$_6$, y) and the largest anisotropic parameter shift was 0·127 Å^2 (C$_3$, B_{11}).

The R factor dropped from 0·21 (least squares, isotropic) to 0·126. The standard deviations* of the atomic coordinates and thermal parameters as computed by the method of Cruickshank (1949, 1950, 1956a) are given in Table 1. The standard deviations of the position parameters were reduced on average by a factor of 0·56 as compared with the isotropic analysis. The observed and calculated structure amplitudes and the phase angle components are given in Table 2. The atomic scattering factors used were those of Viervoll & Øgrim (1949) for sulphur and Berghuis et al. (1955) for carbon. The comparison of observed and calculated curvatures of the atomic peaks is shown in Table 3; these data may be compared with those given in Table 7 in the paper by Kehl & Jeffrey (1958) reporting the results of the isotropic analysis by differential Fourier syntheses. The ratios of

$$\delta^2\varrho_{obs.}/\delta x^2 \quad \text{to} \quad \delta^2\varrho_{calc.}/\delta x^2 \quad \text{etc.}$$

* The standard deviations given in Tables 1 and 6 were computed with equal weights for all ΔFs. With a weight of unity for the centrosymmetrical ΔFs, as compared with two for the general phases, the s.d.s are reduced on average by a factor of 0·7.

Table 2. *Observed and calculated structure factors*

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	A_c	B_c
0	0	2	18.1	15.3	15.3	
0	0	4	16.9	14.2	14.2	
0	1	1		4.2		4.2
0	1	2	10.0	9.8		9.8
0	1	3	12.1	9.7		9.7
0	2	0	33.3	39.7	-39.7	
0	2	1	25.3	26.2	26.2	
0	2	2	9.9	7.5	7.5	
0	2	3	9.2	7.4	-7.4	
0	3	1	66.3	46.5		-46.5
0	3	2	9.6	7.0		-7.0
0	3	3	6.4	5.6		-5.6
0	3	4		.3		-.3
0	4	0	37.0	30.2	-30.2	
0	4	1	12.6	12.4	12.4	
0	4	2	8.0	8.8	8.8	
0	4	3	4.0	3.8	-3.8	
0	5	1	38.0	38.6		38.6
0	5	2	7.3	5.1		-5.1
0	5	3	20.9	16.4		-16.4
0	6	0	18.1	13.7	-13.7	
0	6	1	16.1	13.9	-13.9	
0	6	2	25.3	20.4	20.4	
0	6	3	5.6	5.3	5.3	
0	7	1	8.0	6.1		6.1
0	7	2		3.0		3.0
0	7	3		2.4		-2.4
0	8	0	11.7	10.4	-10.4	
0	8	1	13.7	10.8	-10.8	
0	8	2	37.8	36.1	-36.1	
0	8	3	4.0	4.1	4.1	
0	9	1	4.0	3.8		-3.8
0	9	2		1.2		1.2
0	9	3		1.9		-1.9
0	10	0	5.6	3.4	-3.4	
0	10	1	5.6	4.6	4.5	
0	10	2	7.6	7.9	-7.9	
0	10	3		.6	-.6	
0	11	1	6.0	3.3		3.3
0	11	3	5.6	4.2		4.2
0	12	0		.1	.1	
0	12	1	7.6	7.8	7.8	
0	13	1	10.0	7.8		7.8
0	14	0	9.2	8.6	-8.6	
0	14	1		.8	-.8	
0	15	1		1.1		1.1
0	16	0	4.0	4.8	4.8	
1	0	1	57.8	73.4		73.4
1	0	2	9.2	8.3	8.3	
1	0	3	11.2	9.7		-9.7
1	0	4		.1	-.1	
1	1	0	30.1	46.2		-46.2
1	1	1	58.4	60.6	50.2	-33.9
1	1	2	26.3	25.7	2.3	-25.6
1	1	3	9.3	7.0	6.5	2.6
1	1	4		5.0	-2.7	-4.2
1	2	0	25.3	31.9		-31.9
1	2	1	27.3	30.0	-25.9	-15.3
1	2	2	28.9	27.5	-5.1	27.1
1	2	3	8.8	6.2	-6.1	-.7
1	3	0	5.6	6.5		-6.5
1	3	1	29.7	30.0	-29.3	6.3
1	3	2	12.6	12.3	11.4	4.6
1	3	3	10.4	5.4	-5.4	.1
1	3	4		3.6	-3.5	-.9
1	4	0	53.8	69.3		-69.3
1	4	1	25.7	28.9	-23.9	-16.2
1	4	2	21.9	22.5	.9	-22.5
1	4	3	12.1	9.7	-7.6	6.0
1	5	0	12.1	7.8		-7.8
1	5	1	10.8	10.9	10.8	-1.3
1	5	2		4.8	-4.2	-2.6
1	5	3		12.5	12.4	1.0
1	6	0	16.1	18.1		18.1
1	6	1	24.5	24.7	-14.8	-19.7
1	6	2	13.7	12.8	2.3	-12.6
1	6	3	10.4	8.9	-6.2	6.3
1	7	0	19.7	19.2		19.2
1	7	1	11.7	10.8	-7.6	7.7
1	7	2	10.8	9.9	-4.8	8.7
1	7	3	7.2	6.0	-5.2	-3.1
1	8	0	17.7	18.5		18.5
1	8	1	18.1	18.3	-4.1	17.8
1	8	2	5.2	4.7	-.4	-4.7
1	8	3	4.0	5.5	-.6	-5.4
1	9	0	17.7	19.4		19.4
1	9	1	16.1	16.9	-15.8	-6.1
1	9	2	10.8	8.9	.3	8.9
1	10	0	13.7	14.6		-14.6
1	10	1	7.2	8.1	5.6	5.9
1	10	2		.4	-.4	.1
1	11	0		2.5		-2.5
1	11	1	5.6	5.7	5.7	.4
1	11	2		4.5	3.4	2.8
1	12	0		1.7		1.7
1	12	1		4.6	4.2	-1.9
1	12	2	9.6	9.4	-.1	9.4
1	13	0		2.2		2.2
1	13	1		3.8	-3.8	-.4
1	14	0		3.2		3.2
1	14	1		6.1	3.2	-5.2
1	15	0	1.6	1.2		-1.2
1	15	1		1.0		1.0
2	0	0	34.5	57.7	57.7	
2	0	1	49.2	64.2		-64.2
2	0	2	11.5	8.9	-8.9	
2	0	3	13.7	14.4		-14.4
2	0	4	4.8	5.1	5.1	
2	1	0	39.4	49.8	-49.8	
2	1	1	50.9	51.6	1.0	51.6
2	1	2	13.7	12.7	10.3	7.4
2	1	3	13.3	12.9	.5	12.9
2	1	4	2.4	2.8	-.8	-2.7
2	2	0	27.1	24.7	-24.7	
2	2	1	56.2	48.2	46.2	-13.6
2	2	2	19.5	17.6	-17.6	.7
2	2	3	15.3	13.3	-12.2	-5.3
2	2	4	3.2	2.9	-2.9	.5
2	3	0	29.2	24.6	-24.6	
2	3	1	15.0	11.7	.8	-11.7
2	3	2	25.5	23.6	-23.3	-3.4
2	3	3	10.8	10.3	-1.5	10.2
2	3	4	3.2	4.6	-4.3	1.6
2	4	0	23.1	24.8	-24.8	
2	4	1	10.7	10.0	10.0	.4
2	4	2	8.6	8.0	7.7	-2.2
2	4	3		1.4	.9	-1.0
2	4	4	1.6	3.2	-3.2	.5
2	5	0	45.0	42.6	-42.6	
2	5	1	8.8	5.9	-.9	-5.8
2	5	2	18.5	16.5	-14.2	-8.3
2	5	3	7.2	8.2	3.3	-7.5
2	5	4	4.0	5.0	-4.1	2.7
2	6	0		1.0	1.0	
2	6	1	24.1	22.3	-22.2	2.9
2	6	2	22.1	21.4	21.3	1.7
2	6	3	4.0	4.3	4.2	.9
2	7	0	9.2	7.2	7.2	
2	7	1	28.5	26.7	.4	26.7
2	7	2	9.6	9.6	-9.5	1.1
2	7	3	4.8	5.5	-.1	5.5
2	8	0	7.6	7.8	7.8	
2	8	1	28.1	25.1	-13.4	21.2
2	8	2	10.0	9.8	-9.6	-1.8
2	8	3	6.4	8.9	2.9	8.4
2	9	0	8.0	7.7	-7.7	
2	9	1	9.6	7.9	-.6	-7.9
2	9	2	4.0	4.2	1.9	3.8
2	9	3	4.8	4.7	-.5	-4.7
2	10	0	14.1	14.8	14.8	
2	10	1	15.7	13.6	11.6	7.1
2	10	2		2.8	-2.8	.2
2	10	3	3.2	3.6	-2.1	2.9
2	11	0	8.8	8.2	8.2	
2	11	1	7.6	7.6	1.9	-7.4
2	11	2	4.0	4.1	4.0	.7
2	12	0		1.7	1.7	
2	12	1	3.2	3.4	3.3	1.1
2	12	2	2.4	3.6	3.3	-1.5
2	13	0	4.0	4.8	4.8	
2	13	1	2.4	3.2	-1.7	2.7
2	13	2	4.0	4.8	4.6	-1.4
2	14	0	7.2	8.3	-8.3	
2	14	1		.5	-.4	.2
2	15	0	1.6	2.8	2.8	
2	15	1	1.6	2.4	-.3	-2.4
3	0	1	20.3	21.4		21.4
3	0	2		2.4	-2.4	
3	0	3	7.6	6.4		-6.4
3	0	4		.8	.8	
3	1	0	28.1	34.5		-34.5
3	1	1	18.2	16.7	-15.8	-5.6
3	1	2	5.2	5.5	-4.4	-3.4
3	1	3	14.1	12.8	-12.0	4.5
3	1	4	4.0	2.9	-.6	-2.8
3	2	0	5.4	7.8		7.8
3	2	1	22.5	18.9	13.8	12.8
3	2	2	51.4	52.5	5.2	52.2
3	2	3	6.0	5.2	4.3	-2.8
3	2	4	3.2	3.4	-1.3	3.1
3	3	0	18.7	17.8		17.8
3	3	1	40.7	38.5	-37.8	7.0
3	3	2	16.1	14.6	14.6	-.8
3	3	3	9.1	8.3	-8.2	-1.2
3	3	4	4.0	4.7	-4.4	1.7
3	4	0	10.4	7.2		-7.2
3	4	1	38.0	39.9	-30.8	-25.4
3	4	2	6.4	5.8	-4.3	3.9
3	4	3	9.2	10.2	-7.8	6.6
3	4	4	1.6	1.7	1.7	-.2
3	5	0	4.8	1.9		1.9
3	5	1	19.3	17.1	12.5	-11.6
3	5	2	10.0	9.5	-5.1	-8.0
3	5	3	10.4	11.6	11.6	-.4
3	5	4	1.6	3.0	2.9	-.6
3	6	0	52.6	49.1		49.1
3	6	1	10.4	11.0	4.3	-10.1
3	6	2	6.8	6.5	1.2	6.4
3	6	3	2.4	1.8	-.9	1.6
3	6	4	4.0	5.1	-.2	5.0
3	7	0	5.6	3.1		3.1
3	7	1	20.5	18.4	16.3	8.6
3	7	2	7.6	6.7	-4.7	-4.3
3	7	3	4.8	4.9	4.9	
3	7	4		.6	-.1	.6
3	8	0	34.5	27.6		27.6
3	8	1	10.4	7.7	1.4	7.6
3	8	2	3.2	2.1	-.8	-1.9
3	8	3	3.2	2.8	.8	-2.7
3	8	4	2.4	2.8	.1	2.8
3	9	0		1.4		1.4
3	9	1	9.2	8.8	8.6	-1.8
3	9	2	8.4	7.6	-2.5	7.1
3	9	3		1.8	-1.4	-1.2
3	10	0	27.7	28.4		-28.4
3	10	1	12.1	11.2	-5.2	9.9
3	10	2	3.2	3.3	1.7	-2.9
3	10	3	2.4	3.1	-2.0	-2.4
3	11	0		1.3		1.3
3	11	1	10.8	9.5	9.5	.1
3	11	2	3.2	3.6	3.3	-1.5
3	11	3	2.4	3.7	3.7	.1
3	12	0	5.6	6.0		-6.0
3	12	1	4.8	5.3	4.8	-2.3
3	12	2		1.6	-1.2	1.0
3	12	3	2.4	2.7	2.4	1.2
3	13	0		2.0		2.0
3	13	1	1.6	2.7	-2.0	-1.8
3	13	2		.6	-.2	.6
3	14	0	2.4	3.3		-3.3
3	14	1	2.4	3.5	.8	-3.4
3	14	2	1.6	2.0		-2.0
3	15	0		.1		.1
3	15	1	2.4	3.0	-2.9	.8
4	0	0	39.4	48.5	48.5	
4	0	1	8.8	12.5		12.5
4	0	2	17.4	17.1	-17.1	
4	0	3		3.3		-3.3
4	0	4	2.4	2.3	2.3	
4	1	0	35.5	42.4	42.4	
4	1	1	26.5	26.2	13.7	22.3
4	1	2	30.0	23.3	21.9	7.8
4	1	3	12.4	10.9	-2.0	10.7
4	1	4	4.0	4.6	3.9	-2.5
4	2	0	32.7	32.1	-32.1	
4	2	1	34.3	31.1	26.9	15.5
4	2	2	28.1	26.8	-26.8	-.2
4	2	3	15.7	15.1	-6.5	13.7
4	2	4	4.0	4.2	-3.7	2.0
4	3	0	12.3	9.3	9.3	
4	3	1	16.9	15.6	-11.8	10.2
4	3	2	10.7	10.6	8.1	-6.9
4	3	3	12.5	12.8	1.6	12.7
4	3	4	2.4	.9	.6	.7
4	4	0	45.8	48.6	-48.6	
4	4	1	13.1	10.8	6.2	8.8
4	4	2	12.8	13.1	12.2	-4.8
4	4	3	5.6	5.0	-2.8	-4.2
4	4	4	3.2	3.9	-3.7	-1.4
4	5	0		2.8	-2.8	
4	5	1	16.5	13.7	-5.2	12.6
4	5	2	6.4	6.1	2.3	-5.7
4	5	3		1.4	1.3	-.4
4	5	4	2.4	2.7	.9	2.6
4	6	0	23.7	20.3	20.3	
4	6	1	22.9	20.9	-11.1	-17.8
4	6	2	20.9	20.7	20.4	3.6
4	6	3	5.6	5.0	3.3	-3.7
4	6	4	1.6	2.7	2.7	
4	7	0	30.1	28.2	28.2	
4	7	1	22.1	19.1	-1.3	19.1
4	7	2	10.4	10.6	10.6	.2
4	7	3	3.2	4.1	-.4	4.1
4	7	4	2.4	2.9	2.9	-.4
4	8	0	16.9	13.5	13.5	
4	8	1	14.9	13.2	-13.2	-.2
4	8	2	6.4	5.9	-5.7	1.5
4	8	3	3.2	3.8	3.2	-2.2
4	8	4		1.4		.2
4	9	0	8.4	8.6	-8.6	
4	9	1	9.2	8.1	7.6	-2.8
4	9	2	8.4	7.4	-6.4	3.6
4	9	3	2.4	3.2	-2.2	-2.4
4	9	4	1.6	2.0	-.9	-1.8
4	10	0	17.7	18.2	18.2	
4	10	1	11.7	11.0	6.0	-9.2
4	10	2		1.3	.2	-1.3
4	10	3	2.4	2.7	-2.7	-.5
4	11	0	6.0	6.1	-6.1	
4	11	1	10.0	8.5	-2.7	-8.1
4	11	2	3.2	2.6	-2.2	1.4
4	12	0	2.4	1.3	1.3	
4	12	1	4.8	4.9	4.8	-.8
4	12	2	6.0	5.9	5.9	.6
4	13	0	1.6	1.8	-1.8	
4	13	1	1.6	1.8	.4	-1.8
4	14	0	5.2	7.1	-7.1	
4	14	1	1.6	2.2	.2	2.2
4	15	0	1.6	2.2	-2.2	
5	0	1	38.0	38.6		38.6
5	0	2	4.0	1.1	-1.1	
5	0	3	8.0	8.0		-8.0
5	0	4	3.2	3.1	3.1	
5	1	0	9.1	9.7		9.7
5	1	1	23.3	18.1	16.0	-8.5
5	1	2	20.1	17.5	9.8	14.5
5	1	3	3.2	2.3	-.8	2.1
5	1	4	3.2	2.7	-2.1	1.7
5	2	0	15.5	16.6		-16.6
5	2	1	34.0	29.9	29.9	1.0
5	2	2	20.1	17.7	4.8	17.0
5	2	3	15.7	14.1	14.0	-2.1
5	2	4	4.0	3.7	-3.7	-.5
5	3	0	45.0	47.9		47.9
5	3	1	26.3	24.7	-22.6	-9.9
5	3	2	20.9	19.4	3.5	19.1
5	3	3	6.2	4.8	-4.1	2.5
5	3	4	5.6	5.6	-2.3	5.1
5	4	0	18.5	18.5		-18.5
5	4	1	27.5	25.9	6.5	-25.0
5	4	2	8.8	8.6	-8.6	-.3
5	4	3	8.0	6.7	2.8	6.1
5	4	4	4.0	3.5	2.5	-2.6
5	5	0	26.1	22.3		-22.3
5	5	1	6.8	7.2	5.9	4.0
5	5	2	16.9	15.4	-2.7	-15.2
5	5	3	7.2	8.2	8.0	-1.9
5	5	4	1.6	2.4	-.2	-2.4
5	6	0	18.1	14.4		14.4
5	6	1	24.9	24.4	23.0	-8.1
5	6	2	10.4	8.3	4.6	-6.9
5	6	3	8.0	7.4	6.5	3.7
5	6	4	1.6	1.8	-.9	1.6
5	7	0	9.2	7.1		-7.1
5	7	1	9.2	7.1	1.2	7.0
5	7	2	13.3	11.6	-4.5	-10.7
5	7	3		.4	-.4	-.2
5	7	4	3.2	3.0	2.6	-1.6
5	8	0	17.7	15.0		15.0
5	8	1	16.5	13.5	6.6	11.8
5	8	2	5.6	4.9	-4.1	-2.7
5	8	3	4.0	3.9	1.5	-3.6
5	8	4		1.6	.1	1.6
5	9	0	13.3	13.4		-13.4
5	9	1	4.8	5.1	-5.1	-.6
5	9	2		1.5	.5	1.5
5	9	3	4.0	4.8	-4.8	.3
5	10	0	7.2	6.2		-6.2
5	10	1	13.3	12.3	-10.2	6.9
5	10	2	4.0	3.5	3.4	.7
5	10	3	3.2	3.6	-3.1	-1.8
5	11	0	11.2	10.4		-10.4
5	11	1	6.4	6.1	5.8	2.0
5	11	2	8.4	8.1	1.6	-8.0
5	11	3		1.5	.8	1.2
5	12	0	6.4	5.6		-5.6
5	12	1	4.0	4.3	-2.7	-3.3
5	12	2	4.8	4.4	-.4	4.4
5	13	0	1.6	1.9		1.9
5	13	1		1.4	-1.3	-.5
5	13	2		1.9	1.0	1.6
5	14	0	2.4	1.4		1.4
5	14	1	4.0	4.3	-3.1	-3.1
5	15	0	3.6	4.6		4.6
6	0	0	56.6	66.6	66.6	
6	0	1	13.4	16.2		-16.2
6	0	2	4.8	3.4	3.4	
6	0	3	4.8	4.2		-4.2
6	0	4	6.8	7.2	7.2	
6	1	0		1.0	1.0	
6	1	1	10.2	8.4	6.0	-5.8
6	1	2	19.3	21.6	21.4	3.5
6	1	3	7.6	7.7	-.9	7.6
6	1	4	3.2	3.8	3.0	-2.3
6	2	0	14.2	13.3	13.3	
6	2	1	35.9	33.5	21.9	25.4
6	2	2	8.2	6.9	6.6	-1.9
6	2	3	14.9	13.6	-6.4	11.9
6	2	4	2.4	1.9	1.4	1.3
6	3	0		.6	-.6	
6	3	1	21.7	20.0	-5.9	-19.1
6	3	2	9.6	9.7	9.7	-.5
6	3	3	4.8	5.2	-2.2	-4.8
6	3	4		1.5	-.3	1.5
6	4	0	19.8	19.1	-19.1	
6	4	1	14.5	13.9	8.3	11.1
6	4	2	9.4	7.7	7.6	-1.6
6	4	3	4.4	3.6	-3.0	-2.0
6	4	4	2.4	1.7	-1.6	.5
6	5	0	8.8	7.6	7.6	
6	5	1	25.3	22.3	-1.3	-22.3
6	5	2	6.0	5.8	.2	-5.8
6	5	3	8.0	7.4	3.1	-6.8
6	5	4	2.4	2.4	.9	2.2
6	6	0	18.1	15.8	-15.8	
6	6	1	28.1	27.2	-16.2	-21.9
6	6	2	6.0	6.1	5.3	3.0
6	6	3	7.2	7.7	4.8	-6.0
6	6	4		1.4	-1.3	-.6
6	7	0	29.3	26.8	26.8	
6	7	1	7.6	6.5	-3.9	5.2
6	7	2	6.4	4.9	4.5	1.9
6	7	3	4.8	5.4	.6	-5.5
6	7	4	2.4	3.0	3.0	-.2
6	8	0	4.0	2.9	-2.9	
6	8	1	8.8	7.7	-4.8	6.1
6	8	2	15.3	14.7	-14.6	1.1
6	8	3	2.4	2.5	2.0	1.5
6	9	0	8.8	8.1	-8.1	
6	9	1	5.6	4.8	4.7	-1.1
6	9	2	2.4	3.3	-2.0	2.6
6	9	3	2.4	2.8	-2.3	1.6
6	10	0		.3	-.3	
6	10	1	10.4	8.9	3.7	-8.1
6	10	2	8.8	8.7	-8.7	.3
6	11	0	7.2	5.7	-5.7	
6	11	1		2.2	1.4	1.8
6	12	0		1.6	-1.6	
6	12	1	6.4	6.8	5.8	-3.5
6	13	0		1.2	-1.2	
6	13	1	4.8	4.2	-.5	4.2
6	14	0	2.4	3.1	-3.1	
6	14	1	3.2	3.6	-1.8	3.1
7	0	1	12.9	13.6		13.6
7	0	2	6.2	4.9	4.9	
7	0	3	8.8	8.1		-8.1
7	0	4		1.1	-1.1	
7	1	0	23.5	28.3		-28.3
7	1	1	27.9	26.4	22.5	-13.7
7	1	2	8.8	9.0	6.9	-5.7
7	1	3	7.6	6.2	3.7	5.0
7	1	4	4.0	4.4	-3.0	-3.3
7	2	0	30.5	31.6		-31.6
7	2	1	11.8	10.6	9.0	5.5
7	2	2	11.0	10.0	-.9	10.0
7	2	3	5.6	5.3	5.1	1.5
7	2	4	3.2	3.1	-.8	-2.9
7	3	0	24.1	23.7		23.7
7	3	1	9.6	7.6	7.4	-1.5
7	3	2	8.6	7.8	1.4	7.6
7	3	3	4.8	4.9	4.6	1.5
7	3	4	3.2	2.9	-.6	2.9
7	4	0	37.2	37.2		-37.2
7	4	1	26.8	27.5	-25.1	-11.3
7	4	2	13.7	12.1	-3.3	-11.6
7	4	3	8.8	7.9	-6.8	4.0
7	4	4	3.2	4.3	1.0	-4.1
7	5	0	4.8	2.4		-2.4
7	5	1	10.8	9.7	-9.0	-3.5
7	5	2	12.8	12.0	2.3	-11.8
7	5	3		2.1	2.1	
7	6	0	14.9	7.5		7.5
7	6	1	10.4	10.2	4.8	-9.1
7	6	2	17.7	17.5	.3	-17.5
7	6	3		2.1	-1.2	1.7
7	7	0	6.4	4.2		4.2
7	7	1	15.7	13.1	-6.3	11.4
7	7	2	6.8	7.0	-5.8	4.0
7	7	3	2.4	3.9	-3.5	-1.7
7	8	0	9.6	6.7		6.7
7	8	1	9.2	7.8	3.7	6.9
7	8	2		2.5	1.4	-2.1
7	8	3	2.4	1.7	1.4	-.8
7	9	0	6.4	5.1		5.1
7	9	1	10.0	7.9	-7.5	-2.5
7	9	2	8.8	9.1	2.0	8.9
7	9	3	4.8	5.6	-5.6	-.5
7	10	0	7.3	5.2		-5.2
7	10	1	8.4	6.9	-3.6	5.9
7	10	2		2.4	1.0	2.3
7	10	3	2.4	3.0	-2.0	-2.2
7	11	0	6.4	5.5		-5.5
7	11	1	4.8	4.7	-4.2	-2.1
7	11	2	2.4	2.8	1.3	-2.4
7	12	0		.4		-.4
7	12	1	4.8	4.3	3.8	-2.1
7	12	2	5.6	6.3	-.4	6.2
7	13	0		2.7		2.7
7	14	0	5.6	5.7		5.7
8	0	0	15.7	16.8	16.8	
8	0	1	33.2	35.0		-35.1
8	0	2		5.1	-5.1	
8	0	3	10.0	9.1		-9.1
8	1	0		3.1	3.1	
8	1	1	11.0	10.8	10.1	-3.8
8	1	2	17.9	16.9	16.3	4.6
8	1	3	5.6	4.5	-3.0	3.3
8	2	0	16.3	15.9	15.9	
8	2	1	23.9	18.6	18.0	-4.7
8	2	2		.7	-.7	.1
8	2	3	5.6	3.9	-3.5	-1.7
8	3	0	24.1	22.6	-22.6	
8	3	1	8.3	7.2	-6.1	-3.7
8	3	2	13.9	12.4	-12.4	-1.4
8	3	3		2.2	1.9	1.1
8	4	0	20.1	20.8	-20.8	
8	4	1	7.8	5.7	5.3	2.2
8	4	2	11.5	10.7	10.0	-4.0
8	4	3		2.4	-2.3	-.7
8	5	0	34.5	32.7	-32.7	
8	5	1	12.5	11.9	-9.8	-6.7
8	5	2	16.5	14.6	-13.8	-4.7
8	5	3	4.0	4.0	3.3	-2.2
8	6	0	5.6	3.6	-3.6	
8	6	1	11.2	10.3	-10.3	1.0
8	6	2	4.8	4.2	1.8	3.8
8	6	3	4.8	4.7	4.0	-2.6
8	7	0	22.4	19.0	19.0	
8	7	1	4.8	3.7	3.5	1.3
8	7	2		1.0	-.9	.1
8	7	3	3.2	3.6	-.5	-3.6
8	8	0	4.8	3.4	3.4	
8	8	1	15.7	14.3	-5.5	13.2
8	8	2		3.4	-3.4	-.1
8	8	3	8.8	7.7	2.0	7.4
8	9	0	8.8	5.8	-5.8	
8	9	1	7.2	4.7	4.7	.4
8	9	2	5.6	4.2	-2.6	3.3
8	10	0		3.3	3.3	
8	10	1	6.4	5.0	3.3	3.8
8	10	2	7.2	6.2	-6.2	-1.1
8	11	0		1.1	1.1	
8	11	1		1.9	.1	-1.9
8	11	2	4.0	3.2	3.0	-1.1
8	12	0	3.2	3.0	-3.0	
8	12	1	4.0	4.1	4.1	-.4
8	13	0	4.8	4.6	4.6	
8	13	1	2.4	2.4	-2.3	.8
9	0	1	9.4	9.3		9.3
9	0	2	4.8	3.6	3.6	
9	0	3	4.0	3.3		-3.3
9	0	4		1.0	-1.0	
9	1	0	27.1	30.2		-30.2
9	1	1	8.6	9.1	5.6	-7.2
9	1	2	10.4	9.0	6.3	-6.5
9	1	3	8.0	7.2	-6.3	-3.5
9	1	4	4.0	3.6	.3	-3.6
9	2	0	9.6	10.8		-10.8
9	2	1	10.2	10.5	2.6	10.2
9	2	2	10.7	9.8	.6	9.8
9	2	3	4.8	4.6	4.4	-1.5
9	2	4		.4		-.4
9	3	0	11.5	13.5		13.5
9	3	1	8.8	9.4	-7.1	-6.2
9	3	2		3.2	3.0	1.3
9	3	3		1.5	.7	1.3
9	3	4	2.4	2.2	-1.5	1.6
9	4	0	10.4	11.5		11.5
8	4	1	31.1	32.0	-25.0	-20.0
9	4	2	12.8	12.2	-1.5	12.1
9	4	3	9.2	9.3	-8.0	4.8
9	4	4		1.7	.8	1.4
9	5	0	3.2	3.0		3.0
9	5	1		.1		-.1
9	5	2	11.6	9.9	-2.8	-9.7
9	5	3	3.2	2.4	2.2	-.9
9	6	0	10.4	8.9		8.9
9	6	1		.7	-.7	-.2
9	6	2	4.0	3.3	-1.3	-3.1
9	6	3	3.2	3.1	-3.0	-.1
9	7	0	6.4	4.9		4.9
9	7	1	10.8	9.9	7.1	6.8
9	7	2	4.8	4.5	-.8	4.4
9	7	3	4.0	3.9	3.5	-1.9
9	8	0	9.6	8.0		8.0
9	8	1	5.6	3.8	2.3	3.0
9	8	2		3.1	1.0	-2.9
9	9	0	6.4	4.7		4.7
9	9	1	4.8	5.1	5.1	-.2
9	9	2	11.2	9.9	-1.2	9.8
9	10	0	3.2	3.8		-3.8
9	10	1	7.2	7.3	-4.3	5.8
9	11	0		1.3		-1.3
9	11	1	4.0	2.9	.9	-2.7
9	12	0	8.0	8.3		-8.3
9	12	1	5.6	5.2	4.2	-3.0
9	13	0	3.2	3.3		3.3
10	0	0	9.2	10.0	-10.0	
10	0	1	16.1	15.4		-15.4
10	0	2	16.9	15.9	-15.9	
10	0	3		3.2		-3.2
10	1	0	5.6	4.3	4.3	
10	1	1	10.0	9.1	8.0	-4.3
10	1	2	10.4	10.1	9.8	2.2
10	1	3		2.3	-1.1	2.0
10	2	0		.9	.9	
10	2	1	14.9	14.1	11.6	8.1
10	2	2	12.5	10.7	-9.8	-4.3
10	2	3	5.6	4.4	-1.6	4.1
10	3	0	15.7	13.8	-13.8	
10	3	1	14.1	12.6	-4.8	11.6
10	3	2	6.8	6.7	6.7	-1.1
10	3	3	6.4	7.1	.5	7.1
10	4	0	19.3	21.2	-21.2	
10	4	1	5.6	5.0	2.1	4.6
10	4	2	8.8	7.7	7.6	-.7
10	5	1	16.9	13.7	-5.4	12.6
10	5	2	8.0	7.3	-6.7	-2.9
10	6	0		4.8	4.8	
10	6	1	11.2	11.4	-5.7	-9.9
10	8	0	11.2	12.7	12.7	
10	10	0	7.2	8.5	8.5	
11	0	1	5.6	4.4		4.4
11	0	2		3.7	3.7	
11	0	3	4.8	4.3		-4.3
11	1	0	7.2	3.5		-3.5
11	1	1	8.4	7.5	-6.8	-3.1
11	1	3	5.6	4.6	-4.6	.2
11	2	0	12.5	9.9		-9.9
11	2	1	11.2	10.7	9.7	4.5
11	2	2	7.2	6.6	.8	6.6
11	2	3	5.6	6.7	6.7	-.3
11	3	0	15.3	20.5		20.5
11	3	1	12.1	12.6	2.5	-12.4
11	3	2	6.8	6.9	.7	6.8
11	3	3		3.8	2.0	3.2
11	4	0	6.4	5.4		5.4
11	4	1	8.0	8.6	2.3	-8.3
11	4	2	10.0	8.8	-3.5	8.1
11	5	0		3.3		-3.3
11	5	1	8.8	9.0	-6.4	6.4
11	6	0	8.0	9.8		9.8
11	6	1	8.0	7.8	6.9	-3.6
12	0	0		3.4	3.4	
12	0	1		.5		.5
12	0	2	8.4	7.8	-7.8	
12	0	3	4.0	3.4		3.4
12	1	0	6.8	8.0	8.0	
12	1	1	10.4	9.7	6.4	-7.2
12	1	2	7.2	7.8	7.7	.5
12	2	0	8.4	9.2	9.2	
12	2	1	13.3	11.6	7.4	8.9
12	2	2	5.6	5.3	4.9	-2.0
12	2	3	4.0	4.1	-2.1	3.5
12	3	0		4.1	-4.1	
12	3	1	4.8	4.1	-3.8	-1.6
12	3	2	9.2	10.0	10.0	0.4
12	3	3		1.9	1.8	-.4
12	4	0		4.7	-4.7	
12	4	1		5.2	2.8	4.4
12	5	1	7.2	7.3	-6.9	-2.4
12	6	0	8.8	11.4	-11.4	
12	6	1	8.8	8.8	-6.7	-5.7
12	8	0	3.2	6.1	6.1	
13	0	1	6.8	6.8		6.8
13	0	2		2.1	2.1	
13	1	0		6.5		-6.5
13	1	1	7.2	6.8	5.8	-3.5
13	1	2	4.0	5.1	3.1	4.1
13	2	0	13.7	15.7		-15.7
13	2	1		3.9	3.9	-.2
13	2	3		3.8	3.8	0.5
13	3	0	5.2	7.1		7.1
13	3	1	8.0	8.7	6.6	-5.8
13	3	2		.2	-.1	.1
13	4	0	4.0	4.2		-4.2
13	4	1	5.6	5.1	-3.8	-3.3
13	5	0	6.4	7.7		7.7
13	5	1	7.2	6.4	-6.1	1.9
13	6	0	2.4	2.2		-2.2
14	0	0	7.2	7.2	7.2	
14	0	1	8.8	8.5		-8.5
14	0	2		2.7	-2.7	
14	1	0		5.0	-5.0	
14	1	1	9.2	9.0	4.4	-7.8
14	2	0	6.0	6.6	6.6	
14	2	1		4.4	4.3	-.9
14	3	0	9.6	8.9	-8.9	
14	3	2		1.0	.9	-.5
15	1	0	9.6	10.5		-10.5
15	2	0	5.6	6.6		-6.6
11	5	2	9.6	9.0	-0.5	-9.0

now lie within the range 0·95 to 1·05 as against 0·72 to 1·07 from the isotropic refinement.

The final atomic coordinates in unit-cell fractions and the bond lengths are given in Table 4. The equation of the plane passing through atoms S_1, S_3 and C_4 is $X+0{\cdot}836Y-2{\cdot}463Z = 1{\cdot}392$; the deviations out of that plane for the other atoms are S_2, −0·035; C_3, 0·039; C_5, 0·003; C_6, 0·006 Å; (c.f. $X+0{\cdot}839Y-2{\cdot}485Z = 1{\cdot}379$ and 0·030, −0·023, 0·022, −0·011, respectively, from the isotropic differential synthesis

Table 3. *Observed and calculated peak heights and curvatures in* e.Å^{-3} *and* e.Å^{-5}

		ϱ	Ahh	Akk	All	Akl	Ahl	Ahk
S_1	obs.	20·59	−179·72	−165·82	−137·94	−6·46	3·69	−10·58
	calc.	20·02	−175·00	−161·13	−133·94	−5·88	3·57	−10·05
S_2	obs.	21·57	−198·06	−169·83	−136·13	−0·55	−2·33	−2·22
	calc.	20·96	−191·38	−164·76	−131·93	−0·38	−2·14	−2·07
S_3	obs.	19·41	−167·70	−149·31	−128·58	1·09	−9·19	−15·41
	calc.	19·00	−163·88	−146·04	−125·34	1·34	−8·16	−14·93
C_5	obs.	5·99	−50·93	−41·67	−30·03	−0·06	−2·81	1·44
	calc.	5·95	−50·51	−41·46	−29·89	−0·00	−3·08	1·12
C_4	obs.	6·21	−48·14	−44·62	−43·13	1·64	−1·42	0·08
	calc.	6·58	−50·47	−46·71	−44·81	2·01	−1·64	−0·11
C_3	obs.	6·59	−48·37	−46·95	−38·65	4·26	2·47	0·74
	calc.	6·35	−47·15	−44·98	−37·21	4·22	2·66	0·85
C_6	obs.	4·48	−29·65	−28·07	−20·32	1·23	−2·14	3·50
	calc.	4·24	−28·30	−26·79	−19·34	1·03	−1·88	3·18

Table 4. *Fractional atomic coordinates and bond lengths*

	x	y	z
S_1	0·1511	0·4420	0·5009
S_2	0·0112	0·3897	0·2861
S_3	−0·0311	0·1788	0·0083
C_3	0·0538	0·2601	0·1846
C_4	0·1605	0·2369	0·3017
C_5	0·2145	0·3206	0·4528
C_6	0·2141	0·1311	0·2602

S_1–S_2	2·047 Å	C_3–S_3	1·627 Å
S_2–C_3	1·747	C_3–C_4	1·432
S_1–C_5	1·713	C_4–C_5	1·384
		C_4–C_6	1·483 Å

analysis). This is very close to the 'best' plane through all the atoms, $X + 0 \cdot 849\,Y - 2 \cdot 470\,Z = 1 \cdot 429$.

Computation times on a basic IBM 650

(A) *Structure factors with anisotropic temperature factors*

In an anisotropic refinement the structure factors must be computed either in the general form, i.e. $P1$ or $P\bar{1}$, or in a special modified form (e.g. Rollett & Davies, 1955). In this program we use the general form and therefore have 28 atoms of two kinds in $P1$. The symmetry transformations for the temperature factors were obtained from the tabulation of Trueblood (1956). The calculations were carried out at the rate of 20 sec./structure factor and the total calculation for 672 reflexions required 3·75 hours. The full capacity of the program is fifty atoms of eight different kinds.

(B) *Differential synthesis*

This program computes electron densities, slopes and curvatures at selected points, close to the atomic maxima, for the observed and calculated Fourier syntheses and solves the equations for the positional parameter shifts, at the rate of 28 minutes per atom with 672 reflexions.

(C) *Anisotropic temperature factor refinement*

This computes the summations for Cruickshank's

equations (3·7) and (3·9) by means of which, using equation (3·10), the shift in thermal parameters is calculated from the differences in the curvatures of the atoms in the observed and calculated syntheses. Since these sums may change only slightly during the course of the refinement it is possible in practice to compute them once only. If some of the parameter shifts are large however, this may prolong the convergence of the refinement. In this analysis, we computed the summations in going from cycle I to II and again from II to III, using the latter values for the remainder of the cycles where the shifts were small. With 7 atoms and 672 reflexions in $P2_12_12_1$, the computation times were 2·5 hours for isotropic to anisotropic, I → II, 7·7 hours for anisotropic to anisotropic, II → III.

The programs maintain five-figure accuracy throughout. These times have been reduced by about 20% with small modifications in the programs to employ indexing accumulators and magnetic core storage.

Comparison with the previous isotropic analyses

The first refinement procedure used on this structure was the least squares IBM 704 program of Friedlander, Love & Sayre (1955), which was carried through five cycles until the coordinate and isotropic thermal parameter shifts were negligible. Because the results were 'suspect' for reasons discussed in the previous paper, (Kehl & Jeffrey, 1958), a differential Fourier synthesis calculation was carried out with identical data and some further parameter shifts were obtained. These gave a more acceptable set of bond lengths for the molecule and were favored in the earlier paper as the best refinement solution obtainable at the isotropic stage.

The shifts to the final parameters, given by the anisotropic refinement, from those of the isotropic least squares and the isotropic differential synthesis results are shown in Table 5. These results are interesting in as much as they show that the least-squares coordinates were the slightly better of the

Table 5

Shifts to final parameters in Å from

	Isotropic least squares				Isotropic differential syntheses			
	Δx	Δy	Δz	Mean	Δx	Δy	Δz	Mean
S_1	0·0001	0·0086	0·0047		0·0010	0·0055	0·0111	
S_2	0·0047	0·0002	0·0070	0·0040	0·0014	0·0011	0·0119	0·0051
S_3	0·0023	0·0035	0·0045		0·0026	0·0094	0·0018	
C_3	0·0277	0·0232	0·0322		0·0009	0·0212	0·0254	
C_4	0·0162	0·0218	0·0357	0·0291	0·0047	0·0276	0·0043	0·0168
C_5	0·0321	0·0418	0·0363		0·0236	0·0269	0·0192	
C_6	0·0135	0·0648	0·0042		0·0129	0·0146	0·0208	

two for the sulphur atoms but were considerably poorer for the carbon atoms. This appears contrary to the effect of weighting, since the $1/f$ weights on the Fourier terms, as compared with the least squares, should tend to suppress the influence of the higher order reflexions for which the sulphur contributions will be relatively the more dominant. An alternate explanation is the effect of omission of the least-squares cross-terms in a structure in which the light and heavy atoms are associated rather closely in a compact molecule undergoing thermal motion of comparatively large amplitude. This would imply that the isotropic least-squares refinement had not completely converged and it is relevant to note that in the last two cycles of the least-squares computations the isotropic temperature factors were all changing in the same positive sense by magnitudes on average as big as in the previous cycle ($\Delta B \sim 0\cdot1$), although the coordinate shifts were less than 0·005 Å.

Discussion of the structure

The bond lengths and bond angles are shown in Fig. 1; the values in parenthesis are those obtained from the
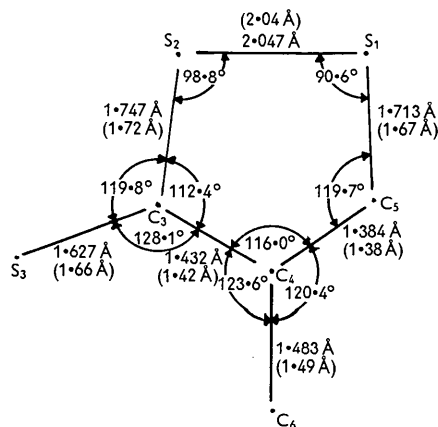
Fig. 1. Structure of the $C_4H_4S_3$ molecule, showing the bond angles and bond lengths.

differential synthesis isotropic analysis. The mean standard deviations of the bond lengths computed by Cruickshank's (1949) method are S–S, 0·007 Å; S–C (ring), 0·017 Å; C–C (ring), 0·024 Å; C–CH₃, 0·035 Å.

As compared with the results of the isotropic analysis, the largest difference, 0·04 Å in S_1–C_5, was less than 2·5 times the standard deviation of the final analysis, and the difference in C–C bonds was less than the standard deviations. Obviously, for the determination of molecular dimensions and bond lengths, the law of diminishing returns has been very much in operation. It is however, gratifying that, with the exception of the C–CH₃ bond, the small changes in bond lengths are all in directions to conform more closely with predictions from chemical theory and observations on related structures. Thus, the S_2–C_3 and S_1–C_5 lengths of 1·75 and 1·71 Å are closer to the values reported from structures in which these bonds occur in similar molecular environments, e.g. thiophthen, II, 1·72, 1·74 Å, (Cox, Gillot & Jeffrey, 1949); β-isoprene sulphone, III, 1·76, 1·74 Å, (Jeffrey, 1951); thiophene, IV, 1·74 Å, (Schomaker & Pauling, 1939); thianthrene, V, 1·74, 1·75, 1·76, 1·78 Å, (Lynton & Cox, 1956; Rowe & Post, 1958).

Similarly the thione bond length, C_3–S_3, 1·63 Å, is now closer to predictions for the double bond length. The discussion in terms of valence bond representation is unchanged from that presented in the earlier paper, (Kehl & Jeffrey, 1958).

II.   III.   IV.

V.
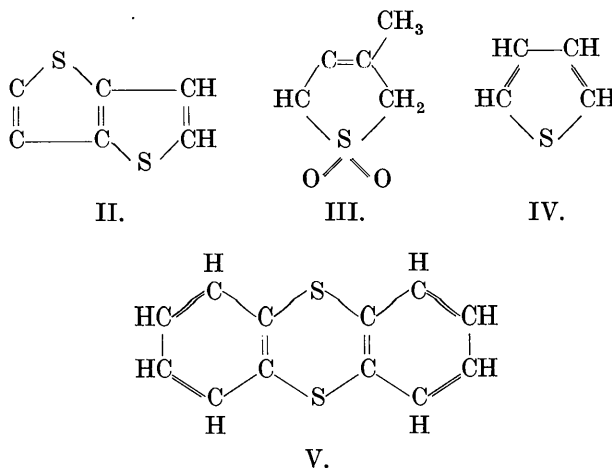
It is interesting to note the comparatively narrow range of bond lengths which are reported for the heterocyclic five membered rings which have in common only that they contain both sulphur and con-

jugated carbon atoms. For compounds I, II, III and IV, the S–C bond lengths lie between 1·72 and 1·76 Å. This is significantly shorter than the well-established C–S single bond length and correspond to bond orders between 1·5 and 1·2 depending somewhat on how one choses to relate order to length (Cox & Jeffrey, 1951).

The C–C bond lengths also show a similar generalization:

Compound	I	II	III	IV
Formal single	1·43	1·41	1·47	1·44
Formal double	1·38	1·36	1·38	1·35

The differences in the lengths of the formal double bonds are certainly within the experimental errors of the analyses and it is questionable whether there are significantly observed differences among the formal single bond lengths. There is also uniformity in the stereochemistry of the five membered ring in that it is planar, within experimental error, and the angles subtended at the sulphur atoms are 95° within ±4°.

Even with the increased precision of this further analysis, however, some of the interesting fine details of the bond length results can only be discussed in terms of 'possible significance'.

The S–S bond is quite accurately measured and agrees so well with many other single bond measurements that it must be described as a pure σ-bond, despite the conjugation throughout the rest of the five membered ring. Since 1·82 Å is a well established C–S single bond length (Cox & Jeffrey, 1951; Abrahams, 1956), the C–S bonds in this molecule are significantly shorter, presumably due to π-character arising from interaction between the d-orbitals of the sulphur atoms and the p-orbitals of the adjacent carbons. The small difference of 0·035 Å between S_1–C_5 and S_2–C_3 is suggestive in that it is associated with adjacent conjugated C–C bonds which are respectively donor and acceptor, but it is too small to be significant.

The thione bond length is so close to the somewhat indeterminate C–S double bond length (e.g. 1·61 Å, Abrahams, 1956) that, for the present, it represents one of the more accurately measured values for this type of bond.

Taking 1·545 and 1·334 Å (c.f. Bastiansen, Hedberg & Hedberg, 1957; Bartell & Bonham, 1957), respectively as single and double carbon lengths and using a Coulson type of bond length/order relationship (Coulson, 1952), the C_3–C_4 and C_4–C_5 bonds have total bond orders of 1·45 and 1·7 respectively. The C–CH$_3$ bond length presents a special problem in that it is associated with the abnormally large thermal parameters of the methyl carbon which is discussed in the next section.

The thermal motion of the methyl carbon atom (C_6)

The results of the anisotropic refinement confirm the observation made at the isotropic stage that the ap-

parent r.m.s. amplitude of vibration of the methyl carbon atom is greater than that of the ring carbon atoms, particularly in the z direction, i.e. 0·41 Å as compared with 0·28 Å for C_3, for example.

There appear to be two interpretations of this observation; one is that the apparent thermal effect is real and at least part of the bond shortening, i.e. 1·48 vis-a-vis 1·54 Å, can be accounted for in consequence, (Cruickshank, 1956b); the other is that it arises from an attempt by the anisotropic refinement procedure to fit the electron distribution of the methyl group with an 'anisotropically spread' carbon atom.

To test the latter possibility we replaced the C_6 scattering factor by one with thermal parameters equal to the mean of those of the carbon atoms in the ring and included the scattering from the three hydrogen atoms. It was assumed that the methyl hydrogen atoms were rotating unhindered about the C–C bond with C–H = 1·09 Å and the tetrahedral angles, so that

$$f = 3f_h \cdot J_0\{4\pi/\lambda \cdot (1\cdot03) \cdot \sin\theta \cdot \sin\psi\}$$

where ψ is the angle between the reflecting plane and the plane containing the hydrogen atoms.

The refinement cycles were then continued to give the results shown in Table 6. In two cycles the shifts

Table 6. Positional and thermal parameters for methyl carbon atom

Col. I, terminal cycle excluding hydrogens (same as final column, Table 1).
Col. II, parameters assuming C_6 has same thermal motion as ring carbon atoms.
Col. III, first cycle including the hydrogen atom contributions (free rotation).
Col. IV, second cycle including the hydrogen atom contributions (free rotation).
Col. V, first cycle including the hydrogen atom contributions (fixed orientation).

	I	II	III	IV	V
X	0·2141	—	0·2124	0·2132	0·2128
Y	0·1311	—	0·1311	0·1315	0·1313
Z	0·2601	—	0·2633	0·2628	0·2622
$\sigma(X)$	0·0023	—	—	0·0022	0·0023
$\sigma(Y)$	0·0022	—	—	0·0022	0·0022
$\sigma(Z)$	0·0085	—	—	0·0080	0·0088
B_{11}	7·13	3·35	6·41	6·59	6·35
B_{22}	6·20	4·88	5·12	5·24	5·46
B_{33}	12·98	5·73	12·18	11·69	12·67
B_{12}	1·47	0·39	1·35	1·33	1·47
B_{23}	−2·69	0·73	−2·95	−2·89	−3·08
B_{31}	1·09	−0·05	0·83	1·05	0·67
R	0·126	0·132	0·120	0·119	0·126

became small and the thermal parameters reverted to values close to the original. The overall change in thermal parameters was less than the standard deviations calculated by Cruickshank's method (1956a). The change in positional parameters was less than one third the standard deviations. The agreement index improved from 0·126 to 0·119, but there was negligible change in the standard deviations.

In view of the interpretation of this 'thermal effect', which is presented below, we also considered the case with the methyl group 'hindered' at the position of minimum repulsion between the hydrogens and the thione sulphur atom. Following the same procedure as described in the preceding paragraphs with the hydrogens in fixed positions (i.e. the one furthest from the sulphur in the plane of the molecule), the first refinement cycle reproduces the original anisotropy of the C_6 atom in much the same way as before; c.f. columns III and V in Table 6. A second cycle of refinement was not computed in this case.

We conclude therefore that, as far as we can judge from this analysis alone, the relatively large thermal parameters of the methyl group is a real effect and not an artifice arising from the model used in the refinement procedure. We have not been able to find reference to any other detailed analysis in which one might expect a similar observation.

It is difficult to believe that the thermal vibration of the substituent methyl carbon atom is appreciably greater than that of the rest of the molecule. The most plausible explanation of this result is that the methyl group is statistically displaced above or below the plane of the molecule by about 0·1 Å due to the non-bonding interaction of the thione sulphur atom in the same molecule, at the unusually close distance of 3·23 Å.

A general description of the relative orientation of the molecules and a listing of intra-molecular distances was given in the earlier paper. The changes in positional parameters resulting from the anisotropic refinement are such that the maximum correction to this list of distances is 0·04 Å. In comparison with our present theoretical knowledge concerning the quantitative details of non-bonded atomic interactions, these differences are negligible.

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