The effect of the thermal motion on the tetrahedral bond angles, for the case of this model, would be small. On the other hand the effects on the Si–O–Si angles would require a knowledge of how the tetrahedra are vibrating relative to each other, which is not available. In any event, it can be qualitatively seen that since the time average values of these angles are so large, almost any type of correlated or noncorrelated motion will cause their instantaneous values to be lower and thus more nearly equal to those found in the room temperature structures quoted above.

## Summary

The structure of the Steinbach tridymite at 220°C is distorted relative to the ideal high-tridymite structure. The distortion consists of a twisting of pairs of tetrahedra about the *a* axis such that tetrahedra joined in the *c*-axis direction are alternately displaced in the positive and negative direction of the *b* axis. The amount of the twist, about 8°, causes the centers of the tetrahedra to be displaced by about 0·2 Å. The atoms show strong thermal motion, especially oxygen atoms in the directions roughly normal to the silicon–oxygen bonds. The tetrahedra are very nearly regular and the interatomic distances (and perhaps also the angles) are not too different from those reported for room-temperature structures, provided the thermal motion is taken into account.

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# The Crystal and Molecular Structure of 2,5-Dimethyl-2,5-*endo*-thio-1,4-dithiane

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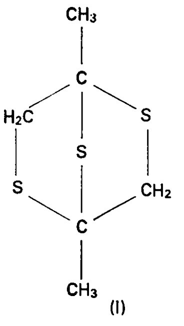
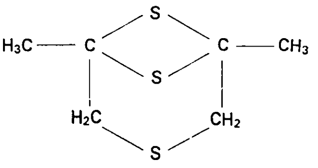
The product $C_6H_{10}S_3$, formed when an alcoholic solution of chloroacetone saturated with hydrogen chloride is treated with hydrogen sulphide has been examined by X-ray single-crystal techniques and shown to have the structure 2,5-dimethyl-2,5-*endo*-thio-1,4-dithiane. The crystals are monoclinic, space group $P2_1/c$, with $a=10{\cdot}970$, $b=6{\cdot}371$, $c=12{\cdot}129$ Å and $\beta=91{\cdot}6°$. The diffraction data were measured using an on-line, automatic, computer-controlled film scanner. Positional and anisotropic thermal parameters of the carbon and sulphur atoms and positional and isotropic thermal parameters of the hydrogen atoms were refined to give a final $R$ value of 0·044.

## Introduction

The reaction between an alcoholic solution of chloroacetone saturated with hydrogen chloride and hydrogen sulphide gives the product $C_6H_{10}S_3$. There has been considerable discussion as to the structure of this product, and several different models have been proposed for it (Rappe & Gustafsson, 1967). Böhme, Pfeiffer & Schneider (1942) isolated the substance and proposed the structure 2,6-dimethyl-2,6-*endo*-thio-1,4-dithiane (II). Brintzinger & Ziegler (1948) reported that, from the reaction of chloroacetone, hydrogen sulphide and hydrogen chloride, they had isolated bis-thioacetonyl sulphide; however, Böhme & Schneider (1949) maintained that this product and the one previously reported by them were identical. On the basis of independent experiments, Hromatka & Engel (1948) suggested that the structure was 2,5-dimethyl-2,5-*endo*-thio-1,4-dithiane (I). More recently, Olsson (1966) attempted to resolve the dilemma using nuclear magnetic resonance techniques; however, no clear solution to the problem could be obtained. An X-ray analysis was therefore undertaken and the correct structure was established as that shown in (I).


(I)


(II)

## Experimental

### *Crystal data*

$C_6H_{10}S_3$, 2,5-dimethyl-2,5-*endo*-thio-1,4-dithiane
Monoclinic, space group $P2_1/c$
$a = 10{\cdot}970 \pm 0{\cdot}010$, $b = 6{\cdot}371 \pm 0{\cdot}006$, $c = 12{\cdot}129 \pm 0{\cdot}010$ Å, $\beta = 91{\cdot}6° \pm 0{\cdot}3°$
($\lambda = 1{\cdot}5418$ Å)
$V = 847{\cdot}4$ Å$^3$
$Z = 4$, $D_m = 1{\cdot}41$ g.cm$^{-3}$, $D_x = 1{\cdot}397$ g.cm$^{-3}$
Absent spectra $0k0$, $k$ odd, $h0l$, $l$ odd
$\mu = 69{\cdot}75$ cm$^{-1}$ for $\lambda = 1{\cdot}5418$ Å.

Crystals suitable for X-ray diffraction studies were obtained by evaporation of an aqueous alcoholic solution of $C_6H_{10}S_3$. The crystals formed as flat plates with their shortest dimension parallel to the *a* axis. Two samples with dimensions $0{\cdot}048 \times 0{\cdot}525 \times 0{\cdot}262$ mm and $0{\cdot}048 \times 0{\cdot}215 \times 0{\cdot}170$ mm were selected for data collection about the *b* and *c* axes respectively. Since the crystals were volatile (m.p. 50 °C) and unstable at room temperature they were sealed in thin walled glass capillaries. Multifilm equi-inclination Weissenberg techniques with Cu $K\alpha$ radiation were used to collect intensities on layers 0 to 4 about the *b* axis and 0 to 6 about the *c* axis.

The data were estimated with the automatic on-line film scanner in this laboratory (Abrahamsson, 1966*a*). Since this was the first attempt at an accurate three-dimensional structure analysis with the use of this instrument the results were carefully analysed so that sources of systematic errors could be detected and, where possible, eliminated. The film factors for all reflexions occurring on adjacent films within a pack were calculated and the film factor distribution as a function of intensity was evaluated for each film pack. Fig. 1 is a plot of the film factor–intensity distribution for the *h*0*l* films. It can be seen that some systematic errors are present in the low intensity terms. This is due to the method of integration used, which results in an underestimation of the weak reflexion intensities. A later version of the film scanner INDEX program (Abrahamsson, 1966*b*) will employ a new method of intensity integration and this source of error should be eliminated. Non-zero layer plots showed similar distributions, although there was some spot shape dependence at high inclination angles. Film factor–intensity distributions of this type were not only useful as a method of detecting systematic errors in the intensity data, but were also valuable in estimating the linear range of measurement. The plateau in the middle range of the graph indicates that intensities in this region have been reliably estimated and only reflexions falling in this range were used in the following data reduction procedures.

The average normal-beam film factor obtained from the *h*0*l* and *hk*0 zones was 2·93, which is in agreement with the results of Morimoto & Uyeda (1963) for Ilford Industrial G film. This value, with the appropriate angular correction for non-zero levels (Grenville-Wells, 1955), was used to reduce the intensity measurements within a pack to a common scale. Lorentz and polarization and general absorption corrections were applied to all reflexions. The interlayer correlation scales were obtained using the method of Hamilton, Rollett & Sparks (1965). The final set of 710 observed structure factors was derived from 4047 individual measurements. An estimate of the standard deviation in each value of $|F_o|$ was derived from the scaling procedure and was used to calculate individual weights for each reflexion in the final stages of the least-squares refinement. Unobserved reflexions were excluded from the analysis.

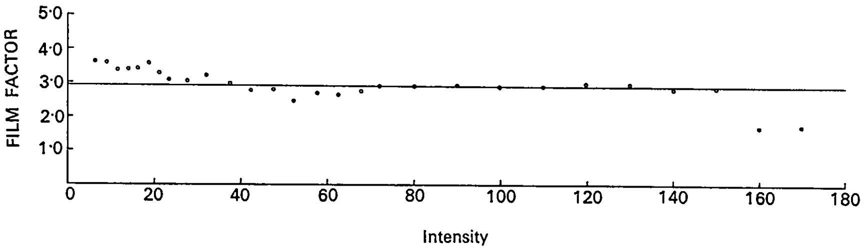


Fig. 1. The distribution of film factors for the *h*0*l* films plotted as a function of intensity. The scale of the intensity values is arbitrary.

## Solution and refinement

The structure solution was obtained by three-dimensional Patterson and Fourier synthesis techniques. A Patterson function, sharpened to correspond to point atoms at rest (Abrahamsson & Maslen, 1963) revealed the positions of the three sulphur atoms. The six carbon atoms of the structure were readily located from a three-dimensional sulphur-phased Fourier synthesis.

The structure refinement was carried out by the block diagonal least-squares method. Reflexion weights were initially derived from the function

$$w=1/(1+[(|F_o|-8|F_{\min}|)/5|F_{\min}|)]^2)\;.$$

However, in the final stages of the refinement individual

Table 1. *Observed and calculated structure factors*

The values in the Table have been multiplied by 100.

| H | K | L | FOBS | FCALC |
|---|---|---|---|---|
| 0 | 0 | 2 | 8807 | -8958 |
| 0 | 0 | 4 | 1809 | -1807 |
| 0 | 0 | 6 | 2775 | -2719 |
| 0 | 0 | 8 | 5306 | 5461 |
| 0 | 0 | 10 | 3577 | -3535 |
| 0 | 0 | 14 | 1195 | -1265 |
| 0 | 1 | 1 | 4981 | -5630 |
| 0 | 1 | 2 | 853 | 835 |
| 0 | 1 | 3 | 4226 | 4271 |
| 0 | 1 | 4 | 869 | 877 |
| 0 | 1 | 5 | 983 | 985 |
| 0 | 1 | 6 | 2700 | 2703 |
| 0 | 1 | 7 | 2873 | -2837 |
| 0 | 1 | 13 | 894 | 1035 |
| 0 | 2 | 1 | 6316 | 6755 |
| 0 | 2 | 2 | 2841 | 2786 |
| 0 | 2 | 3 | 2908 | 2818 |
| 0 | 2 | 4 | 4373 | -4430 |
| 0 | 2 | 5 | 3471 | -3466 |
| 0 | 2 | 6 | 4324 | 4295 |
| 0 | 2 | 7 | 900 | -985 |
| 0 | 2 | 8 | 2303 | -2212 |
| 0 | 3 | 2 | 2640 | -2663 |
| 0 | 3 | 4 | 1884 | 1876 |
| 0 | 3 | 5 | 2313 | -2268 |
| 0 | 3 | 6 | 2026 | 2061 |
| 0 | 3 | 7 | 633 | 810 |
| 0 | 3 | 9 | 1844 | 1871 |
| 0 | 3 | 13 | 688 | -881 |
| 0 | 4 | 1 | 3849 | 3839 |
| 0 | 4 | 2 | 2650 | -2673 |
| 0 | 4 | 3 | 1182 | -1176 |
| 0 | 4 | 4 | 3820 | 3821 |
| 0 | 4 | 5 | 1149 | -1130 |
| 0 | 4 | 6 | 613 | -690 |
| 0 | 4 | 7 | 1278 | -1289 |
| 0 | 4 | 9 | 1331 | 1399 |
| 0 | 4 | 10 | 1020 | -1049 |
| 0 | 4 | 11 | 643 | -738 |
| 0 | 4 | 12 | 1494 | 1432 |
| 0 | 5 | 2 | 1023 | -1110 |
| 0 | 6 | 2 | 859 | 734 |
| 1 | 0 | -12 | 1140 | 1167 |
| 1 | 0 | -10 | 849 | 1095 |
| 1 | 0 | -8 | 2011 | -2037 |
| 1 | 0 | -4 | 2936 | 2843 |
| 1 | 0 | -2 | 9224 | 8568 |
| 1 | 0 | 2 | 9209 | -8895 |
| 1 | 0 | 4 | 1684 | -1661 |
| 1 | 0 | 6 | 3942 | 3879 |
| 1 | 0 | 8 | 3152 | -3148 |
| 1 | 0 | 10 | 1053 | -1195 |
| 1 | 0 | 14 | 715 | 1019 |
| 1 | 1 | -13 | 694 | -869 |
| 1 | 1 | -12 | 676 | 762 |
| 1 | 1 | -10 | 2200 | -2040 |
| 1 | 1 | -8 | 1746 | 1778 |
| 1 | 1 | -6 | 1726 | -1816 |
| 1 | 1 | -5 | 1333 | -1337 |
| 1 | 1 | -4 | 2816 | 2944 |
| 1 | 1 | -3 | 3117 | 3250 |
| 1 | 1 | -2 | 2374 | -2480 |
| 1 | 1 | -1 | 7860 | -9196 |
| 1 | 1 | 0 | 2377 | 2446 |
| 1 | 1 | 1 | 8047 | 9140 |
| 1 | 1 | 2 | 1016 | 1018 |
| 1 | 1 | 3 | 3915 | 4040 |
| 1 | 1 | 4 | 6636 | 6447 |
| 1 | 1 | 5 | 3113 | -3245 |
| 1 | 1 | 6 | 4169 | -4170 |
| 1 | 1 | 7 | 2295 | -2353 |
| 1 | 1 | 9 | 3911 | 3948 |
| 1 | 1 | 12 | 1220 | 1236 |
| 1 | 2 | -11 | 1216 | 1321 |
| 1 | 2 | -10 | 991 | -994 |
| 1 | 2 | -9 | 1109 | 1071 |
| 1 | 2 | -8 | 797 | 791 |
| 1 | 2 | -7 | 940 | -935 |
| 1 | 2 | -6 | 1700 | 1710 |
| 1 | 2 | -5 | 3582 | -3554 |
| 1 | 2 | -4 | 1262 | -1268 |
| 1 | 2 | -2 | 619 | -607 |
| 1 | 2 | -1 | 1743 | 1746 |
| 1 | 2 | 0 | 1747 | 1794 |
| 1 | 2 | 1 | 217 | 390 |
| 1 | 2 | 2 | 2556 | -2693 |
| 1 | 2 | 3 | 2806 | -2903 |
| 1 | 2 | 6 | 1458 | 1462 |
| 1 | 2 | 7 | 2497 | 2603 |
| 1 | 2 | 8 | 1462 | -1600 |
| 1 | 3 | -12 | 1152 | -1228 |
| 1 | 3 | -9 | 1307 | 1315 |
| 1 | 3 | -8 | 1672 | -1725 |
| 1 | 3 | -7 | 2818 | -2695 |
| 1 | 3 | -6 | 2525 | 2383 |
| 1 | 3 | -4 | 2186 | -2201 |
| 1 | 3 | -3 | 1282 | 1323 |
| 1 | 3 | -2 | 5104 | 5245 |
| 1 | 3 | -1 | 268 | 155 |
| 1 | 3 | 0 | 5722 | -6045 |
| 1 | 3 | 1 | 4471 | -4768 |
| 1 | 3 | 2 | 4549 | 4503 |
| 1 | 3 | 3 | 2374 | 2461 |
| 1 | 3 | 4 | 636 | 628 |
| 1 | 3 | 6 | 848 | 928 |
| 1 | 3 | 7 | 1944 | 1894 |
| 1 | 3 | 8 | 4117 | -4167 |
| 1 | 3 | 9 | 1056 | -1146 |
| 1 | 3 | 10 | 2287 | 2229 |
| 1 | 4 | -12 | 720 | -818 |
| 1 | 4 | -6 | 2649 | 2567 |
| 1 | 4 | -5 | 1457 | 1389 |
| 1 | 4 | -4 | 3333 | -3234 |
| 1 | 4 | -3 | 1906 | -1989 |
| 1 | 4 | -2 | 1292 | -1246 |
| 1 | 4 | 0 | 1494 | 1513 |
| 1 | 4 | 1 | 555 | 623 |
| 1 | 4 | 2 | 1168 | 1151 |
| 1 | 4 | 3 | 1059 | -1131 |
| 1 | 4 | 4 | 754 | -705 |
| 1 | 4 | 5 | 1539 | -1494 |
| 1 | 4 | 7 | 1816 | 1797 |
| 1 | 5 | -6 | 1626 | -1626 |
| 1 | 5 | -3 | 2460 | 2537 |
| 1 | 5 | -2 | 849 | 1007 |
| 1 | 5 | -1 | 1251 | -1505 |
| 1 | 5 | 0 | 822 | 912 |
| 1 | 5 | 2 | 3154 | -3065 |
| 1 | 5 | 3 | 1357 | -1356 |
| 1 | 5 | 4 | 2083 | 2129 |
| 1 | 5 | 5 | 1823 | 1818 |
| 1 | 5 | 6 | 710 | -832 |
| 1 | 6 | -6 | 706 | -850 |
| 1 | 6 | -5 | 1529 | 1502 |
| 1 | 6 | -1 | 1528 | -1527 |
| 1 | 6 | 0 | 798 | 902 |
| 1 | 6 | 1 | 948 | 975 |
| 1 | 7 | -4 | 1375 | -1331 |
| 1 | 7 | -3 | 1099 | -1071 |
| 1 | 7 | -2 | 1561 | 1536 |
| 1 | 7 | -1 | 1122 | 1086 |
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| 2 | 0 | -8 | 1229 | -1200 |
| 2 | 0 | -6 | 6844 | 6677 |
| 2 | 0 | -4 | 9276 | -9558 |
| 2 | 0 | -2 | 6959 | 7455 |
| 2 | 0 | 0 | 8626 | -8149 |
| 2 | 0 | 2 | 1475 | 1371 |
| 2 | 0 | 4 | 5564 | -5279 |
| 2 | 0 | 6 | 5442 | 5002 |
| 2 | 0 | 8 | 4979 | -5036 |
| 2 | 0 | 10 | 4047 | 4032 |
| 2 | 1 | -13 | 757 | -800 |
| 2 | 1 | -12 | 1335 | -1475 |
| 2 | 1 | -10 | 1463 | 1538 |
| 2 | 1 | -9 | 1010 | 1042 |
| 2 | 1 | -7 | 2453 | -2491 |
| 2 | 1 | -6 | 580 | 681 |
| 2 | 1 | -5 | 966 | 993 |
| 2 | 1 | -4 | 5557 | -5800 |
| 2 | 1 | -3 | 5151 | 5365 |
| 2 | 1 | -2 | 4915 | 5102 |
| 2 | 1 | -1 | 2159 | 2233 |
| 2 | 1 | 0 | 3135 | 3154 |
| 2 | 1 | 2 | 1573 | 1587 |
| 2 | 1 | 4 | 5143 | -5055 |
| 2 | 1 | 5 | 2715 | -2773 |
| 2 | 1 | 7 | 2176 | 2248 |
| 2 | 1 | 8 | 924 | 981 |
| 2 | 1 | 11 | 755 | -870 |
| 2 | 1 | 12 | 912 | -748 |
| 2 | 2 | -13 | 827 | 1084 |
| 2 | 2 | -11 | 680 | 642 |
| 2 | 2 | -10 | 1425 | -1376 |
| 2 | 2 | -9 | 3323 | -3280 |
| 2 | 2 | -8 | 2540 | 2577 |
| 2 | 2 | -7 | 960 | -974 |
| 2 | 2 | -6 | 1162 | -1192 |
| 2 | 2 | -5 | 2947 | 2948 |
| 2 | 2 | -4 | 1419 | -1369 |
| 2 | 2 | -3 | 349 | -232 |
| 2 | 2 | -2 | 3223 | -3099 |
| 2 | 2 | -1 | 1575 | -1635 |
| 2 | 2 | 0 | 5066 | 5384 |
| 2 | 2 | 1 | 2268 | 2259 |
| 2 | 2 | 2 | 6817 | -6977 |
| 2 | 2 | 3 | 2539 | 2516 |
| 2 | 2 | 4 | 3446 | 3470 |
| 2 | 2 | 5 | 1529 | 1572 |
| 2 | 2 | 6 | 1297 | -1370 |
| 2 | 2 | 8 | 970 | 1174 |
| 2 | 2 | 9 | 1698 | -1760 |
| 2 | 2 | 10 | 817 | -983 |
| 2 | 2 | 12 | 1373 | 1387 |
| 2 | 2 | 13 | 1007 | 1045 |
| 2 | 3 | -8 | 2920 | 2851 |
| 2 | 3 | -7 | 735 | -934 |
| 2 | 3 | -6 | 1971 | -1970 |
| 2 | 3 | -5 | 2077 | 2061 |
| 2 | 3 | -3 | 529 | -624 |
| 2 | 3 | -2 | 371 | 459 |
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| 2 | 3 | 1 | 1094 | 1221 |
| 2 | 3 | 2 | 2007 | -1996 |
| 2 | 3 | 3 | 3410 | 3356 |
| 2 | 3 | 5 | 1258 | -1218 |
| 2 | 3 | 6 | 2251 | -2231 |
| 2 | 3 | 8 | 1266 | 1336 |
| 2 | 4 | -10 | 1578 | 1562 |
| 2 | 4 | -8 | 1069 | -1114 |
| 2 | 4 | -7 | 860 | -936 |
| 2 | 4 | -5 | 2075 | 1946 |
| 2 | 4 | -4 | 2433 | -2491 |
| 2 | 4 | -3 | 3574 | -3514 |
| 2 | 4 | -2 | 3216 | 3187 |
| 2 | 4 | -1 | 1538 | 1572 |
| 2 | 4 | 0 | 1010 | -1068 |
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| 2 | 5 | 3 | 1166 | 1246 |
| 2 | 5 | 4 | 2023 | 1989 |
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| 2 | 6 | 3 | 2015 | -1914 |
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| 3 | 1 | -4 | 1052 | 979 |
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| 3 | 1 | -2 | 6924 | 7263 |
| 3 | 1 | -1 | 6344 | -6381 |
| 3 | 1 | 0 | 7538 | -7516 |
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| 3 | 1 | 2 | 978 | 995 |
| 3 | 1 | 3 | 2121 | 2169 |
| 3 | 1 | 5 | 5129 | -5181 |
| 3 | 1 | 6 | 2485 | 2534 |
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| 3 | 1 | 8 | 2052 | -2147 |
| 3 | 1 | 10 | 834 | 923 |
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| 3 | 2 | -7 | 2192 | 2349 |
| 3 | 2 | -6 | 545 | -644 |
| 3 | 2 | -5 | 1197 | 1205 |
| 3 | 2 | -4 | 3067 | -2957 |
| 3 | 2 | -3 | 4062 | -4155 |
| 3 | 2 | -2 | 3239 | 3273 |
| 3 | 2 | -1 | 2948 | 2957 |
| 3 | 2 | 0 | 490 | 513 |
| 3 | 2 | 1 | 4943 | 4951 |
| 3 | 2 | 2 | 2270 | -2189 |
| 3 | 2 | 4 | 2069 | 2022 |
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| 3 | 2 | 6 | 956 | 971 |
| 3 | 2 | 7 | 636 | -746 |
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| 3 | 3 | 6 | 2597 | -2537 |
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| 3 | 3 | 12 | 730 | 966 |
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| 3 | 4 | -2 | 1783 | -1826 |
| 3 | 4 | 0 | 538 | 633 |
| 3 | 4 | 1 | 2173 | 2157 |
| 3 | 4 | 2 | 869 | -978 |
| 3 | 4 | 3 | 3080 | -3217 |
| 3 | 4 | 4 | 2788 | 2753 |
| 3 | 4 | 5 | 1660 | 1869 |
| 3 | 4 | 6 | 1356 | -1356 |
| 3 | 4 | 8 | 826 | -877 |
| 3 | 5 | -4 | 892 | -921 |
| 3 | 5 | -1 | 2206 | 2131 |
| 3 | 5 | 0 | 2390 | -2490 |
| 3 | 5 | 1 | 1273 | -1287 |
| 3 | 5 | 2 | 2743 | 2730 |
| 3 | 6 | -6 | 1343 | 1394 |
| 3 | 6 | 0 | 988 | -1112 |
| 3 | 7 | -3 | 827 | 1054 |
| 3 | 7 | -1 | 798 | -752 |
| 4 | 0 | -12 | 722 | 793 |
| 4 | 0 | -10 | 1559 | -1373 |
| 4 | 0 | -8 | 1112 | 1123 |
| 4 | 0 | -6 | 1333 | -1398 |
| 4 | 0 | -4 | 5365 | 5266 |
| 4 | 0 | -2 | 801 | 706 |
| 4 | 0 | 0 | 4521 | -4521 |
| 4 | 0 | 2 | 5942 | -5811 |
| 4 | 0 | 4 | 9878 | 9919 |
| 4 | 0 | 6 | 3890 | -3902 |
| 4 | 0 | 8 | 1159 | -1222 |
| 4 | 0 | 12 | 1498 | 1594 |
| 4 | 1 | -13 | 852 | -944 |
| 4 | 1 | -10 | 2369 | -2367 |
| 4 | 1 | -8 | 1093 | 1148 |
| 4 | 1 | -5 | 1620 | -1630 |
| 4 | 1 | -4 | 3827 | 3901 |
| 4 | 1 | -3 | 2265 | -2261 |
| 4 | 1 | -2 | 4430 | -4237 |
| 4 | 1 | -1 | 1581 | -1542 |
| 4 | 1 | 0 | 2729 | 2742 |
| 4 | 1 | 1 | 3372 | 3527 |
| 4 | 1 | 2 | 715 | -673 |
| 4 | 1 | 3 | 4266 | -3988 |
| 4 | 1 | 4 | 2936 | 2841 |
| 4 | 1 | 6 | 3179 | -3112 |
| 4 | 1 | 7 | 2774 | 2775 |
| 4 | 1 | 8 | 715 | 731 |
| 4 | 1 | 9 | 1028 | 1148 |
| 4 | 1 | 11 | 974 | -1146 |
| 4 | 2 | -9 | 1363 | 1491 |
| 4 | 2 | -7 | 612 | -656 |
| 4 | 2 | -5 | 1415 | -1403 |
| 4 | 2 | -4 | 1730 | -1765 |
| 4 | 2 | -2 | 5428 | 5266 |
| 4 | 2 | -1 | 6095 | 5922 |
| 4 | 2 | 0 | 3096 | -3175 |
| 4 | 2 | 1 | 3846 | -3658 |
| 4 | 2 | 2 | 1597 | 1585 |
| 4 | 2 | 3 | 5597 | -5212 |
| 4 | 2 | 5 | 1142 | 1108 |
| 4 | 2 | 6 | 1464 | 1429 |
| 4 | 2 | 7 | 1920 | 1979 |
| 4 | 2 | 8 | 2955 | -3016 |
| 4 | 2 | 9 | 1151 | -1187 |
| 4 | 2 | 10 | 1837 | 1851 |
| 4 | 2 | 12 | 952 | -1058 |
| 4 | 3 | -12 | 1385 | -1333 |
| 4 | 3 | -9 | 1108 | -1192 |
| 4 | 3 | -8 | 1034 | -1297 |
| 4 | 3 | -7 | 861 | -880 |
| 4 | 3 | -6 | 2128 | 2126 |
| 4 | 3 | -5 | 1736 | 1674 |
| 4 | 3 | -4 | 1399 | -1431 |
| 4 | 3 | -2 | 574 | 627 |
| 4 | 3 | -1 | 2195 | -2206 |
| 4 | 3 | 0 | 2450 | -2443 |
| 4 | 3 | 1 | 2072 | 2025 |
| 4 | 3 | 2 | 5003 | 4963 |
| 4 | 3 | 4 | 1480 | -1548 |
| 4 | 3 | 10 | 1262 | 1364 |
| 4 | 3 | 12 | 617 | -786 |
| 4 | 4 | -11 | 616 | 790 |
| 4 | 4 | -9 | 956 | -924 |
| 4 | 4 | -8 | 1940 | 1825 |
| 4 | 4 | -7 | 1311 | 1379 |
| 4 | 4 | -6 | 1553 | -1546 |
| 4 | 4 | -5 | 695 | -814 |
| 4 | 4 | -4 | 777 | -919 |
| 4 | 4 | 0 | 3482 | 3519 |
| 4 | 4 | 2 | 1849 | -1782 |
| 4 | 4 | 3 | 2107 | -2055 |
| 4 | 4 | 5 | 2286 | 2288 |
| 4 | 4 | 6 | 1024 | -1071 |
| 4 | 4 | 8 | 1539 | 1405 |
| 4 | 5 | -6 | 1491 | -1557 |
| 4 | 5 | -1 | 1518 | -1582 |
| 4 | 6 | -3 | 1870 | -1737 |
| 4 | 7 | 0 | 1155 | -1115 |
| 5 | 0 | -12 | 2335 | -2174 |
| 5 | 0 | -10 | 891 | 1050 |
| 5 | 0 | -8 | 1510 | 1493 |
| 5 | 0 | -6 | 2576 | 2553 |
| 5 | 0 | -4 | 6231 | -6153 |
| 5 | 0 | -2 | 1215 | 1279 |
| 5 | 0 | 0 | 2634 | -2611 |
| 5 | 0 | 2 | 3284 | 3113 |
| 5 | 0 | 4 | 2289 | -2166 |
| 5 | 0 | 6 | 772 | -856 |
| 5 | 0 | 10 | 2539 | 2541 |
| 5 | 0 | 12 | 1414 | -1464 |
| 5 | 1 | -11 | 796 | 844 |
| 5 | 1 | -9 | 1373 | -1427 |
| 5 | 1 | -8 | 1532 | 1535 |
| 5 | 1 | -7 | 1130 | -1267 |
| 5 | 1 | -6 | 1523 | -1550 |
| 5 | 1 | -5 | 1865 | 1926 |
| 5 | 1 | -4 | 2366 | 2389 |
| 5 | 1 | -2 | 2899 | -2738 |
| 5 | 1 | 0 | 3216 | 3185 |
| 5 | 1 | 1 | 981 | 945 |
| 5 | 1 | 2 | 2387 | -2295 |
| 5 | 1 | 3 | 1592 | -1586 |
| 5 | 1 | 5 | 2021 | 1936 |
| 5 | 1 | 6 | 2200 | -2196 |
| 5 | 1 | 7 | 1921 | 2002 |
| 5 | 1 | 8 | 2638 | 2641 |
| 5 | 1 | 9 | 1928 | -2037 |
| 5 | 1 | 10 | 873 | -1098 |
| 5 | 2 | -9 | 1543 | -1435 |
| 5 | 2 | -8 | 1528 | 1436 |
| 5 | 2 | -7 | 702 | 679 |
| 5 | 2 | -6 | 2035 | -2009 |
| 5 | 2 | -5 | 1098 | 1154 |
| 5 | 2 | -4 | 1203 | 1192 |
| 5 | 2 | -2 | 1114 | 1148 |
| 5 | 2 | -1 | 2049 | -2026 |
| 5 | 2 | 0 | 938 | -893 |
| 5 | 2 | 2 | 1632 | -1673 |
| 5 | 2 | 4 | 2319 | 2157 |
| 5 | 2 | 5 | 1657 | 1774 |
| 5 | 2 | 6 | 2013 | -1933 |
| 5 | 2 | 7 | 797 | -891 |
| 5 | 3 | -10 | 1299 | 1382 |
| 5 | 3 | -5 | 883 | 908 |
| 5 | 3 | -3 | 2629 | -2479 |
| 5 | 3 | -2 | 1437 | 1513 |
| 5 | 3 | -1 | 685 | 717 |
| 5 | 3 | 0 | 880 | -1017 |
| 5 | 3 | 1 | 2854 | 2818 |
| 5 | 3 | 2 | 1971 | 1894 |
| 5 | 3 | 4 | 3155 | -3038 |
| 5 | 3 | 5 | 2772 | -2720 |
| 5 | 3 | 6 | 793 | 790 |
| 5 | 3 | 7 | 1039 | 1071 |
| 5 | 4 | -11 | 824 | -1010 |
| 5 | 4 | -10 | 936 | 1040 |
| 5 | 4 | -8 | 1790 | -1765 |
| 5 | 4 | -3 | 3163 | -3004 |
| 5 | 4 | -2 | 3669 | 3573 |
| 5 | 4 | -1 | 2037 | 2035 |
| 5 | 4 | 0 | 3225 | -3354 |
| 5 | 4 | 1 | 1472 | -1422 |
| 5 | 4 | 3 | 1488 | 1633 |
| 5 | 4 | 6 | 905 | 1023 |
| 5 | 4 | 8 | 1746 | -1568 |
| 5 | 4 | 9 | 715 | -835 |
| 5 | 5 | -4 | 1878 | 1774 |
| 5 | 5 | 1 | 1410 | 1257 |
| 5 | 5 | 4 | 993 | 1115 |
| 5 | 5 | 6 | 1544 | -1502 |
| 5 | 6 | -5 | 1452 | -1444 |
| 5 | 6 | -2 | 865 | -1020 |
| 5 | 6 | -1 | 1076 | 1097 |
| 5 | 6 | 3 | 1317 | -1268 |
| 5 | 6 | 5 | 1012 | 1042 |
| 6 | 0 | -10 | 2200 | 2046 |
| 6 | 0 | -6 | 4369 | -4246 |
| 6 | 0 | -2 | 2985 | 3069 |
| 6 | 0 | 0 | 3430 | -3566 |
| 6 | 0 | 4 | 1555 | 1512 |
| 6 | 0 | 6 | 759 | 859 |
| 6 | 0 | 12 | 1541 | -1535 |
| 6 | 1 | -10 | 925 | 822 |
| 6 | 1 | -8 | 1774 | -1711 |
| 6 | 1 | -7 | 1077 | 1236 |
| 6 | 1 | -6 | 1947 | 1996 |
| 6 | 1 | -5 | 2598 | 2506 |
| 6 | 1 | -3 | 3909 | -3853 |
| 6 | 1 | -2 | 1305 | 1235 |
| 6 | 1 | 0 | 4588 | -4497 |
| 6 | 1 | 1 | 2223 | 2281 |
| 6 | 1 | 2 | 2678 | 2592 |
| 6 | 1 | 4 | 1735 | -1703 |
| 6 | 1 | 6 | 1986 | 1963 |
| 6 | 1 | 8 | 1388 | -1331 |
| 6 | 1 | 9 | 890 | -959 |
| 6 | 1 | 10 | 1076 | 1249 |
| 6 | 2 | -7 | 1335 | 1398 |
| 6 | 2 | -6 | 1847 | -1704 |
| 6 | 2 | -5 | 2986 | -2920 |
| 6 | 2 | -4 | 2283 | 2106 |
| 6 | 2 | -3 | 1047 | 1064 |
| 6 | 2 | -2 | 665 | -713 |
| 6 | 2 | -1 | 1145 | 1255 |
| 6 | 2 | 0 | 1259 | -1290 |
| 6 | 2 | 3 | 1714 | -1731 |
| 6 | 2 | 4 | 3371 | 3154 |
| 6 | 2 | 5 | 1795 | 1652 |
| 6 | 2 | 6 | 2951 | -2756 |
| 6 | 2 | 8 | 1145 | 1243 |
| 6 | 3 | -10 | 717 | -1002 |
| 6 | 3 | -6 | 923 | -778 |
| 6 | 3 | -4 | 3663 | 3386 |
| 6 | 3 | -2 | 3801 | -3797 |
| 6 | 3 | -1 | 2360 | 2347 |
| 6 | 3 | 2 | 739 | -812 |
| 6 | 3 | 3 | 3307 | -3199 |
| 6 | 3 | 4 | 1541 | 1542 |
| 6 | 3 | 6 | 1495 | -1519 |
| 6 | 3 | 7 | 1232 | 1252 |
| 6 | 3 | 8 | 974 | 1065 |
| 6 | 3 | 10 | 692 | -779 |
| 6 | 4 | -6 | 1516 | 1494 |
| 6 | 4 | -5 | 927 | -1052 |
| 6 | 4 | -1 | 2495 | 2495 |
| 6 | 4 | 0 | 1502 | -1441 |
| 6 | 4 | 1 | 1184 | -1186 |
| 6 | 4 | 2 | 1765 | 1728 |
| 6 | 4 | 5 | 852 | 776 |
| 6 | 4 | 10 | 1132 | 1134 |
| 6 | 5 | 2 | 1473 | 1383 |
| 6 | 5 | 4 | 1546 | -1500 |
| 6 | 6 | 0 | 1177 | 1132 |
| 6 | 6 | 5 | 1337 | 1340 |
| 7 | 0 | -12 | 813 | 1083 |
| 7 | 0 | -10 | 2000 | -1794 |
| 7 | 0 | -6 | 2015 | -1901 |
| 7 | 0 | -4 | 4493 | 4408 |
| 7 | 0 | -2 | 2869 | -2892 |
| 7 | 0 | 2 | 1030 | 923 |
| 7 | 0 | 4 | 3550 | 3505 |
| 7 | 0 | 6 | 3299 | -3159 |
| 7 | 1 | -6 | 1592 | 1673 |
| 7 | 1 | -5 | 2216 | -2303 |
| 7 | 1 | -4 | 2578 | -2686 |
| 7 | 1 | -3 | 913 | -823 |
| 7 | 1 | -1 | 2203 | 2322 |
| 7 | 1 | 2 | 2525 | 2524 |
| 7 | 1 | 3 | 3748 | -3670 |
| 7 | 1 | 4 | 2852 | -2819 |
| 7 | 1 | 5 | 2070 | 2005 |
| 7 | 1 | 6 | 1449 | 1514 |
| 7 | 2 | -7 | 846 | -870 |
| 7 | 2 | -3 | 1281 | 1529 |
| 7 | 2 | -2 | 1179 | 1247 |
| 7 | 2 | 0 | 2392 | -2375 |
| 7 | 2 | 1 | 3424 | -3229 |
| 7 | 2 | 2 | 3561 | 3423 |
| 7 | 2 | 3 | 1305 | 1280 |
| 7 | 2 | 4 | 1325 | -1356 |
| 7 | 2 | 5 | 1035 | 1046 |
| 7 | 2 | 9 | 1113 | -1200 |
| 7 | 2 | 10 | 881 | 1108 |
| 7 | 3 | -9 | 791 | -936 |
| 7 | 3 | -5 | 1086 | 1085 |
| 7 | 3 | -4 | 1100 | -1298 |
| 7 | 3 | -2 | 1867 | -1838 |
| 7 | 3 | 0 | 2411 | 2397 |
| 7 | 3 | 3 | 722 | -1016 |
| 7 | 3 | 4 | 1377 | -1432 |
| 7 | 3 | 5 | 1076 | 1252 |
| 7 | 3 | 8 | 1639 | 1548 |
| 7 | 4 | -8 | 990 | 1093 |
| 7 | 4 | -7 | 699 | 809 |
| 7 | 4 | -6 | 1737 | -1620 |
| 7 | 4 | -5 | 771 | -849 |
| 7 | 4 | -4 | 776 | 712 |
| 7 | 4 | -3 | 1822 | 1787 |
| 7 | 4 | 0 | 1030 | 1157 |
| 7 | 4 | 2 | 1331 | -1358 |
| 7 | 4 | 5 | 975 | 984 |
| 7 | 4 | 6 | 1001 | -1160 |
| 7 | 4 | 7 | 1863 | -1761 |
| 7 | 4 | 8 | 1744 | 1691 |
| 7 | 5 | -5 | 1015 | 1051 |
| 7 | 5 | 4 | 944 | -1111 |
| 7 | 5 | 6 | 740 | 941 |
| 7 | 6 | -2 | 982 | 1082 |
| 7 | 6 | 0 | 1063 | -1080 |
| 8 | 0 | -10 | 878 | 826 |
| 8 | 0 | 2 | 2735 | 2730 |
| 8 | 0 | 4 | 2278 | -2309 |
| 8 | 0 | 6 | 1359 | -1416 |
| 8 | 0 | 8 | 1247 | 1269 |
| 8 | 1 | -9 | 1382 | -1247 |
| 8 | 1 | -6 | 2164 | -2171 |
| 8 | 1 | -4 | 1441 | 1340 |
| 8 | 1 | 0 | 1878 | 1947 |
| 8 | 1 | 2 | 2722 | -2744 |
| 8 | 1 | 4 | 1753 | 1696 |
| 8 | 1 | 5 | 1692 | 1732 |
| 8 | 1 | 8 | 1088 | 1266 |
| 8 | 1 | 10 | 1723 | -1774 |
| 8 | 2 | -3 | 1369 | -1543 |
| 8 | 2 | -1 | 966 | -1159 |
| 8 | 2 | 0 | 1047 | -1159 |
| 8 | 2 | 2 | 1437 | 1427 |
| 8 | 2 | 3 | 2907 | 2988 |
| 8 | 2 | 4 | 1413 | -1546 |
| 8 | 2 | 5 | 1192 | -1249 |
| 8 | 2 | 7 | 840 | -844 |
| 8 | 2 | 10 | 712 | 296 |
| 8 | 3 | -8 | 1507 | -1489 |
| 8 | 3 | -3 | 1707 | -1704 |
| 8 | 3 | -2 | 1712 | 1802 |
| 8 | 3 | -1 | 1262 | 1356 |
| 8 | 3 | 1 | 841 | -928 |
| 8 | 3 | 4 | 1452 | -1460 |
| 8 | 3 | 6 | 2009 | 1940 |
| 8 | 3 | 8 | 872 | -959 |
| 8 | 4 | -4 | 1282 | 1178 |
| 8 | 4 | 0 | 965 | -1026 |
| 8 | 4 | 1 | 805 | -798 |
| 8 | 4 | 4 | 1005 | 1107 |
| 8 | 5 | -5 | 996 | -1107 |
| 8 | 5 | -2 | 1827 | -1600 |
| 8 | 5 | 0 | 1415 | 1303 |
| 8 | 5 | 3 | 1403 | -1498 |
| 9 | 0 | -10 | 1233 | 1098 |
| 9 | 0 | -8 | 2308 | -2155 |
| 9 | 0 | -2 | 894 | 951 |
| 9 | 0 | 0 | 2631 | -2740 |
| 9 | 0 | 2 | 2307 | 2443 |
| 9 | 0 | 4 | 1639 | -1687 |
| 9 | 0 | 6 | 586 | 766 |
| 9 | 1 | -2 | 850 | -871 |
| 9 | 1 | -1 | 2144 | 2331 |
| 9 | 1 | 1 | 1102 | -1179 |
| 9 | 1 | 4 | 1063 | 1234 |
| 9 | 2 | -9 | 617 | 805 |
| 9 | 2 | -6 | 875 | -873 |
| 9 | 2 | -5 | 1662 | -1700 |
| 9 | 2 | -4 | 1995 | 1962 |
| 9 | 2 | -2 | 2577 | -2599 |
| 9 | 2 | -1 | 651 | 773 |
| 9 | 2 | 0 | 879 | 938 |
| 9 | 2 | 6 | 1133 | -1271 |
| 9 | 2 | 8 | 1656 | 1687 |
| 9 | 3 | -2 | 995 | -972 |
| 9 | 3 | 0 | 748 | 852 |
| 9 | 3 | 1 | 723 | -874 |
| 9 | 3 | 5 | 1204 | 1173 |
| 9 | 4 | -7 | 922 | -1011 |
| 9 | 4 | -6 | 738 | 804 |
| 9 | 4 | -4 | 853 | -919 |
| 9 | 4 | -3 | 617 | 816 |
| 9 | 4 | 1 | 1299 | -1300 |
| 9 | 4 | 2 | 1582 | 1544 |
| 9 | 4 | 3 | 1168 | 1229 |
| 9 | 4 | 4 | 1507 | -1418 |
| 9 | 5 | 0 | 1165 | 1248 |
| 10 | 0 | -2 | 2419 | -2423 |
| 10 | 0 | 0 | 1892 | 2004 |
| 10 | 0 | 2 | 721 | 864 |
| 10 | 0 | 4 | 1324 | -1313 |
| 10 | 0 | 8 | 914 | 1050 |
| 10 | 1 | -6 | 640 | 787 |
| 10 | 1 | -4 | 1546 | -1584 |
| 10 | 1 | -3 | 957 | 1142 |
| 10 | 1 | -2 | 682 | 805 |
| 10 | 1 | -1 | 816 | 856 |
| 10 | 1 | 1 | 1933 | -1960 |
| 10 | 1 | 2 | 1222 | 1332 |
| 10 | 1 | 4 | 1322 | -1416 |
| 10 | 1 | 5 | 753 | 930 |
| 10 | 1 | 6 | 744 | 901 |
| 10 | 1 | 8 | 770 | -985 |
| 10 | 2 | -3 | 993 | 1024 |
| 10 | 2 | -2 | 827 | -767 |
| 10 | 2 | -1 | 920 | -1005 |
| 10 | 2 | 4 | 811 | -808 |
| 10 | 3 | -7 | 948 | 934 |
| 10 | 3 | -1 | 645 | -883 |
| 10 | 3 | 0 | 1689 | 1653 |
| 10 | 3 | 2 | 1533 | -1559 |
| 10 | 3 | 5 | 541 | 758 |
| 10 | 4 | -1 | 1211 | -1204 |
| 10 | 4 | 3 | 880 | 849 |
| 10 | 4 | 5 | 675 | -676 |
| 11 | 0 | 0 | 2056 | 2063 |
| 11 | 0 | 2 | 1419 | -1459 |
| 11 | 1 | -1 | 859 | -1045 |
| 11 | 1 | 3 | 1067 | 1108 |
| 11 | 2 | -6 | 847 | 953 |
| 11 | 2 | 2 | 1137 | 1236 |
| 11 | 2 | 4 | 1450 | -1510 |
| 11 | 2 | 5 | 850 | -960 |
| 11 | 2 | 6 | 1339 | 1368 |
| 11 | 3 | -5 | 813 | -906 |
| 11 | 3 | -2 | 757 | 916 |
| 11 | 3 | -1 | 574 | 768 |
| 11 | 3 | 4 | 478 | 577 |
| 11 | 4 | -2 | 1125 | -992 |
| 12 | 1 | 0 | 658 | 810 |
| 12 | 1 | 4 | 580 | 492 |
| 12 | 2 | -2 | 634 | -720 |
| 12 | 2 | 0 | 836 | 848 |

weights estimated from the data scaling procedure were introduced (Fig. 2).

Atomic scattering factors for carbon and sulphur, the latter being corrected for the real part of the anomalous dispersion coefficient, were taken from *International Tables for X-ray Crystallography* (1962). The hydrogen form-factor curve used was that derived by Stewart, Davidson & Simpson (1965) from the spherical approximation of hydrogen in the hydrogen molecule.

In the early stages of the refinement positional and isotropic temperature parameters for the carbon and sulphur atoms were varied. At $R=0{\cdot}17$ anisotropic thermal parameters of the form

$$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33} + 2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13})]$$

were introduced. A difference Fourier synthesis evaluated at $R=0{\cdot}10$ indicated the positions of the ten hydrogen atoms of the structure. These were included in the structure factor calculations with isotropic temperature factor coefficients, $B=4{\cdot}0$ Å$^2$.

The refinement proceeded smoothly to $R=0{\cdot}05$, when several cycles of least-squares refinement of the hydrogen positional and isotropic thermal parameters were calculated. These appeared to produce physically reasonable shifts and resulted in a significant improvement in the structure factor agreement. The refinement was concluded with two cycles of least squares on the carbon and sulphur atoms only. None of the final parameter shifts exceeded $0{\cdot}1\sigma$ for the carbon and sulphur atoms or $0{\cdot}25\sigma$ for the hydrogen atoms. The final $R$ index was 0·044. The observed and calculated structure factors are listed in Table 1 and the final positional and thermal parameters are shown in Tables 2, 3 and 4.

Table 2. *Non-hydrogen atom coordinates and (in parentheses) their standard deviations*

All values have been multiplied by $10^5$.

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| S(1) | 37764 (10) | 38081 (15) | 12177 (8) |
| S(4) | 08428 (10) | 45552 (16) | 16103 (8) |
| S(7) | 27656 (8) | 72640 (14) | 24688 (6) |
| C(2) | 31127 (34) | 44904 (53) | 25565 (27) |
| C(3) | 18616 (33) | 33900 (53) | 26495 (26) |
| C(5) | 19140 (30) | 66284 (46) | 12021 (24) |
| C(6) | 28659 (35) | 57023 (54) | 04275 (26) |
| C(8) | 39950 (34) | 39214 (54) | 34973 (27) |
| C(9) | 12390 (32) | 84807 (48) | 07000 (29) |

Table 3. *Hydrogen atom coordinates (multiplied by* $10^4$*) and isotropic thermal parameters*

The isotropic thermal parameters are expressed in the form $\exp[-(B\sin^2\theta/\lambda^2)]$.

The first digit in the hydrogen atom identification number refers to the parent carbon atom number.

| | $x/a$ | $y/b$ | $z/c$ | $B$(Å$^2$) |
|---|---|---|---|---|
| H(31) | 2011 | 2009 | 2542 | 5·1 |
| H(32) | 1638 | 3438 | 3309 | 3·5 |
| H(61) | 2427 | 4840 | −132 | 7·4 |
| H(62) | 3466 | 6867 | 167 | 2·6 |
| H(81) | 3684 | 4225 | 4223 | 6·6 |
| H(82) | 4774 | 4727 | 3508 | 5·9 |
| H(83) | 4165 | 2446 | 3531 | 5·2 |
| H(91) | 1758 | 9557 | 606 | 6·1 |
| H(92) | 564 | 8879 | 1170 | 6·0 |
| H(93) | 854 | 8110 | −4 | 7·0 |

$\sigma(x)=25$, $\sigma(y)=40$, $\sigma(z)=20$. $\sigma(B)=0{\cdot}8$ Å$^2$.

## Discussion

### *Accuracy*

The final $R$ index is 0·044. Table 5 shows the structure factor agreement for ranges of $|F_o|$. The tendency, shown in Fig. 2 and discussed above, for the weak intensities to be underestimated is clearly evident for values of $|F_o|$ less than 10 electrons. The agreement between observed and calculated structure factors above 10 electrons is, however, generally good and the $\Sigma\,|F_c|/\Sigma\,|F_o|$ ratios differ from unity only by about 1%.

The mean coordinate standard deviations are 0·0009, 0·0033 and 0·026 Å for the sulphur, carbon and hydro-

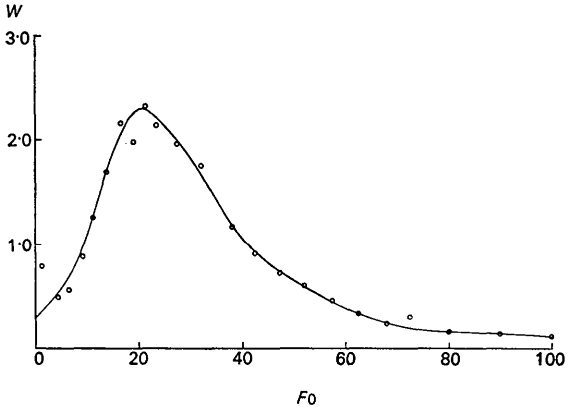

Fig. 2. Reflexion weights (arbitrary scale), derived from the intensity scaling, plotted as a function of $|F_o|$.

Table 4. *Non-hydrogen atom thermal parameters and (in parentheses) their standard deviations*

All values have been multiplied by $10^4$.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{31}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 814 (8) | 719 (8) | 501 (7) | 1 (5) | 143 (6) | 350 (6) |
| S(4) | 580 (6) | 623 (7) | 890 (8) | 88 (6) | −208 (6) | −153 (6) |
| S(7) | 543 (5) | 403 (6) | 467 (5) | −56 (5) | −66 (4) | −2 (5) |
| C(2) | 404 (21) | 453 (23) | 341 (21) | −20 (16) | 43 (17) | 62 (17) |
| C(3) | 617 (26) | 469 (25) | 553 (25) | 129 (17) | −2 (20) | 12 (19) |
| C(5) | 508 (23) | 422 (22) | 376 (22) | −24 (16) | −53 (17) | 27 (19) |
| C(6) | 790 (30) | 593 (27) | 446 (24) | −9 (19) | 15 (21) | 152 (22) |
| C(8) | 645 (27) | 695 (29) | 545 (26) | 172 (20) | −42 (21) | 73 (22) |
| C(9) | 616 (28) | 545 (25) | 661 (27) | 52 (20) | −119 (22) | 62 (21) |

Table 5. *Structure factor agreement*

| $F_o$ range | $n$ | $\Sigma\|F_o\|$ | $\Sigma\|F_c\|$ | $\Sigma\|F_c\|/\Sigma\|F_o\|$ | $R$ |
|---|---|---|---|---|---|
| 0–10 | 186 | 1468 | 1602 | 1·09 | 12·8 |
| 10–20 | 281 | 3956 | 4009 | 1·01 | 4·5 |
| 20–30 | 132 | 3220 | 3199 | 0·99 | 2·6 |
| 30–50 | 76 | 2844 | 2835 | 1·00 | 2·4 |
| 50–100 | 35 | 2312 | 2333 | 1·01 | 4·3 |

gen atoms respectively. The mean bond length standard deviations are 0·0033, 0·0045 and 0·03 Å for the C–S, C–C and C–H bonds. These error estimates were derived from the least-squares inverse matrix and are probably underestimated since no account was taken of the systematic errors in the low intensity terms, the cell parameter errors or positional shifts due to thermal libration effects.

The isotropic thermal coefficients of the hydrogen atoms have values which vary from $B=2{\cdot}6$ to $B=7{\cdot}4$ Å$^2$. It is difficult to assess the physical significance of these parameters; however, there was no tendency for the coefficients to become negative during the least-squares refinement as often happens when the free hydrogen atom scattering curve is used. In this respect the use of the curve proposed by Stewart, Davidson & Simpson (1965) can be considered to lead to more realistic hydrogen atom parameters.

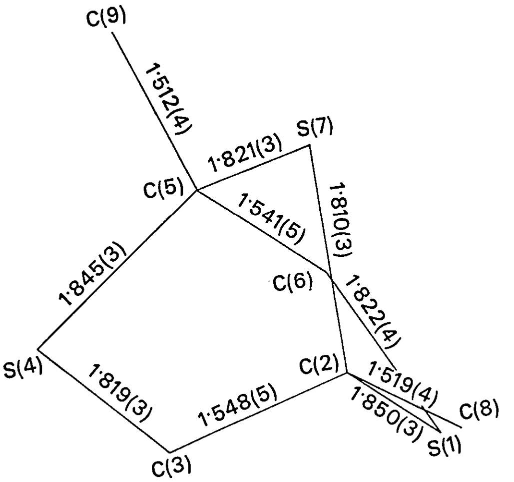

Fig. 3. Intramolecular bond lengths involving non-hydrogen atoms.

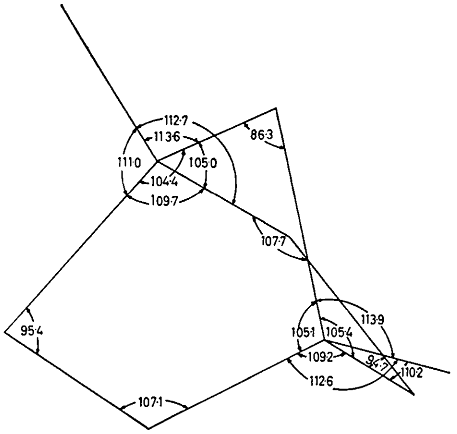

Fig. 4. Intramolecular bond angles involving non-hydrogen atoms. The mean e.s.d. in these angles is 0·25°.

### *Bond lengths and angles*

Interatomic distances and angles involving non-hydrogen atoms are shown diagrammatically in Figs. 3 and 4. The bond distances and angles involving hydrogen atoms are listed in Tables 6 and 7. The largest deviation between chemically equivalent bonds, corresponding to 3·5$\sigma$, is that between S(7)–C(2) and S(7)–C(5). However, this difference cannot be considered significant since, as discussed above, the standard deviations calculated from the least-squares matrix are probably underestimated. Furthermore, there is a strong correlation between these two distances since the bridging sulphur atom is common to both bonds. None of the differences between the remaining interatomic distances involving non-hydrogen atoms exceeds 2$\sigma$.

Table 6. C–H *bond lengths*

| | |
|---|---|
| C(3)–H(31) | 0·90 Å |
| C(3)–H(32) | 0·84 |
| C(6)–H(61) | 0·99 |
| C(6)–H(62) | 1·05 |
| C(8)–H(81) | 0·96 |
| C(8)–H(82) | 0·97 |
| C(8)–H(83) | 1·00 |
| C(9)–H(91) | 0·98 |
| C(9)–H(92) | 0·97 |
| C(9)–H(93) | 0·90 |

The mean e.s.d. in these distances is 0·03 Å.

Table 7. *Bond angles involving hydrogen atoms*

| | |
|---|---|
| C(2)—C(3)–H(31) | 105° |
| C(2)—C(3)–H(32) | 110 |
| S(4) —C(3)–H(31) | 114 |
| S(4) —C(3)–H(32) | 117 |
| H(31)–C(3)–H(32) | 103 |
| C(5)—C(6)–H(61) | 108 |
| C(5)—C(6)–H(62) | 111 |
| S(1) —C(6)–H(61) | 104 |
| S(1) —C(6)–H(62) | 107 |
| H(61)–C(6)–H(62) | 119 |
| *C(2)—C(8)–H | 114 |
| *H——C(8)–H | 105 |
| *C(5)—C(9)–H | 110 |
| *H——C(9)–H | 109 |

The mean e.s.d. of these angles is 2°.

* Only the mean value of the angles at the methyl groups are given.

The C(2)–S(1) and C(5)–S(4) bonds, which have an average value of 1·848 Å, are 0·02–0·03 Å longer than the expected distance based on the carbon and sulphur covalent radii (Pauling, 1960). The remaining four C–S bonds are normal. The C–$CH_3$ distances (1·516 Å) are shorter than the normal single $sp^3$–$sp^3$ carbon bond; however, thermal oscillational effects have probably resulted in some bond shortening. Corrections according to the method of Busing & Levy (1964), assuming that each methyl carbon atom rides on the carbon atom to which it is bonded, results in the C(2)–C(3) and C(5)–C(9) bond lengths being increased by 0·024 and 0·016 Å to 1·543 and 1·528 Å, respectively. However, this vibrational model is probably an oversimplified one and therefore these corrections should be viewed with some scepticism.

There is a variation from 0·84 to 1·05 Å in the C–H distances. The mean bond length (0·96 Å) is similar to that obtained in recent X-ray refinements, and is about 0·1 Å shorter than C–H distances determined by other methods.

The C–S–C angles (95·1 and 86·3°) fall within the range expected for divalent sulphur (Abrahams, 1956) although the latter value is somewhat smaller than usually found in molecules of this type (Hosoya, 1963). There is some distortion of the tetrahedral angles at C(2) and C(5). This is probably due to strain introduced by the fusion of the S(7) bridge between C(2) and C(5). The angles made by the bonds C($H_3$)–C with the remaining three atoms of the tetrahedron are all larger than the normal value. S(1)–C(2)–C(3) and S(4)–C(5)–C(6) are, as would be expected, unaffected by this strain and the remaining angles at C(2) and C(5) are all about 4° less than those usually found in a tetrahedral system. The C–C–S angles within the dithiane ring are all significantly smaller than similar angles in *trans*-2,5-dibromo-1,4-dithiane (Kalff & Romers, 1966), *trans*-2,3-dichloro-1,4-dithiane (Kalff & Romers, 1965) and 1,4-dithiane (Marsh, 1955). This may be due to strain caused by the compression of the boat conformation by the sulphur bridge as discussed above.

### *Molecular geometry and packing*

The molecule has a twofold symmetry axis passing through S(1) and the intersection of the ring diameters S(1)–S(4) and C(3)–C(6). It is interesting to note that the methyl groups retain this symmetry even though they have different intermolecular environments, indicating that the intramolecular environment is the dominating factor in determining the methyl group rotations. Apparently, the intermolecular packing forces have little influence on the hydrogen configuration and the molecules pack in such a way that the molecular symmetry is retained.

Fig. 5 shows the molecular packing viewed in the direction of the *b* axis. The eight non-hydrogen intermolecular contacts less than 4·0 Å are listed in Table 8. The only close contact is that between the symmetry related methyl groups C(9)($XYZ$) and C(9′)($\bar{X}\bar{Y}\bar{Z}$). Assuming a methyl group van der Waals radius of 2·0 Å (Pauling, 1960), this approach distance is 0·29 Å less than the expected value. However, the hydrogen atoms are staggered to accommodate this contact and none of the H–H distances is less than 2·80 Å.

### *Residual electron density*

Sections of the final difference synthesis calculated in the approximately planar parts of the molecule are shown in Fig. 6. The synthesis has been averaged over chemically equivalent regions to reduce the affect of random errors. The reflexions 111 and 11$\bar{1}$, which appeared to suffer from extinction effects, were omitted from these calculations. Fig. 6(*a*) corresponds to the mean residual density through the planes S(7)–C(2)–C(8) and S(7)–C(5)–C(9) and Fig. 6(*b*) to the mean residual density through C(2)–S(1)–C(6)–C(5) and C(5)–S(4)–C(3)–C(2). (In the notation used below S′(1) refers to the atomic site corresponding to S(1) and its chemically equivalent atom S(4) *etc.*).

Table 8. *Non-hydrogen atom intermolecular contacts less than* 4·0 Å

| | | |
|---|---|---|
| S(1)–C(8) | I | 3·97 Å |
| S(1)–C(8) | II | 3·74 |
| S(4)–C(3) | III | 3·96 |
| S(7)–C(6) | IV | 3·81 |
| S(7)–C(8) | V | 3·92 |
| C(8)–C(6) | VI | 3·98 |
| C(9)–C(3) | VII | 3·97 |
| C(9)–C(3) | VIII | 4·00 |
| C(9)–C(9) | IX | 3·71 |

I–IX refer to the equivalent positions
$1-X, \frac{1}{2}+Y, \frac{1}{2}-Z$; $X, \frac{3}{2}-Y, -\frac{1}{2}+Z$;
$\bar{X}, -\frac{1}{2}+Y, \frac{1}{2}-Z$; $X, \frac{1}{2}-Y, \frac{1}{2}-Z$;
$1-X, -\frac{1}{2}+Y, \frac{1}{2}-Z$; $X, \frac{3}{2}-Y, \frac{1}{2}+Z$;
$X, -1+Y, Z$; $\bar{X}, -\frac{1}{2}+Y, \frac{1}{2}-Z$; $\bar{X}, \bar{Y}, \bar{Z}$;

Each bond contains a region of positive residual density near its centre which can be attributed to the aspherical nature of the electron density in bonded atoms. The low value of the residual peak in the S′(1)–C′(6) bond is probably due to radial shifts of the sulphur and carbon atoms resulting from their asymmetric environment. Shifts of a similar nature have been shown to exist in the carbon atom positions in benzene, resulting in the near elimination of bonding electron features (O'Connell, Rae & Maslen, 1966). The remaining four C–C and C–S bonds each have positive residual electron density peaks of about 0·1 e.Å$^{-3}$ near their centres.

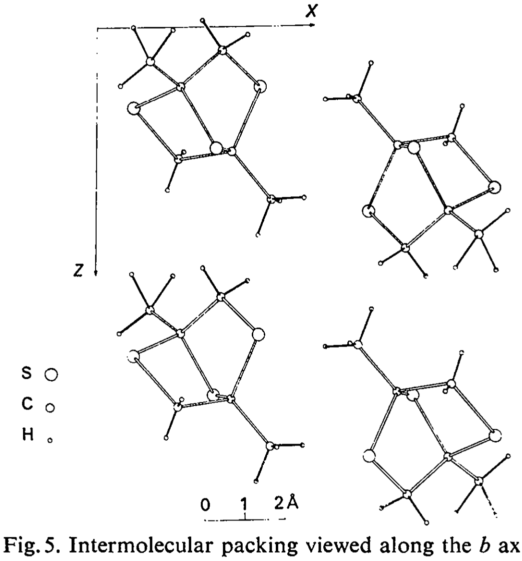

Fig. 5. Intermolecular packing viewed along the *b* axis.

In the recent studies of β-sulphanilamide (O'Connell & Maslen, 1967) and orthanilic acid (Hall & Maslen, 1967) it was found that the tetrahedrally bonded sulphur atoms were situated in negative regions of residual electron density with minima of −0·4 to −0·5 e.Å$^{-3}$ at the atomic sites. This was attributed to errors in the sulphur atom scattering factor. In view of these results it is interesting to note that in the present analysis the sulphur atomic sites have a positive mean residual density of about 0·1 e.Å$^{-3}$. This may be due to systematic errors in the intensity data; however, it may also be related to the different valence states of the sulphur atoms in the present structure as compared to those previously mentioned. The fully substituted $sp^3$ carbon atom C′(2) has a mean density of −0·12 e.Å$^{-3}$ at its atomic site; however, it is not clear if this is an artefact resulting from data or refinement errors or a real effect due to electron redistribution at bonding.

## Conclusion

The X-ray analysis has established the structure as that shown in (I) above. The analysis is of particular interest since it represents the first attempt at an accurate structure refinement using data measured with the automatic computer controlled film scanner in this laboratory. The accuracy of the intensity measurements is generally good, although some systematic errors in the weak reflexions are evident. With more experience in data processing techniques and improved method of intensity integration it is expected that errors of this type can be largely eliminated. For proteins, and other structures having large unit-cell dimensions, where many thousands of reflexions must be measured, this instrument should provide a useful means of structure analysis since the time taken to measure the diffraction data is independent of the number of reflexions on the film.

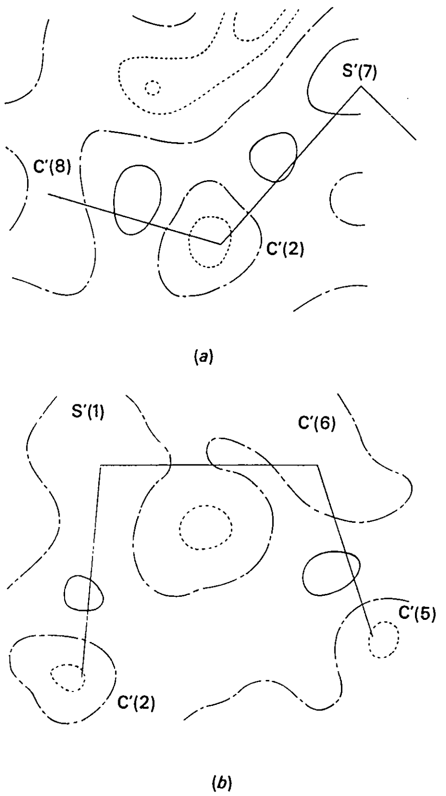

Fig. 6. (*a*) The mean residual electron density distribution for the planes S(7)–C(2)–C(8) and S(7)–C(5)–C(9). (*b*) The mean residual electron density distribution for the planes C(2)–S(1)–C(6)–C(5) and C(5)–S(4)–C(3)–C(2). Zero contour chain dotted, negative contours dashed, positive contours full lines; at intervals of 0·1 e.Å$^{-3}$.

All calculations were performed on a Datasaab D21 computer with programs developed by Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdahl (1965) and additional routines written by the author. Financial support was obtained from the Swedish Medical Research Council, the Swedish National Science Research Council and the U.S. Public Health Service (GM11653).

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