# Structure of Solid Carbon Disulphide between 5 and 150 K

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## Abstract

The crystal structure of $CS_2$ has been determined at six temperatures from 5·3 to 150 K using the neutron powder profile refinement technique. The results confirm the general features of the structure determined earlier at high temperatures. The space group is *Cmca* at all temperatures with four molecules per unit cell, and the lattice parameter, $c$, decreases as the temperature increases. Specific parameters of the structure differ from the earlier determination, and the C–S bond length in the solid appears to be shorter than in the gas phase. At 5·3 K the bond length is 1·546 (2) Å and the lattice parameters are $a = 6·0864$ (3), $b = 5·2866$ (3) and $c = 9·4623$ (5) Å. At 150 K the corresponding values are 1·529 (4), 6·4141 (7), 5·5787 (7) and 8·8928 (11) Å.

## Introduction

Carbon disulphide is a linear molecule which crystallizes, at 161·7 K, in a structure which has no known phase transitions. The present determination of the crystal structure of solid carbon disulphide ($CS_2$) is part of a programme to study the intermolecular dynamics of $CS_2$ (Grout & Leech, 1979; Pawley, Dolling, Powell & Torrie, 1981) and of other simple molecular crystals by the technique of inelastic neutron scattering. In order to interpret the experimental neutron intensities and to provide complementary structural data for the theoretical analysis, the detailed crystal structure of $CS_2$ must be known. With this objective the present work was undertaken using the neutron powder profile refinement technique.

Previous measurements by X-ray diffraction from single crystals (Baenziger & Duax, 1968) showed that $CS_2$ is orthorhombic (space group *Cmca*) with four linear molecules per unit cell. The molecules lie in planes perpendicular to the $a$ axis. A complete determination of the crystal structure was carried out

by these authors at 148 and 133 K while the lattice parameters were measured at six temperatures in the range 98 to 148 K. These latter measurements showed a marked anisotropy in the thermal expansion, with the lattice parameter $c$ increasing with decreasing temperature.

For calculations of the intermolecular dynamics it is preferable to have values of the lattice parameters and atomic positions determined at as low a temperature as possible since, in general, it is only at low temperatures that anharmonic effects become small enough for the quasiharmonic approximation to be reasonable. In addition it became apparent, as the inelastic neutron experiments progressed, that our lattice parameters did not agree with those from the X-ray results. The present neutron diffraction measurements were used to determine the crystal structure at six temperatures between 5·3 and 150 K. The results confirm the general features of the structure and the decrease with increasing temperature of the lattice parameter $c$ as determined earlier, but the specific details are different.

## Experimental details

The polycrystalline sample was prepared by dripping liquid $CS_2$ (supplied by Fisher Scientific) into a thin-walled vanadium can immersed in liquid nitrogen. The solid $CS_2$ condensed in the can was mechanically ground into a fine powder before more liquid was added. The vanadium can (7·5 cm long × 1·67 cm diameter) was filled with polycrystalline $CS_2$ in this manner and was mounted in a cryostat without the temperature of the $CS_2$ exceeding 90 K. The quality of the polycrystalline nature of the sample was checked by measuring the intensity of the Debye–Scherrer peak 111 as a function of specimen orientation about the cylinder axis (*i.e.* an axis perpendicular to the scattering plane). Measurements of the peak intensity (at 30 K) were made at intervals of 10° in specimen orientation and the intensities were distributed about their mean

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value with a standard deviation of 2%. This quality check was repeated at the conclusion of the experiment at a temperature of 150 K. and the result was unchanged. As an added precaution the sample was rotated continuously throughout the experiment to minimize any residual errors in the intensities due to the finite grain size of the sample.

The powder diffraction measurements were made on the L3 triple-axis spectrometer. operating in a two-axis mode. at the NRU reactor. Chalk River. The monochromator planes were Ge(113) and Soller-slit collimators with horizontal divergences of 0·44 and 0·36° were placed before and after the sample respectively. The spectrometer was calibrated using aluminium powder as a standard. The neutron wavelength was determined to be 1·407 Å and initial values for the zero of the scattering-angle scale and for the three half-width parameters were derived from the calibration. The spectrometer resolution function was determined to be Gaussian to a very good approximation. The intensity of the diffracted neutrons was measured as a function of scattering angle ($2\theta$) in steps of 0·1° from 10° to at least 105°. The counting time at each angle was ~120 s. At least 149 Debye–Scherrer peaks were measured at each of the six temperatures 5·3. 30. 77·3. 100. 125. and 150 K. The powder profiles for the lowest and highest temperatures are shown in Fig. 1.

## Analysis

The experimental powder diffraction profiles were analysed by means of the program *EDINP* (Pawley. 1980). In this modification of the Rietveld profile analysis program (Rietveld. 1969) the molecular orientation and the C—S bond length can be constrained during the initial cycles of refinement. At 5·3 K the background intensity in the scan is independent of scattering angle and the assumption of a flat background is well satisfied |see Fig. 1(a)|. At high temperatures. however. this is no longer true and the background intensity not only increases in magnitude but also becomes dependent on the scattering angle. This effect is most pronounced at the highest temperature and it can be seen in Fig. 1(b) that the background has a broad peak at $2\theta \sim 70°$. This type of dependence on scattering angle is characteristic of a background produced by orientationally averaged thermal diffuse scattering. In view of the well-known correlation between the assumed background variation and the values derived for the thermal parameters (Albinati. Cooper. Rouse. Thomas & Willis. 1980) three different assumptions were made for the dependence of background intensity on scattering angle. The first refinement was carried out with a flat (*i.e.* independent of scattering angle) background. This was clearly a poor approximation at the higher temperatures. The

next refinements assumed the background to be linearly dependent on scattering angle. *i.e.* background = $B + C(2\theta)$ where $B$ and $C$ are adjustable parameters. and the final refinements assumed the background to have the form background = $B + CQ^2 \exp(-c'Q^2)$ where $B$. $C$ and $c'$ are adjustable parameters and $|Q| = 4\pi \sin \theta/\lambda$. *i.e.* a dependence characteristic of thermal diffuse scattering (TDS). The crystal structure at all six temperatures was refined using each of these expressions for the background in turn and assuming both isotropic and anisotropic thermal factors. At low temperatures all three background assumptions resulted in similar values for the $R$ factor $|R = \sum_i |y_i^{obs} - y_i^{calc}|/\sum_i y_i^{obs}$. where $y_i^{obs}$ ($y_i^{calc}$) is the observed (calculated) intensity at scattering angle $2\theta_i$| and similar values for the parameters specifying the crystal
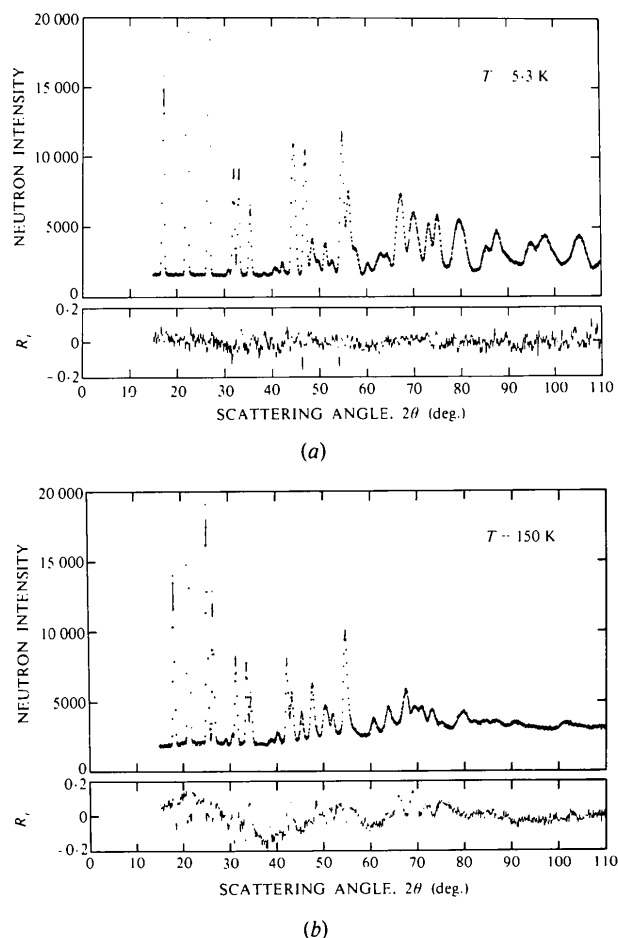


Fig. 1. Comparison of the observed and calculated diffraction profiles for solid $CS_2$. The temperatures are (a) $T = 5·3$ K. (b) $T = 150$ K. The crosses show the experimental intensities and the line through them is the calculated intensity. In (a) the experimental peak intensity of the 111 powder peak ($2\theta = 22·1°$) is 46900 while that of the combined 112 and 002 peaks ($2\theta = 27·3°$) is 44100. The plot of $R_i$ *versus* $2\theta_i$ is a quantitative measure of the discrepancies between the observed ($y_i^{obs}$) and calculated ($y_i^{calc}$) intensities at $2\theta_i$. $R_i = (y_i^{obs} - y_i^{calc})/y_i^{obs}$.

structure. At high temperatures the assumption of a flat background resulted in significantly larger $R$ factors than for either of the other two background variations and in crystal-structure parameters which differed appreciably from those obtained with the more complex background dependences.

The shape of the two lowest-angle, resolved Debye–Scherrer peaks was confirmed to be Gaussian and we assume that all other peaks also have this shape. The half-width is given by $H$ where $H^2 = U \times \tan^2 \theta + V \tan \theta + W$. Initial values for the parameters $U$, $V$ and $W$ were derived from the calibration of the spectrometer. These parameters were refined during the crystal-structure determination at 5·3 K and the final values at this temperature were used for all other temperatures.

In order to ensure a steady decrease in the $R$ factor as the crystal-structure parameters are refined, the order in which the parameters are varied is important. The scale factor and the parameters specifying the background were the first to be varied. The thermal parameters (isotropic or anisotropic) were added as the next variable parameters followed by the lattice parameters and the effective zero of the scattering angle. The molecular orientation and the C—S bond length were finally included and all parameters then varied together. At each step convergence was achieved with three cycles of refinement.

A correction for the effective absorption of the cylindrical sample was calculated for application at the completion of the refinements, following the method given by Hewat (1979). For our $CS_2$ sample the transmission was 90% and the product $\mu r$ was found to be equal to 0·042, leading to $\Delta B = -0·0044$ Å$^2$. The resulting correction to the thermal parameters is within the errors given by the refinements and so no correction was applied.

As expected, the best fit to the observed profiles was obtained for the lowest temperature and the worst fit for the highest temperature. This is evident from the comparisons shown in Fig. 1. A more quantitative measure of the difference between the observed and calculated profiles is given by the normalized dif-

ference, $R_i = (y_i^{obs} - y_i^{calc})/y_i^{obs}$. At $T = 5·3$ K the mean $R_i$ is essentially zero, which indicates that the variation of background with scattering angle has been adequately described. The accuracy of the structural determination ($R$ factor $= 2·4$%) is shown by the small values of $R_i$, whose absolute value exceeds 0·1 at only six values of $2\theta_i$. At $T = 150$ K the mean value of $R_i$ has a definite variation with scattering angle, particularly for $2\theta \leq 60°$. This indicates that the background variations are not completely represented by the simple TDS-type functional dependence, although even here $|R_i| \leq 0·2$. The fluctuations of $|R_i|$ superimposed on this oscillating mean value of $R_i$ are again generally less than 0·1 however. This suggests that the structure may be determined rather better than the value of the $R$ factor (3·9%) for this temperature would indicate. The corresponding plots for the other four temperatures show a smooth change from the low-temperature to the high-temperature behaviour. The smallest $R$ factors were obtained for the TDS-type background assuming anisotropic thermal parameters and the results are quoted for these refinements. The assumption of isotropic thermal parameters with the same background variation increased each corresponding $R$ factor by 0·1 or 0·2%.

## Results and discussion

Use of the three different forms for the background gave a measure of the sensitivity of the various parameters to the background correction. The linear and TDS-type backgrounds gave results which are in agreement, within the calculated standard deviations. On the other hand, the refinement assuming a flat background gave bond lengths and orientations which differed from those obtained with the other two assumptions for background variation by several standard deviations at the higher temperatures, while the anisotropic thermal parameters differed by factors of 2 and 3 in the worst cases. The structural parameters obtained from refinements assuming a TDS-type background and anisotropic thermal parameters are given in Table 1, together with the corresponding $R$

Table 1. *The R factors for the refinements of the crystal structure of* $CS_2$, *and the temperature dependence of the lattice parameters, the* C–S *bond length and the orientation angle,* $\varphi$, *between the molecular axis and the* **b** *direction*

The errors shown are from the profile refinement program. The unit-cell volume and the corrected C—S bond length are also given.

| Temperature (K) | 5·3 | 30 | 77 | 100 | 125 | 150 |
|---|---|---|---|---|---|---|
| R factor (%) | 2·4 | 2·3 | 3·0 | 3·0 | 3·4 | 3·9 |
| Lattice　　　　$a$ | 6·0864 (3) | 6·0983 (3) | 6·1764 (4) | 6·2417 (4) | 6·3347 (5) | 6·4141 (7) |
| parameters　　$b$ | 5·2866 (3) | 5·2970 (3) | 5·3653 (5) | 5·4271 (5) | 5·5158 (5) | 5·5787 (7) |
| (Å)　　　　　$c$ | 9·4623 (5) | 9·4388 (5) | 9·3186 (7) | 9·1898 (8) | 9·0028 (8) | 8·8928 (11) |
| Orientation angle $\varphi$ (°) | 48·19 (5) | 47·97 (5) | 46·91 (7) | 45·65 (7) | 44·26 (10) | 43·21 (13) |
| C—S bond length (Å) | 1·546 (1) | 1·545 (1) | 1·538 (2) | 1·532 (2) | 1·530 (2) | 1·518 (3) |
| Unit-cell volume (Å³) | 304·46 (5) | 304·90 (5) | 308·80 (7) | 311·30 (8) | 314·57 (8) | 318·21 (11) |
| Corrected C—S bond length (Å) | 1·546 (2) | 1·546 (2) | 1·542 (3) | 1·536 (3) | 1·538 (3) | 1·529 (4) |

factors and the unit-cell volume, $V$, derived from the lattice parameters. The $R$ factors may be compared with $R_{\text{expected}} = 1 \cdot 6\%$ where $R_{\text{expected}} = |N/\sum_i y_i^{\text{obs}}|^{1/2}$ and $N$ is the number of degrees of freedom. The thermal parameters for both isotropic and anisotropic assumptions with a TDS-type background are given in Table 2. Correlations between the parameters describing the background and the thermal parameters are found to be small, supporting the conclusion that errors in the latter are not strongly dependent on this particular assumption for background variation. The temperature dependence of the structural parameters and of the isotropic thermal parameters, $B$, is shown in Fig. 2.

The errors quoted in Tables 1 and 2 are the standard deviations produced by the profile refinement program. Sakata & Cooper (1979) compared the errors produced by the profile technique to those from a single-crystal analysis and suggested that for cases in which the profile peaks are well resolved the refinement leads to errors which are underestimated by at least a factor of 2. Pawley (1980) has suggested that the errors should be calculated on the basis of the number of equivalent peaks rather than the number of points in the powder pattern. In our case this would give errors which are nine times larger than the standard deviations. When the Debye–Scherrer peaks overlap, as in our case, it is difficult to give a good estimate of the errors. On the basis of the consistency of the parameter values in Table 1, and the variation of these values when the background, the form of the thermal parameters, isotropic and anisotropic, and the values of $U$, $V$ and $W$ are varied, we feel that the quoted standard deviations should be multiplied by a factor of three to give reasonable estimates of the errors in the parameters.

The lattice-parameter values given in Table 1 do not agree with those measured by Baenziger & Duax (1968) from X-ray diffraction. The values of $a$ and $b$ obtained by the latter authors are systematically smaller than those given in Table 1 by $\sim 0 \cdot 6\%$, while the values of $c$ are larger by $\sim 0 \cdot 9\%$. The discrepancies are not uniform, however, but vary in magnitude from $\sim 1 \cdot 1\%$ in lattice parameter $c$ at 138 K to zero in lattice
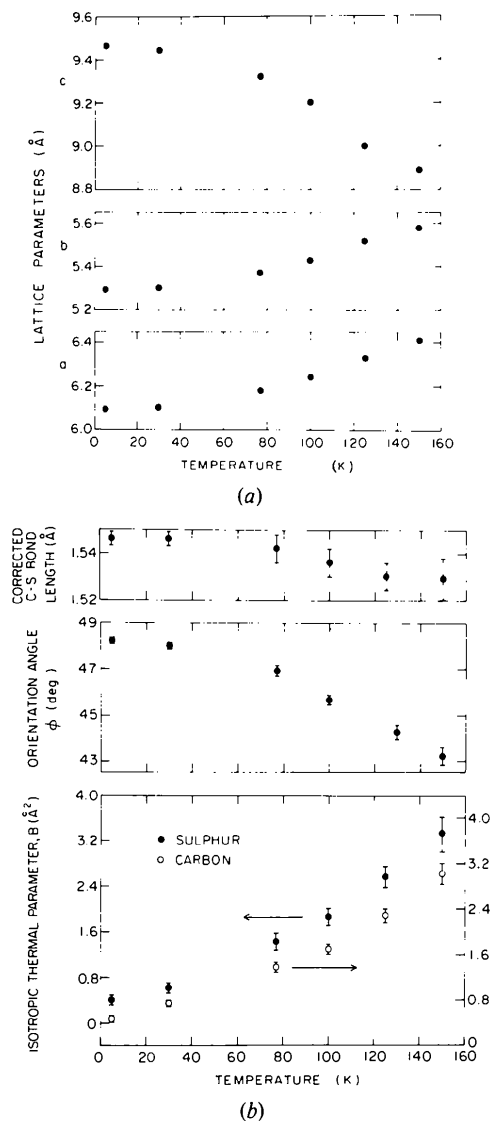


(a)



(b)

Fig. 2. Temperature dependence of the structural and thermal parameters of solid $CS_2$. (a) The lattice parameters. The errors are smaller than the points. (b) The corrected C–S bond length, the orientation angle ($\varphi$), and the isotropic thermal parameters $B(S)$, $B(C)$. The errors shown are those from the refinement program multiplied by a factor of three (see text).

Table 2. *The temperature dependence of the isotropic thermal parameters* $B(C)$, $B(S)$ *and the anisotropic thermal parameters* $U_{ij}$

The errors shown are from the refinement program.

| Temperature (K) | | 5·3 | 30 | 77 | 100 | 125 | 150 |
|---|---|---|---|---|---|---|---|
| Isotropic parameters | $B(S)$ (Å$^2$) | 0·40 (3) | 0·61 (3) | 1·42 (5) | 1·86 (5) | 2·56 (6) | 3·31 (10) |
| | $B(C)$ (Å$^2$) | 0·47 (2) | 0·74 (2) | 1·37 (3) | 1·69 (3) | 2·28 (4) | 3·01 (6) |
| Anisotropic parameters | $U_{11}(S)$ | 0·0056 (9) | 0·0068 (10) | 0·0183 (17) | 0·0250 (15) | 0·0313 (21) | 0·0422 (30) |
| | $U_{22}(S)$ | 0·0074 (11) | 0·0104 (12) | 0·0173 (19) | 0·0245 (19) | 0·0330 (24) | 0·0425 (33) |
| | $U_{33}(S)$ | 0·0059 (9) | 0·0079 (10) | 0·0216 (18) | 0·0250 (18) | 0·0385 (26) | 0·0552 (39) |
| | $U_{23}(S)$ | −0·0035 (8) | −0·0055 (8) | −0·0119 (14) | −0·0118 (14) | −0·0154 (18) | −0·0257 (27) |
| | $U_{11}(C)$ | 0·0083 (5) | 0·0104 (6) | 0·0182 (8) | 0·0221 (9) | 0·0294 (13) | 0·0401 (17) |
| | $U_{22}(C)$ | 0·0052 (6) | 0·0066 (7) | 0·0150 (12) | 0·0173 (11) | 0·0304 (14) | 0·0374 (22) |
| | $U_{33}(C)$ | 0·0074 (4) | 0·0107 (5) | 0·0195 (9) | 0·0271 (9) | 0·0307 (15) | 0·0420 (19) |
| | $U_{23}(C)$ | −0·0013 (7) | 0·0007 (8) | −0·0027 (13) | −0·0037 (12) | −0·0026 (15) | −0·0048 (20) |

parameter $b$ at 150 K. In the present experiment a 'standard' temperature sensor was calibrated at the melting point of $CS_2$. The sensor used to control the specimen temperature was then compared with this 'standard' sensor over the range 77 to 150 K and the discrepancy between the two did not exceed 0·3 K. Consequently, we believe the temperatures quoted in the present paper are accurate to better than 0·5 K. We are unable to suggest an explanation for the discrepancies between the present results and those from X-ray diffraction.

The bond lengths determined from the refinement must be corrected for foreshortening due to the librational motion of the $CS_2$ molecules. Corrections were applied by Baenziger & Duax (1968) to their X-ray results following the procedure developed by Cruickshank (1956), and using the Raman frequencies of the librational modes. These corrections increased the bond length by 0·006 or 0·007 Å at 150 K. We have corrected the bond lengths by rotating the tensor of anisotropic thermal parameters to molecular axes and utilizing Cruickshank's method. An additional correction to foreshortening can be produced by internal-mode motions, but this contribution was found to be negligible by Baenziger & Duax (1968). At 150 K the foreshortening correction is 0·01 ± 0·01 Å where the error is based on standard deviations multiplied by three as discussed above. Corrected bond lengths at all temperatures are given in Table 1 and the temperature dependence is plotted in Fig. 2($b$).

The corrected bond lengths are shorter than the corresponding X-ray values (1·559 ± 0·003 Å) or the gas-phase values (1·559 ± 0·002 Å) of Morino & Iijima (1962) and the bond length decreases with increasing temperature. It is not unreasonable that the bond length

in condensed phases is shorter than in the gas phase because attractive forces between molecules will act to compress the molecules. Reductions in bond lengths of 2 to 3% have been observed in liquid $N_2$ and $O_2$ (Clarke, Dore & Sinclair, 1975) and similar reductions are likely found with the solids, although the accuracy of the measured bond lengths is not high enough to be conclusive. The temperature dependence of the C—S bond length should be viewed with some caution, since at higher temperatures the representation of the background by simple analytic functions is less accurate and the possibility of systematic error cannot be discounted.

The unusual temperature dependence of the lattice parameter $c$ leads to a significant change in the shape of the unit cell. While $c$ decreases by ~6% in going from 5·3 to 150 K, both $a$ and $b$ increase by ~5·5%. As a result the unit-cell volume increases by only ~4·5% in this temperature range. Since the orientation of the linear $CS_2$ molecule changes by ~5° and the C—S bond length decreases by only ~1% the environment of a molecule changes markedly with temperature. This is illustrated in Fig. 3 which shows the unit cell projected on to the $bc$ plane. The temperature dependence of the crystal structure of solid $CS_2$ reported here should provide a sensitive test for models of the intermolecular potentials proposed to interpret the dynamics of this and other simple molecular solids.
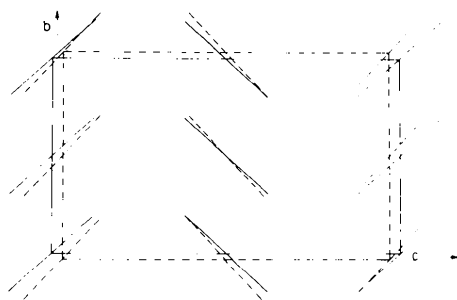
Fig. 3. Projection of the unit cell of $CS_2$ on to the $bc$ plane. The linear molecules are represented by lines and molecules at the centre of each edge are at $a/2$. The solid line is for $T$ 5·3 K and the dashed line for $T$ 150 K.

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