

NH...O (2.9 Å). Such distortions, resulting from the substitution of a thio-base for the natural base, may be of sufficient magnitude to disrupt certain biological processes.

Mrs Helene Sternglanz kindly prepared crystals of the compound. We thank Miss Catherine Sims and Miss Mary Ann Comer for assistance with the preparation of the drawings and manuscript. This work was supported by NIH fellowship 5F22CA-02784 and by NIH research grants CA-12159, CA-13148 and DE-02670.

References

- BUGG, C. E. & THEWALT, U. (1970). *J. Amer. Chem. Soc.* **92**, 7441–7445.
- BUGG, C. E., THOMAS, J. M., SUNDARALINGAM, M. & RAO, S. T. (1971). *Biopolymers*, **10**, 175–219.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DAWSON, B. (1960). *Acta Cryst.* **13**, 403–408.
- DONOHUE, J. & TRUEBLOOD, K. N. (1960). *J. Mol. Biol.* **2**, 363–371.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- IWAMOTO, R. H., ACTON, E. M. & GOODMAN, L. (1963). *J. Med. Chem.* **6**, 684–688.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LEPAGE, G. A. (1968). *Canad. J. Biochem.* **46**, 655–661.
- LEPAGE, G. A., JUNGA, I. G. & BOWMAN, B. (1964). *Cancer Res.* **24**, 835–840.
- SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 1067–1077.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUNDARALINGAM, M. (1971). *J. Amer. Chem. Soc.* **93**, 6644–6647.
- THEWALT, U. & BUGG, C. E. (1972). *J. Amer. Chem. Soc.* **94**, 8892–8898.
- THEWALT, U., BUGG, C. E. & MARSH, R. E. (1970). *Acta Cryst.* **B26**, 1089–1101.
- THEWALT, U., BUGG, C. E. & MARSH, R. E. (1971). *Acta Cryst.* **B27**, 2358–2363.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1977). **B33**, 3681–3684

Solid-State Phase Transition in Carbon Tetrabromide CBr₄. I. The Crystal Structure of Phase II at Room Temperature

BY M. MORE, F. BAERT AND J. LEFEBVRE

Laboratoire de Physique des Solides, Equipe de Dynamique des Cristaux Moléculaires associée au CNRS (n° 465), Université de Lille I, BP 36, 59650 Villeneuve d'Ascq, France

(Received 15 March 1977; accepted 13 May 1977)

Phase II of CBr₄ is monoclinic, space group *C2/c*, with $a = 21.43$, $b = 12.12$, $c = 21.02$ Å, $\beta = 110.88^\circ$, $Z = 32$. The structure was solved by direct methods and refined to $R = 7.0\%$ for 856 counter data. The monoclinic system can be converted into a pseudocubic system which facilitates the description of the structure.

Introduction

At atmospheric pressure, CBr₄ undergoes a transition at 47°C; phase I is stable between 92°C (melting point) and 47°C, phase II below 47°C. Finbak & Hassel (1937) have shown that phase II is monoclinic with $a = 21.12$, $b = 12.26$, $c = 24.14$ Å, $\beta = 125^\circ 3'$, $Z = 32$. These results disagree with those of Mark (1924). Harris (1962) gives $a_1 = 20.9$, $a_2 = 21.2$, $a_3 =$

12.1 Å, $\beta = 110^\circ 30'$. He suggests that the space group is *C2/c* but did not determine the structure.

Phase I is face-centred cubic with $Z = 4$ (Wyckoff, 1964), and is characterized by molecular reorientations ('plastic' crystal). It is interesting to consider why and how the transition occurs.

In this paper, the structure of phase II at room temperature is reported. An attempt to prove the pseudocubic structure is given [the structure of the

plastic phase I will be reported elsewhere (More & Lefebvre, 1977)].

Experimental

Sample preparation

The compound (Koch Light Laboratories) was purified by sublimation *in vacuo* to remove traces of free Br. Single crystals were found in the sublimate, but most were twinned. Examination with a polarizing microscope allowed us to select untwinned crystals.

The specimen retained for the study (approximately spherical, diameter 150 μ) was transparent. The crystal was mounted in a glass capillary to prevent sublimation.

Data collection

Data were collected at room temperature on a Philips PW 1100 automatic four-circle diffractometer. Details are: Mo $K\alpha$ radiation with pyrolytic-graphite monochromator, θ - 2θ scan up to $\theta = 25^\circ$, scan width = 1.2° , scan speed $0.01^\circ \text{ s}^{-1}$, Na(Tl)I detector. The background was counted for half the total scan time on each side of the $K\alpha$ position. Three standard reflexions were monitored; no significant change in their intensities was observed. 3304 reflexions were measured, of which only 856 had $I > 3\sigma(I)$.

An absorption correction was applied ($\mu = 270 \text{ cm}^{-1}$, $\mu R = 2.03$) (spherical crystal: *International Tables for X-ray Crystallography*, 1962). A Wilson-statistics calculation was used to normalize the structure factors to the content of one unit cell. The final distribution of E 's suggested a centrosymmetric structure.

Analysis of the data

Crystallographic data

The lattice constants (Table 1) were calculated by least squares from 25 reflexions. The systematic absences hkl for $h + k \neq 2n$, $h0l$ for $l \neq 2n$, $0k0$ for $k \neq 2n$, with the assumption that the structure is centrosymmetric, lead to the space group $C2/c$.

Table 1. *Crystallographic data*

Lattice: monoclinic	Space group: $C2/c$
$a = 21.43 \pm 0.04 \text{ \AA}$	$\mu = 270 \text{ cm}^{-1}$
$b = 12.12 \pm 0.02$	$V = 5100.3 \text{ \AA}^3$
$c = 21.02 \pm 0.04$	$Z = 32$
$\beta = 110.88 \pm 0.3^\circ$	$D_x = 3.42 \text{ g cm}^{-3}$

Structure determination

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). From 32 phase sets generated from eight starting reflexions, the set with the best figure of merit was developed into a complete phased set for 300 reflexions with $E > 1.6$ and the 2000 strongest Σ_2 relations. An E map based on weighted E 's was calculated and 19 atoms were found. Only one C atom was missing.

Least-squares refinement

Refinement was by least squares with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The scattering factors were those of *International Tables for X-ray Crystallography* (1962). Values for the imaginary part of the dispersion correction for Br were introduced. R ($= \sum |F_o| - |F_c| / \sum |F_o|$) was 13.6% with isotropic and 7.0% with anisotropic temperature coefficients for Br atoms. R_w [$= (\sum W|F_o| - |F_c|)^2 / \sum WF_o^2$]^{1/2} was 7.0%.

Description of the structure

(i) Positional parameters

The asymmetric unit contains four molecules (Table 2). Each C atom is assumed to lie at the centre of mass of its four Br atoms and to move isotropically.

(ii) Atomic thermal parameters and rigidity of the molecule

The vibrational motions were analysed in terms of the rigid-body tensors **T**, **L** and **S** (Schomaker &

Table 2. *Atomic positional parameters ($\times 10^4$) as given by least-squares refinement, with standard deviations in parentheses*

	x	y	z
C(1)	3450 (30)	7090 (70)	8710 (40)
Br(1)	3545 (5)	7726 (8)	7904 (5)
Br(2)	2697 (4)	7690 (9)	8935 (6)
Br(3)	4248 (4)	7368 (10)	9488 (6)
Br(4)	3322 (5)	5591 (8)	8527 (7)
C(2)	6260 (30)	1840 (70)	6230 (40)
Br(5)	7064 (4)	1023 (8)	6432 (5)
Br(6)	6296 (4)	2636 (6)	7038 (4)
Br(7)	5516 (3)	892 (7)	6002 (5)
Br(8)	6167 (4)	2821 (7)	5458 (5)
C(3)	3790 (30)	-590 (70)	6200 (40)
Br(9)	4578 (5)	-1497 (9)	6389 (7)
Br(10)	3906 (5)	411 (7)	6930 (5)
Br(11)	3029 (4)	-1581 (9)	6035 (6)
Br(12)	3656 (5)	272 (9)	5451 (5)
C(4)	5960 (30)	4680 (70)	8780 (40)
Br(13)	6025 (4)	5475 (7)	8037 (4)
Br(14)	6762 (4)	4902 (10)	9542 (5)
Br(15)	5214 (4)	5257 (8)	8942 (5)
Br(16)	5844 (6)	3107 (9)	8608 (6)

Trueblood, 1968). The elements of these tensors may be derived from a least-squares fit of the atomic β_{ij} 's.* Values of **T** and **L** are given in Table 3. The cross-tensor **S**, which accounts for correlation of translational and librational motions, has no significant values. Molecule 2 has values with large standard deviations but this is probably meaningless. The tensors are nearly diagonal. U^{ij} 's were calculated in two different ways: first (U_0^{ij}) starting from the β_{ij} 's, second (U_c^{ij}) with the TLS coefficients. Table 3 compares root mean square values of $\Delta U^{ij} = U_0^{ij} - U_c^{ij}$ with estimated standard deviations $\sigma(U_c^{ij})$. In view of the agreement, we may conclude that the rigid-body model is a good approximation.

(iii) Interatomic distances and angles

The arrangement of the four molecules is represented in Fig. 1. Interatomic distances and angles are given in Table 4. The molecules show departures from regular tetrahedral symmetry (high value of e.s.d. of the intramolecular length Br—Br). However, the mean intramolecular Br—Br distance is compatible with the mean

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32751 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Rigid-body tensors: elements of the mean square tensors and their standard deviations

	T ($\text{\AA}^2 \times 10^4$)			L ($\text{rad}^2 \times 10^4$)		
Molecule 1						
413 (65)	75 (68)	3 (52)	158 (51)	28 (53)	-29 (40)	
	483 (56)	-47 (70)		148 (28)	36 (57)	
		504 (65)			173 (56)	
	R.m.s. (ΔU_{ij}) = 0.0049 \AA^2		$\sigma(U_{ij}) = 0.0086 \text{\AA}^2$			
Molecule 2						
402 (164)	-105 (103)	-120 (169)	101 (127)	47 (44)	-37 (152)	
	474 (192)	38 (101)		225 (147)	26 (41)	
		577 (162)			84 (127)	
	R.m.s. (ΔU_{ij}) = 0.012 \AA^2		$\sigma(U_{ij}) = 0.0207 \text{\AA}^2$			
Molecule 3						
446 (49)	-19 (31)	-52 (57)	68 (35)	55 (13)	-40 (47)	
	511 (58)	79 (31)		172 (55)	1 (13)	
		559 (50)			132 (35)	
	R.m.s. (ΔU_{ij}) = 0.0037 \AA^2		$\sigma(U_{ij}) = 0.0064 \text{\AA}^2$			
Molecule 4						
459 (72)	40 (76)	-61 (61)	117 (53)	-4 (71)	-86 (42)	
	515 (60)	-54 (74)		103 (40)	28 (65)	
		505 (77)			112 (53)	
	R.m.s. (ΔU_{ij}) = 0.0055 \AA^2		$\sigma(U_{ij}) = 0.0096 \text{\AA}^2$			

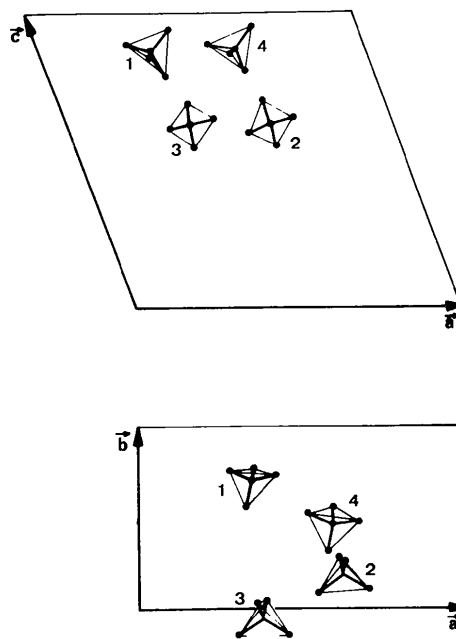


Fig. 1. Projections of the four molecules of the asymmetric unit.

Table 4. Distances and angles with their e.s.d.'s

Intramolecular distances and angles	
C—Br	1.912 (39) \AA
Br—Br	3.123 (71)
Br—C—Br	$109.48 \pm 2.50^\circ$
Shortest intermolecular distance	
Br—Br	3.776 (16) \AA

C—Br distance, 1.912 \AA . For this length, Kitaigorodsky (1955) gave 1.85 and *International Tables for X-ray Crystallography* (1962) 1.94 \AA . The shortest intermolecular distance, Br—Br = 3.776 \AA , is twice the van der Waals radius (Scott & Scheraga, 1965).

(iv) The pseudocubic cell

Many facts lead one to suppose that the symmetry is higher than monoclinic. The number of intense diffraction peaks is relatively low; thermal tensors **T** and **L** are nearly scalar; Fig. 1 shows that there are two kinds of molecule: (1,4) and (2,3).

Finbak & Hassel (1937) have given an incorrect version of the pseudocubic cell since their β was $125^\circ 3'$; the measured value is 110.88° .

If we write

$$\begin{aligned} \mathbf{A} &= -2\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3 & \mathbf{A}, \mathbf{B}, \mathbf{C} : \text{monoclinic} \\ \mathbf{B} &= \mathbf{a}_2 + \mathbf{a}_3 & \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 : \text{cubic} \\ \mathbf{C} &= 2\mathbf{a}_1 + \mathbf{a}_2 - \mathbf{a}_3 \end{aligned}$$

we obtain the results given in Table 5 which are most consistent with experiment. In particular, we obtain $\beta =$

109.47°, close to the experimental value. Calculations are based on the cubic lattice constant $a = 8.82 \text{ \AA}$ of phase I at 52°C (More & Lefebvre, 1977).

We can now describe the lattice with these new parameters. A vector \mathbf{OM} can be written:

$$\mathbf{OM} = X\mathbf{A} + Y\mathbf{B} + Z\mathbf{C} = \mathbf{OO}' + x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

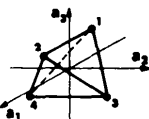
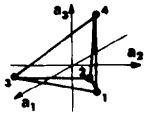
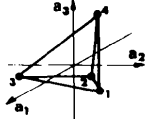
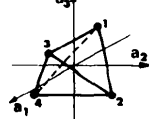
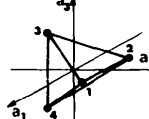
where O and O' are the origins of the monoclinic and cubic lattices respectively.

Table 5. *Calculated lattice constants from the cubic model ($a = 8.82 \text{ \AA}$).*

	Calculated	Experimental	Finbak & Hassel (1937)
a	21.60 \AA	21.43 \AA	24.94 \AA
b	12.47	12.12	12.47
c	21.60	21.02	21.60
β	109.47°	110.88°	125.26°

Table 6. *Reduced coordinates ($\times 10^3$) of some atoms in the cubic system*

The origin is taken on C(1). The coordinates of bromine atoms are taken with regard to those of their centre of mass (carbon atom). C(1') is obtained from C(1) by application of the symmetry operation: $\bar{x}, y, \frac{1}{2} - z$.

	x	y	z	
C(1)	0	0	0	
Br(1)	-180	-8	135	
Br(2)	195	6	113	
Br(3)	-4	184	-129	
Br(4)	-11	-182	-118	
C(2)	-1057	-492	-557	
Br(5)	-121	18	-183	
Br(6)	154	163	-5	
Br(7)	102	-192	2	
Br(8)	-136	11	184	
C(3)	-570	-986	-551	
Br(9)	-119	7	-188	
Br(10)	123	185	16	
Br(11)	120	-191	-6	
Br(12)	-123	-2	175	
C(4)	-487	17	-498	
Br(13)	-162	10	147	
Br(14)	-8	177	-135	
Br(15)	181	-2	115	
Br(16)	-12	-187	-129	
C(1')	-1104	-1933	1933	
Br(1')	181	135	-8	
Br(2')	-195	113	6	
Br(3')	4	-130	184	
Br(4')	11	-119	-182	

$$\begin{aligned} \mathbf{OM} &= (-2X + 2Z)\mathbf{a}_1 + (X + Y + Z)\mathbf{a}_2 \\ &\quad + (-X + Y - Z)\mathbf{a}_3 \\ &= (x + x_0)\mathbf{a}_1 + (y + y_0)\mathbf{a}_2 + (z + z_0)\mathbf{a}_3 \end{aligned}$$

where $\mathbf{OO}' = x_0\mathbf{a}_1 + y_0\mathbf{a}_2 + z_0\mathbf{a}_3$.

We choose the origin O' of the cubic lattice on C(1). This gives ($x_0 = 1.05$, $y_0 = 1.92$, $z_0 = -0.51$). Referring to this origin, the coordinates of the others C atoms can be calculated (Table 6). Translations between C atoms and origin are nearly those of a f.c.c. structure. In Table 6, we have also reported the coordinates of the Br atoms with respect to those of the corresponding C atom. All molecular sites have approximately $\bar{4}2m$ symmetry. For example, in molecule (1), Br(1) and Br(2) lie approximately in the (010) plane, Br(3) and Br(4) in the (100) plane. One 4 molecular axis is aligned with the \mathbf{a}_3 fourfold lattice axis. The other 4 tetrahedral axes are in the directions of the twofold lattice axes. We will call such a molecule A_3 . We can see that all the molecules obtained from $C2/c$ symmetry are of type $\pm A_1, \pm A_2, \pm A_3$.

The molecular orientations are correlated with the twofold axis $\mathbf{B} = \mathbf{a}_2 + \mathbf{a}_3$ which favours the [011] direction. We can expect that in phase I the six twofold axes have the same importance. The low-temperature phase can now be regarded as a single domain corresponding to one particular twofold axis.

The authors thank Professor R. Fouret for useful discussions.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- FINBAK, C. & HASSEL, O. (1937). *Z. phys. Chem. (B)*, **36**, 301–308.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HARRIS, M. T. (1962). *X-ray Diffraction Studies of Carbon Tetrabromide and Alloantin Dihydrate*, Thesis, New Brunswick, New Jersey. Ann Arbor, Michigan: University Microfilms Inc.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KITAIGORODSKY, A. I. (1955). *Organic Chemical Crystallography*. New York: Consultants Bureau.
- MARK, H. (1924). *Ber. dtsh. Chem. Ges.* **57**, 1820–1827.
- MORE, M. & LEFEBVRE, J. (1977). To be published.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCOTT, R. A. & SCHERAGA, H. A. (1965). *J. Chem. Phys.* **42**, 2209–2215.
- WYCKOFF, R. W. G. (1964). *Crystal Structures*. New York, London, Sydney: Interscience.