

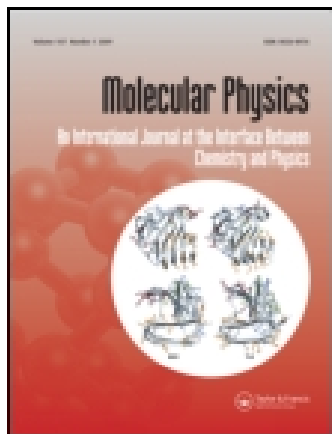
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Crystal structure of chloriodomethane

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The crystal structure of phase III of chloriodomethane- d_2 was determined at 13 K using Rietveld refinement of neutron powder profiles. The space group is $Pnma$ (D_{2h}^{16}) and there are four molecules in its orthorhombic unit cell with dimensions $a = 6.383(4) \text{ \AA}$, $b = 6.706(1) \text{ \AA}$ and $c = 8.867(4) \text{ \AA}$. The molecules form a 'herringbone' pattern in layers perpendicular to the b axis, similar to that in the halogen and the hydrogen halides crystals.

1. Introduction

In a recent paper [1] from this laboratory the Raman and far-infrared spectra of crystalline chloriodomethane were reported. The spectra showed that the crystal has four solid phases. From the melting point of 245 K to a temperature of 195 K the crystal has a plastic phase (phase I). Quenching the sample in liquid nitrogen or slow cooling to 170–180 K produces a transformation to phase III, which could be retained down to liquid-helium temperature. When phase III is annealed at a temperature above 165 K, the sample transforms to one of the other phases depending on the strains frozen into the sample. A quenched sample transforms from phase III to phase II near 165 K, whereas phase III derived from slow cooling transforms back to phase I near 190 K or in some cases to phase IV near 187 K.

The spectra showed that phases II–IV are completely ordered, but the lattice peaks in phase III, being broader than in the other two phases, suggested that there is some residual disorder in this phase. The spectra indicated that the structures of phases II and III have a centre of symmetry with at least four molecules in the primitive unit cell. For phase IV the spectra suggested a non-centrosymmetric unit cell with at least eight molecules in the cell.

In this paper we report the crystal structure of phase III as determined with neutron powder profiles using Rietveld [2] refinement techniques. To our knowledge there is no report of any crystal structure work on this compound in the literature.

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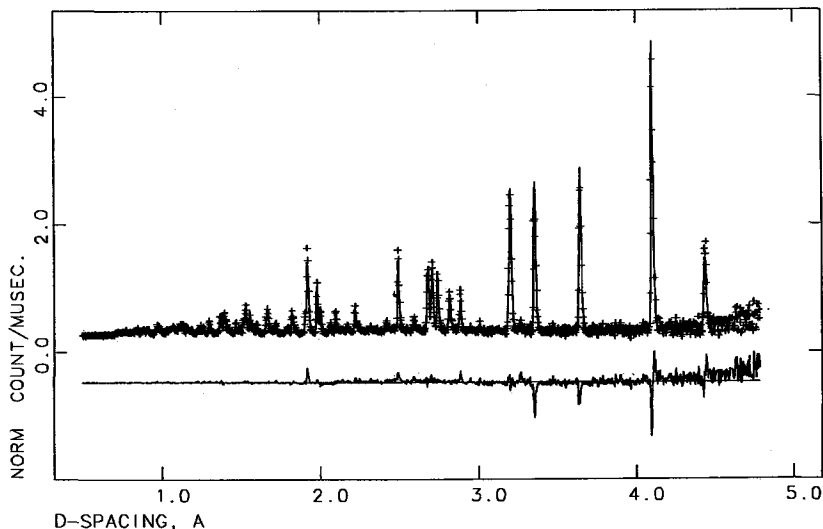


Figure 1. Observed, calculated and difference profiles for chloriodomethane- d_2 at 13 K.

2. Experimental details

Deuterated chloriodomethane (CD_2CI) was obtained from Cambridge Isotope Laboratories (98% deuterated) and was used as supplied. The liquid was loaded into a vanadium can 1.0 cm in diameter by 6.4 cm long and mounted on a closed-cycle refrigerator. The sample was cooled to 180 K and annealed at that temperature for about 1 h to obtain phase III. The solid was then further cooled to 13 K and held for about 1 h before starting the measurements. The neutron powder profiles were recorded using the high intensity powder diffractor at the Los Alamos Neutron Scattering Center, Los Alamos National Laboratory. Detector banks at 153° and 90° gave resolutions of $\Delta d/d = 0.3$ and 0.5% respectively on this time-of-flight machine. A representative section of the 13 K profiles for the 153° bank is shown in figure 1.

Efforts to produce the other phases were not successful. The experiments were repeated a year later and again only phase III profiles were successfully recorded. One problem is the grain growth which takes place at the high annealing temperatures. In the spectroscopic experiments discussed in the introduction, an average is taken over many grains but the averaging process is less effective in a neutron powder profile experiment and preferred orientation is observed.

3. Analysis

Some 20 high- d -value lines were used in the indexing program TREOR4 [3], which yielded an orthorhombic unit cell with four molecules per cell. Systematic absences showed that the crystal belongs to the space group Pnma . The refinement of the profiles was carried out with the program GSAS [4]. The rigid body routine in GSAS was used in the initial stages of the refinement with the molecule constrained to have a geometry similar to that of the methylene halides [5].

For the initial positioning of the molecule in the unit cell, a short program was written that calculated the interatomic distances between a molecule and its nearest neighbours. The position and orientation of the molecule were varied in a systematic manner and the lattice energies were calculated using Buckingham potentials with the

CD₂ClI, phase III at 13 K.

R_{expected}	1.78%			
R_{wp}	4.50%			
R_p	2.90%			
Space group	Pnma (D_{2h}^{16})			
Z	4			
Lattice parameters Å				
a	6.383(4)			
b	6.706(1)			
c	8.867(4)			
Atomic parameters				
Atom	x	y	z	100 U_{iso}
C	0.2088(2)	$\frac{1}{4}$	0.0804(2)	0.18(3)
D	0.2507(2)	0.3804(2)	0.1419(1)	1.86(3)
Cl	-0.0600(2)	$\frac{1}{4}$	0.0451(1)	0.84(3)
I	0.3962	$\frac{1}{4}$	-0.1206(2)	0.42(4)
Bond lengths Å				
	Crystal (CD ₂ ClI at 13 K)		Gas phase [8]	
	C-D	1.064(1)	C-H	1.062
	C-Cl	1.744(2)	C-Cl	1.774
	C-I	2.147(2)	C-I	2.137
Bond angles/degrees				
	Crystal (CD ₂ ClI at 13 K)		Gas phase [8]	
	D-C-D	110.5(2)	H-C-H	111.00
	D-C-Cl	109.8(1)	H-C-Cl	108.67
	Cl-C-I	113.5(1)	Cl-C-I	112.80
	D-C-I	106.6(1)		

parameters of Gavezotti [6] for those positions and orientations that produced the closest non-bonded interatomic distances that were similar to but less than the sum of the van der Waals radii. The position that produced the deepest minimum in the lattice energy was used as a starting point in the refinement procedure using the rigid-body constraint. This position was obviously close to the correct position since the refinement rapidly converged. In the final stages of the refinement the rigid-body constraint was removed and the atomic coordinates were allowed to vary independently of each other. The final parameters were also used for the refinement of the profiles recorded at an earlier time.

4. Results and discussion

The results obtained for the refinement of the powder profiles of the two samples (recorded a year apart) were basically the same. However, the values obtained for the lattice constants and the fractional coordinates differed by more than the estimated standard deviations (ESDs) calculated in the refinement program. The average absolute deviation was 0.003 Å whereas the average ESD was 0.0002 Å. Aside from the fact that the ESDs are believed to be underestimated by a factor of about three [7], the discrepancy in the lattice constants could be due to a small temperature difference between the two samples or to calibration differences with the time-of-flight machine. Discrepancies in the fractional coordinates, on the other hand, are most probably caused by the different crystallinities of the two powder samples.

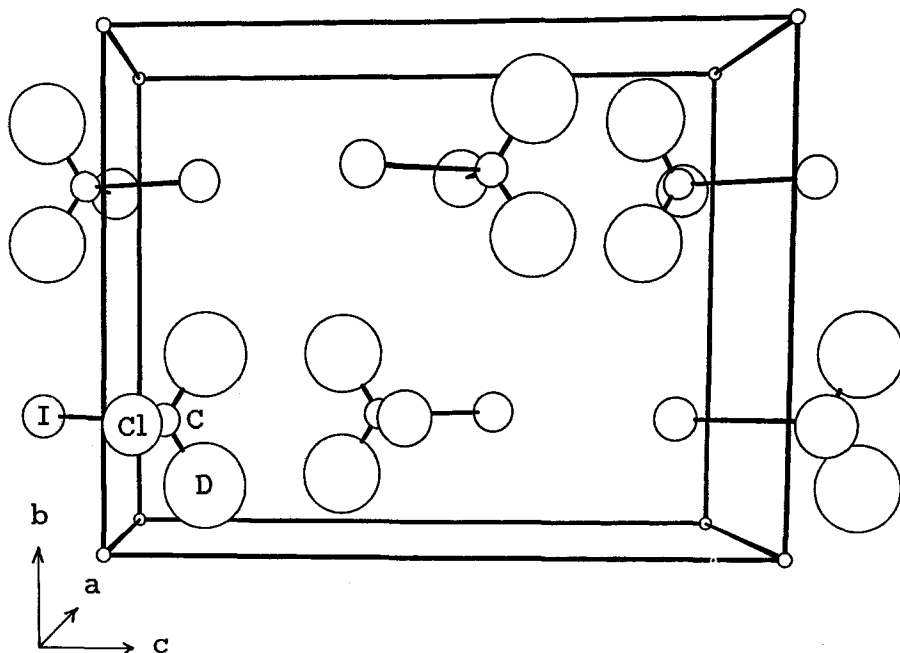


Figure 2. Unit cell contents for chloriodomethane- d_2 at 13 K. The radii of the circles are proportional to the thermal parameters. The circles represent, in order of decreasing radii, deuterium, chlorine, iodine and carbon respectively.

The final results shown in the table represent a refinement of four banks, two from each sample. The ESDs quoted there come from the refinement program, but a more realistic estimate of the uncertainty would multiply these by a factor of approximately 15 based on the difference between the two runs mentioned above. The lattice constants listed in the table, however, represent average values obtained from a refinement of the two 153° banks separately, and the uncertainties quoted are the half-range values. Because of systematic errors in the 90° banks, these values of the lattice parameters are more accurate than those obtained from the refinement of the four banks together. The observed and calculated profiles for one of the 153° banks together with a different plot are displayed in figure 1. Figure 2 shows the contents of the unit cell and figure 3 shows a projection of the crystal on the a - c plane.

The fitted profile and the difference plot show a serious mismatch in intensity for a few peaks. Examination of the relative intensities of the peaks in the raw histograms from different banks for a given sample showed that preferred orientation was a cause of this problem. The standard cryogrinding technique [9] that we have used elsewhere with other samples was not applied here but the effect of the cryogrinding would probably have been reversed by the high-temperature anneal in any case. The refinement program, GSAS, has a preferred orientation option and this was used in an attempt to correct the mismatch in the intensities. The preferred orientation directions were varied manually and, although the R factors improved slightly, the mismatch in intensities remained basically unchanged. Despite this problem, the quality of the fit as indicated by the R factors is reasonable and, by averaging over four banks, the effect of preferred orientation is reduced.

We have also carried out a refinement of the four banks separately to obtain a

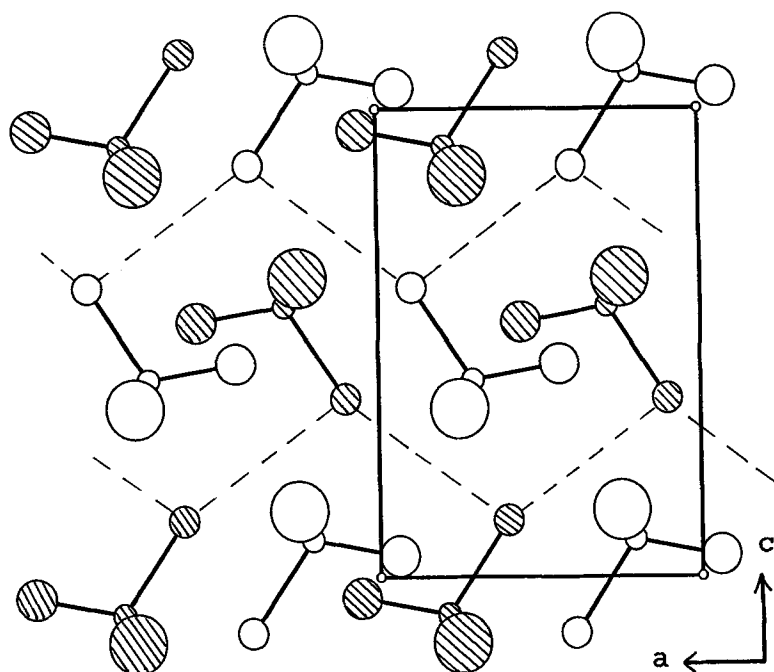


Figure 3. Projection of the crystal CD_2ClI on the a - c plane to display the 'herringbone' arrangement of the molecules in a layer. The striped molecules are in a layer displaced by $\frac{1}{2}b$.

better measure of the effects of preferred orientation. The fitted profiles were basically the same as those obtained from a refinement of the four banks together. The mismatch in intensities for the high- d -value lines was also evident in these profiles. The positional parameters derived from the four individual banks gave average values nearly the same as those shown in the table, and the range of values for each parameter fell approximately within the realistic uncertainty (15ESD) of the listed value. The lattice constants obtained were 6.382(7), 6.703(5) and 8.863(9) Å for a , b and c respectively, where the uncertainties here represent half the range of values from the four banks. These results agree well with the corresponding values listed in the table of 6.383(4), 6.706(1) and 8.867(4) Å but there is a systematic difference as expected.

There is no evidence for disorder in this crystal. The structure is similar to that of the halogens [10] and the lowest temperature phase of the hydrogen halides HCl and HBr [11, 12] in that the molecules form a 'herringbone' pattern in layers perpendicular to the b axis. The iodine atom in one molecule makes contact with the iodine in another molecule in the layer, thus forming a zigzag chain parallel to the a axis. In the hydrogen halides, which are ferroelectric, the chains are all parallel to a crystal axis, whereas in this case the chains in adjacent layers are antiparallel.

The intrachain iodine-iodine distance is 3.931(2) Å, which is slightly shorter than the sum of the van der Waals radii, 3.96 Å. The shortest Cl-Cl distance, 3.531(1) Å, is slightly larger than the sum of the van der Waals radii of 3.50 Å and occurs between atoms in adjacent layers. The shortest Cl-I distances are 3.769(2) and 3.774(2) Å and are between atoms in the same layer.

The geometry of the molecule in the crystal shows no appreciable change from

that in the gas phase as determined by microwave techniques [11]. The slight shortening of the C–Cl bond length in the solid state is probably not significant when due account is taken of the realistic uncertainties mentioned earlier. A refinement using two banks for one of the samples yielded a C–Cl bond length close to the gas phase value.

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