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# POLYMORPHISM IN ORDERED CARBON TETRABROMIDE

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## ABSTRACT

The ordered form of $CBr_4$ has been found to crystallize in two space groups (C2/m and C2/c) with nearly identical unit cell parameters. These two forms can be distinguished from each other using single-crystal x-ray diffraction methods, but not on the basis of powder measurements.

## I. INTRODUCTION

Globular or pseudo-spherical molecules are known to form orientationally disordered (plastic) phases (I) at temperatures near their melting points. It has recently been shown that, in some cases, the sample container or size and the presence of impurities in the sample can result in the formation of several polymorphs of these orientationally disordered phases.[1,2] The specific parameters responsible for the formation of these polymorphs are still under investigation.

In general, the ordered phase (II), which is formed as the temperature is lowered, is a "normal" crystalline phase. However, in some cases crystals of phase II exhibit several unusual crystallographic properties. For example,[3] Phase II of $CCl_4$, stable below -48°C, crystallizes in the monoclinic system, space group C2/c with 32 molecules per unit cell. The X-ray diffraction pattern is characterized by many "non-systematic" absences. It has been shown[4] that this phase can be related to Phase II of $(CH_3)CCl_3$, a compound with a similar globular shape, which crystallizes in the orthorhombic system with only 4 molecules per unit cell. Eight unit cells of the latter compound fit exactly into one unit cell of $CCl_4$. Thus, the $CCl_4$ structure can be looked upon as a super-lattice of a smaller unit cell.

In an attempt to investigate this phenomenon in greater detail, the isostructural[3] $CBr_4$ was selected for investigation. During the course of preparing single crystals of $CBr_4$ (by several different methods), it became apparent that "Phase II" of $CBr_4$ crystallizes in two different polymorphs - with nearly identical unit cells but different space groups. Thus, a globular molecule has now been shown to form two different ordered crystalline modifications. These observations are consistent with the previously reported model for the $CCl_4$ and $CBr_4$ structures: the two phases are related by a shift in the stacking of the smaller sub-cells.

## II. EXPERIMENTAL

The carbon tetrabromide used in this investigation included new samples obtained from Aldrich Chemicals and Eastman Kodak, and one

Aldrich sample that had been stored for several years in the laboratory.

Crystals were grown by vacuum sublimation at room temperature, by sublimation in a refrigerator, and by slow recrystallization from solvent (methanol and ethanol).

Approximately thirty individual specimens were studied. They were examined between crossed poloroids, so that all twinned specimens were rejected, and only single crystals were mounted in thin-walled capillary tubes for X-ray investigation, using Weissenberg and precession techniques (at room temperature and at -50°C).

## III. RESULTS

Both types of crystals had the same unit-cell parameters (within the limits of experimental error) but displayed different systematic absences. The averaged results of measurements on several crystals of each type are shown in Table I (unit-cell dimensions to 1% accuracy).

It is not possible to state unequivocally which crystal-growing method will give rise to a specific polymorphic form. In general, the newly purchased samples of $CBr_4$ resulted in higher quality crystals than the older sample. Thus the presence of impurities is seen to affect the crystal growth ($CBr_4$ is know to decompose readily and is difficult to purify[5]). With a little experience it is possible to visually select crystals of the desired space group.

Table I. Unit-Cell Parameters for $CBr_4$ Polymorphs (1% Accuracy)

| Space Group | C2/c | C2/m |
|---|---|---|
| a (Å) | 21.11 | 20.84 |
| b (Å) | 12.20 | 12.41 |
| c (Å) | 20.71 | 20.46 |
| β (°) | 110.47 | 110.10 |
| Z | 32 | 32 |
| Volume ($Å^3$) | 4997 | 4969 |
| X-Ray Density (g/mℓ) | $3.52_6$ | $3.54_5$ |
| Systematic Absences: | | |
| hkℓ | h + k odd | h + k odd |
| h0ℓ | (h odd)<br>ℓ odd | (h odd) |
| 0k0 | (k odd) | (k odd) |

However, the usual criteria for crystal selection for X-ray diffraction investigations, e.g., small, clear samples with well developed faces, are characteristic of the C2/c crystals and may explain why this space group was observed in all previous X-ray diffraction investigations. The C2/m crystals did not have as sharply defined faces.

Since there are significant differences in the intensity distributions of data collected from single crystals of these two phases, one can definitively distinguish between the two forms on the basis of a rotation photograph of an aligned crystal.

However, the gross similarities of the strong reflections and the nearly identical unit-cell parameters prohibits the identification of these phases through the use of standard powder diffraction techniques.

A differential scanning calorimetric study of these phases was carried out on a Perkin-Elmer DSC-1B calorimeter. Both samples showed the same melting point (94.0°C), but somewhat different transition temperatures (II- I, 49.8°C and 47.5°C, for C2/c and C2/m, respectively). Although these figures are reproducible, they fall within the temperature error range ascribed to this instrument.

It was also noted that the C2/c crystals were more stable in the X-ray beam (to both $CuK_\alpha$ and $MoK_\alpha$ radiations) than the C2/m crystals. The latter tended to deteriorate and gave the appearance of having melted after 20-40 hours in the X-ray beam, even for those samples studied at -50°C.

As a result of this work recent investigations of the physical properties of $CBr_4$ may have to be re-evaluated in terms of the exact space group of the sample studied. This will be particularly difficult for studies of powdered specimens.

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