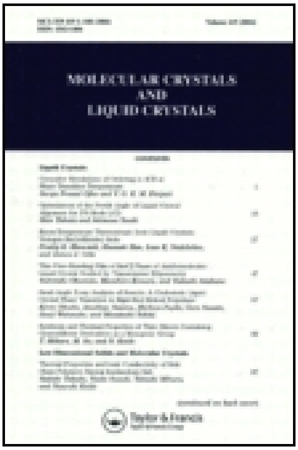

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A Variable Temperature X-ray Diffraction Study of 4,7-Dioxatricyclo[3.2.1.0^{3,6}]-octane and Characterization of the High Temperature (> 268 K) Plastic Crystalline Phase

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The low temperature phase of 4,7-Dioxatricyclo[3.2.1.0^{3,6}]octane (I) has been characterized by X-ray diffraction at four temperatures from 190 to 268 K. Over this range, the monoclinic (space group *C2/m*) unit cell volume changes linearly with temperature. At 268 K a phase change is observed to give a cubic unit cell (space group $Fm\bar{3}m$) with a 10% increase in cell volume. The scattered X-ray intensities and solid state NMR data are in close agreement with a cubic close packed structure of isotropically rotating molecules, however, there is evidence for some deviation from free rotation.

Keywords: Plastic crystal; phase transition; X-ray diffraction

INTRODUCTION

The structure of 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane (**I**) at 190 K was recently reported [1] in space group *C2/m* with $Z = 4$, the molecules having *m* symmetry. While growing crystals of this material by sublimation *in situ* at ca. 273 K, it was observed that the crystals self-destructed on cooling. Hence, in the previous publication, the crystals were grown at ca. 253 K before cooling to 190 K. In order to investigate the nature of the apparent

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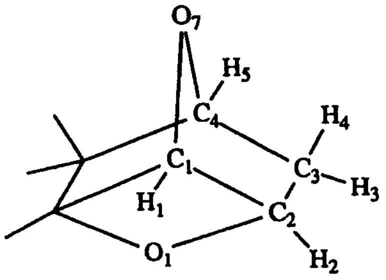
phase change and to characterize the high temperature phase, we have repeated this experiment, first growing the low temperature phase as before and determining the unit cell parameters at four different temperatures. The high temperature phase was then grown from the same sample, the unit cell redetermined and a complete sphere of intensity data collected. Additional solid state NMR experiments have also been used to characterize the high temperature phase.



I

EXPERIMENTAL

A small sample of **I** was sealed into a thin walled glass capillary under vacuum. The sample was mounted on an Enraf-Nonius CAD4 diffractometer and cooled to ca. 253 K with a nitrogen gas stream cooling device. By repeated small modifications of the temperature and position of the capillary over several days, a slab shaped single crystal of approximate dimensions 0.35 × 0.25 × 0.20 mm formed. Unit cell parameters were determined at four different temperatures (Tab. I). Below the lowest temperature recorded, the crystal underwent an apparent phase change with loss of crystallinity. The experiment was repeated to obtain a similar crystal as before at ca. 253 K, the sample warmed to close (268 K) to the previously

TABLE I Unit cell parameters as a function of temperature

$T(K)$	190(1)	221(1)	250(1)	268(1)	269(1)
a(Å)	9.634(3)	9.658(3)	9.679(3)	9.695(3)	8.409(2)
b(Å)	6.5478(8)	6.5529(6)	6.5575(8)	6.5607(9)	
c(Å)	8.474(1)	8.5036(9)	8.5382(7)	8.567(1)	
β(°)	98.86(2)	98.80(2)	98.74(2)	98.67(2)	
V(Å^3)	528.2(3)	531.8(2)	535.6(5)	538.7(4)	594.7(4)

observed [1] high temperature phase transition and the unit cell again determined. On warming by 1K the transition was reached (269 K) and the crystal disintegrated. On standing for several hours at this temperature, the material sublimed to fill the end of the capillary with a pointed cylindrical single crystal approximately 0.30 mm long and 0.30 mm in diameter at its widest point. The unit cell of the new phase was determined (Tab. I) and a complete sphere of intensity data (2518 total reflections) collected to $\sin\theta/\lambda = 0.61\ \text{Å}^{-1}$. There were, however, no observable reflections for $\sin\theta/\lambda > 0.43\ \text{Å}^{-1}$. All equivalent reflections with $I > 0$ were averaged ($R_{\text{int}} = 0.020$) to give a total of 20 unique data. The space group was assumed to be $Fm\bar{3}m$ (based on the systematic absences, the internal R value and the discussion below) with four molecules in the unit cell.

An additional sample was condensed under vacuum into a boiling point tube which was sealed and then centered in a 5 mm NMR tube. The ^{13}C NMR spectrum was obtained at ambient temperature on the static sample with a Varian VXR 400 spectrometer. The solution ^{13}C NMR spectrum was obtained in $CDCl_3$ using the same spectrometer.

RESULTS AND DISCUSSION

As shown in Figure 1, the unit cell volume of the low temperature phase changes smoothly with temperature until reaching the phase transition (269 K), whereupon the volume increases by 10.4%. Associated with the volume change is a change in crystal system from monoclinic (space group $C2/m$) to cubic (space group $Fm\bar{3}m$). This type of change is often associated with the formation of a plastic crystalline phase [2]. Such phases are frequently characterized as containing rotating, globular shaped molecules which pack as spheres (commonly cubic close packed as here, however, examples of hexagonal close packing are also known). We will show below that this dynamic behavior is a reasonable model in the case of 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane, however, a better description of the molecular motion may be that of a hindered rotor.

The disintegration of the crystal during the phase transition at 269 K may be associated with the large deviation of the monoclinic cell dimensions from those of the cubic cell ($C2/m$ is a subgroup of $Fm\bar{3}m$) and with the large deviation of the molecular centroids (0.334, 0, 0.2117) from the ideal values of 0.25, 0, 0.25, in the low temperature ordered form. The phase transition from monoclinic to cubic thus requires the molecules to occupy a sphere of rotation about the molecular centroid which also shifts by ca. 0.8 Å in the x

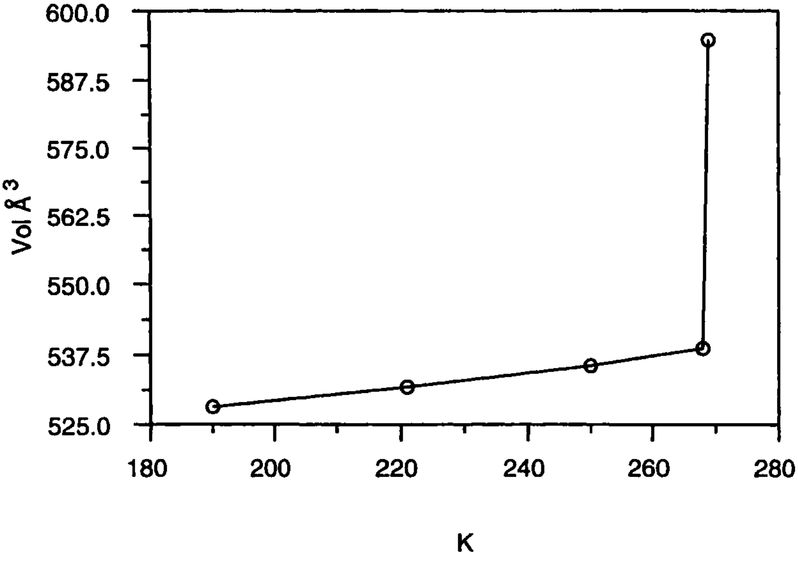


FIGURE 1 Variation of the unit cell volume of **I** with temperature.

direction, significant expansion of *b* and contraction of *a*, plus an 8.7° change in *β*.

It is well known that the observation of well resolved NMR signals in solution is due to the rapid tumbling of the molecules. Well resolved NMR spectra of solid state samples are usually obtained by the use of magic angle spinning. However, if the barrier to rotation in the solid is low enough, then molecules will also tumble in the solid state and hence it should be possible to observe an NMR signal even on a static sample. The classic example of this type of behavior is adamantane [3]. In Figure 2 we show the ^{13}C NMR spectrum obtained for a static solid sample of **I** superimposed on the analogous spectrum obtained from $CDCl_3$ solution. The signals from the solid are broad, however, they are observable and have the same chemical shifts as the solution spectrum. This thus indicates rapid reorientational degrees of freedom in the solid at ambient temperature, although the tumbling is clearly not as rapid as in solution.

Plastic crystalline phases are usually associated with dynamic orientational disorder. This may be caused by isotropic rotational motion or rapid changes between a number of discrete orientations. Intermediate between these two extremes is the hindered rotor. The known structure of **I** [1]

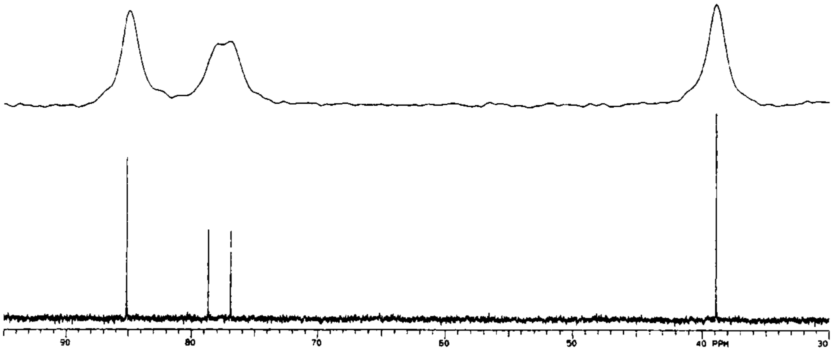


FIGURE 2 Ambient temperature ^{13}C NMR spectrum of solid **I** (upper trace) and a $CDCl_3$ solution (lower trace). Chemical shifts with respect to TMS.

indicates a globular molecule of *m* symmetry with no hydrogen bonding or other strong intermolecular interactions. Starting from the known molecular dimensions, the scattering factor for the molecule freely rotating about its center of gravity may be calculated as

$$f = \sum_i f_i \frac{\sin\ 4\pi r_i \sin\theta/\lambda}{4\pi r_i \sin\theta/\lambda}$$

where the sum is over all the atoms in the molecule, f_i being the atomic scattering factor for atom i and r the distance of each atom from the center of mass [4]. The values for r are listed in Table II. The derived function is shown in Figure 3 with the experimental points superimposed. Taking the center of the mass of the molecule to be at the origin of the unit cell (Wyckoff position *a*), the experimental points are scaled observed structure factors where the positive or negative root has been taken to correspond to the scattering factor curve. A marginally better fit is obtained by applying an isotropic temperature factor $B = 4.4\,\text{Å}^{-1}$ (see Fig. 3). The observed and calculated structure factors are also reported in Table III.

From the fit of the X-ray data and the observation of the NMR signals, it is clear that there is dynamic orientational disorder. However, the quality of the fit observed in Figure 3 (especially for reflections 115 and 333 which should have the same intensity), the traditional $R = 0.21$ and the width of the NMR signals indicate that free rotation is only an approximate model.

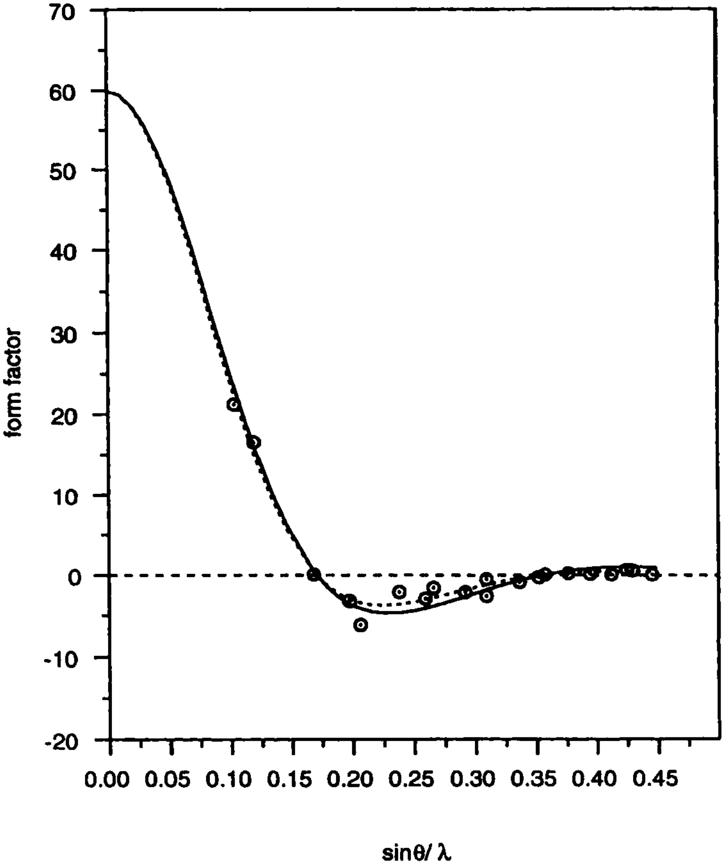


FIGURE 3 Scattering factor curve for a freely rotating molecule of **I** and the observed structure factors (—— no additional thermal motion, ----- with $B = 4.4\,\text{Å}^2$).

TABLE II Atomic distances from the center of mass for **I**

Atom	*r(Å)*	*Atom*	*r(Å)*
O1	1.764	H1	2.032
O7	1.476	H2, H2′	2.261
C1	1.059	H3, H3′	2.314
C2, C2′	1.302	H4, H4′	2.261
C3, C3′	1.578	H5	2.297
C4	1.328		

Some form of hindered rotor or rapid exchange between a number of discrete orientations, such as described for cyclohexane [5], would perhaps provide a better description.

TABLE III Observed and calculated structure factors for I[1]

h	*k*	*l*	*sl*	*f*	*fc*	*fo*	*sig*
1	1	1	0.1030	23.38	22.30	21.22	0.20
0	0	2	0.1189	16.07	15.10	16.58	0.20
0	2	2	0.1682	0.49	0.43	0.07	0.11
1	1	3	0.1972	−3.56	−2.99	−3.18	0.06
2	2	2	0.2060	−4.13	−3.42	−6.11	0.08
0	0	4	0.2378	−4.63	−3.60	−2.10	0.05
3	3	1	0.2592	−4.09	3.03	−2.91	0.07
0	2	4	0.2659	−3.82	−2.79	−1.58	0.04
2	2	4	0.2913	−2.67	−1.83	−2.13	0.04
1	1	5	0.3090	−1.82	−1.19	−0.51	0.02
3	3	3	0.3090	−1.82	−1.19	−2.61	0.05
0	4	4	0.3363	−0.65	−0.40	−0.85	0.03
1	5	3	0.3518	−0.11	−0.06	−0.26	0.10
2	4	4	0.3568	0.04	0.02	0.06	0.20
0	2	6	0.3761	0.53	0.28	0.22	0.10
2	2	6	0.3945	0.83	0.42	0.12	0.14
4	4	4	0.4120	0.98	0.46	0.07	0.19
5	5	1	0.4246	1.01	0.45	0.64	0.04
0	4	6	0.4288	1.01	0.45	0.57	0.03
2	4	6	0.4450	0.95	0.39	0.06	0.21

[1] sl = $\sin\theta/\lambda$, *f* = spherical form factor, *fc* = form factor modified for thermal motion ($B = 4.4\,\text{Å}^2$), *fo* = observed scattering factor scaled to *fc* (× 4 to obtain absolute scale) with phases assigned from *fc*.

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