

LETTER TO THE EDITOR

The Low-Temperature Crystal Structure of RS-Camphor

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The crystal structure of the low-temperature phase of RS-camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, C₁₀H₁₆O) has been solved at 100 K by high-resolution powder X-ray diffraction using synchrotron radiation. The structure is orthorhombic, space group *Cmcm*, with $a = 6.8341(2)$ Å, $b = 11.6584(3)$ Å, $c = 11.5000(3)$ Å, and $Z = 4$. The structure has four-fold disorder of the molecules. Left-handed and right-handed molecules are situated on the same crystallographic site, with an additional two-fold rotational disorder of the molecules. The structure was obtained from a combination of auto indexing, direct methods, and a grid search of molecular orientations. © 1997 Academic Press

INTRODUCTION

Camphor is a simple chiral bicyclic molecule whose enantiomers are miscible in all proportions in the solid state. The binary phase diagram shows the presence of three solid phases (1, 2), of which I and II are orientationally disordered plastic crystalline phases, with face-centered cubic and hexagonal structures, respectively (2). The transition between phase II and the more ordered lowest temperature phase III is strongly dependent on composition. Hence, for the pure enantiomers (S-camphor or R-camphor) the transition temperature is 244.19 K, whereas for the 1:1 racemic solid solution (RS-camphor) the transition temperature is reported to be in the range 203–210 K (3). The transition temperature has a minimum value of around 190 K for the 3:1 solid solutions.

In the lowest temperature phase III, the powder X-ray diffraction patterns of the pure enantiomers and the racemic solid solution are different (4). Other physical measurements indicate differences in behavior during the II → III phase transition. NMR experiments (4, 5), dielectric (6–8) and thermal conductivity investigations (9, 10), and heat capacity measurements (3) show that for R- or S-camphor ordering occurs at the transition. However, residual disorder persists with RS-camphor. Marked variations in

the specific heat and the transition temperature are observed after RS-camphor is annealed at low temperature (3). For a sample that was annealed in a series of heating cycles lasting almost a month, a transition temperature of 218.2 K was found between phases III and II. Excess entropy of 1.6 ± 0.4 J K⁻¹ mol⁻¹ at 0 K has been calculated for the nonannealed sample compared to the well-annealed sample. The residual disorder seen in nonannealed RS camphor has been explained in terms of positional disorder of the enantiomers coupled with orientational disorder (3).

Owing to the ordering of the molecules, large volume changes of around 10% accompany the II → III transition, so single-crystal diffraction studies have not been possible. Previous powder diffraction studies have been largely qualitative. The detection of only six diffraction peaks in RS-camphor at 77 K was interpreted as indicating that little long-range order is present (4). Here we report the results of high-resolution powder diffraction studies using synchrotron radiation to investigate nonannealed RS-camphor. The crystal structure of phase III has been solved, and indeed exhibits the positional disorder of enantiomers and additional rotational disorder suggested from the heat capacity measurements (3).

EXPERIMENTAL

RS-camphor (Lancaster, 97%) was gently ground in a pestle and mortar under liquid nitrogen in a glove bag and loaded into a flat copper sample holder, 25 mm in diameter and 2 mm deep. The sample was cooled to 50 K in a precooled liquid-helium cryostat. A powder diffraction pattern was measured in $\theta/2\theta$ mode on diffractometer 2.3 (11, 12) at the Synchrotron Radiation Source, Daresbury Laboratory, as the sample was spun about its normal. The powder diffraction pattern was quite different from that of a sample of S-camphor measured under similar conditions (13). The pattern was indexed as orthorhombic from the positions of 20 low-angle peaks using the program Fzon

(14). All 20 reflections were accounted for with a figure of merit M_{20} of 119. The unit cell volume indicates four molecules per unit cell. From the systematic absences, hkl : $h + k = 2n + 1$ absent, $h0l$: $l = 2n + 1$ absent, the space group appears to be $Cmcm$ (No. 63), or a C-centered subgroup, $C2cm$ (No. 40), $Cmc2_1$ (No. 36), monoclinic $C2/c$ (No. 15) or Cc (No. 9). The number of general (x, y, z) positions in each of these space groups is 16, 8, 8, 8, and 4, respectively. Hence they represent various degrees of disorder for the molecules, i.e., four-fold disorder for $Cmcm$, fully ordered for Cc , and two-fold disorder for the others, with different combinations of two-fold rotational disorder and/or superposition of the left-handed and right-handed molecules. Attempts to solve the structure by direct methods using the program SHELXS (15) in space group $Cmcm$ indicated possible fragments of the molecule around the position $4c$ $(0, y, \frac{1}{4})$, with $y \approx 0.25$, which is a site with

TABLE 1
Final Parameters for RS-Camphor, (1,7,7-Trimethylbicyclo [2.2.1]heptan-2-one, $C_{10}H_{16}O$, $M = 152.23$), at 100 K

Atom	Site symmetry	x	y	z	B (iso)	N
C(1)	16 h 1	-0.093(2)	0.3910(6)	0.2543(7)	8.7(2)	4
C(2)	16 h 1	0.018(2)	0.4840(3)	0.3186(9)	8.7(2)	4
C(3)	16 h 1	0.190(2)	0.429(1)	0.379(1)	8.7(2)	4
C(4)	16 h 1	0.163(2)	0.3031(9)	0.3417(9)	8.7(2)	4
C(5)	16 h 1	-0.008(3)	0.2550(7)	0.4095(6)	8.7(2)	4
C(6)	16 h 1	-0.185(2)	0.317(1)	0.3537(9)	8.7(2)	4
C(7)	16 h 1	0.081(1)	0.3125(5)	0.2169(6)	8.7(2)	4
C(8)	16 h 1	0.222(2)	0.373(1)	0.130(1)	8.7(2)	4
C(9)	16 h 1	0.018(2)	0.1960(5)	0.1632(7)	8.7(2)	4
C(10)	16 h 1	-0.236(2)	0.432(1)	0.165(1)	8.7(2)	4
O(1)	16 h 1	-0.022(4)	0.5825(3)	0.3117(6)	8.7(2)	4
H(1)	16 h 1	0.325(2)	0.463(2)	0.347(2)	8.7(2)	4
H(2)	16 h 1	0.180(3)	0.438(1)	0.471(1)	8.7(2)	4
H(3)	16 h 1	0.293(2)	0.253(1)	0.348(1)	8.7(2)	4
H(4)	16 h 1	-0.018(4)	0.1646(6)	0.398(1)	8.7(2)	4
H(5)	16 h 1	0.004(4)	0.276(1)	0.4993(6)	8.7(2)	4
H(6)	16 h 1	-0.286(2)	0.257(1)	0.319(1)	8.7(2)	4
H(7)	16 h 1	-0.255(3)	0.371(1)	0.416(1)	8.7(2)	4
H(8)	16 h 1	0.20(2)	0.464(1)	0.14(1)	8.7(2)	4
H(9)	16 h 1	0.371(2)	0.35(1)	0.152(8)	8.7(2)	4
H(10)	16 h 1	0.19(2)	0.35(1)	0.044(2)	8.7(2)	4
H(11)	16 h 1	-0.138(2)	0.191(3)	0.162(7)	8.7(2)	4
H(12)	16 h 1	0.07(1)	0.190(3)	0.077(2)	8.7(2)	4
H(13)	16 h 1	0.08(1)	0.1275(5)	0.214(4)	8.7(2)	4
H(14)	16 h 1	-0.26(2)	0.521(3)	0.178(8)	8.7(2)	4
H(15)	16 h 1	-0.18(1)	0.42(1)	0.080(1)	8.7(2)	4
H(16)	16 h 1	-0.369(8)	0.385(9)	0.173(9)	8.7(2)	4

Note. Parameters refined in the orthorhombic space group $Cmcm$ (No. 63) by the Rietveld method from powder X-ray diffraction data collected using synchrotron radiation with $\lambda = 1.40053 \text{ \AA}$. The molecular geometry was restrained in the refinement to that assumed for the camphor molecule in Ref. (18). The atom numbering scheme is shown in Fig. 2. $a = 6.8341(2) \text{ \AA}$, $b = 11.6584(3) \text{ \AA}$, $c = 11.5000(3) \text{ \AA}$, $V = 916.3 \text{ \AA}^3$, $Z = 4$, $D_c = 1.103 \text{ g cm}^{-3}$. $R_{wp} = 4.9\%$, $R_{exp} = 3.3\%$, and $R_1 = 4.9\%$.

point symmetry $m2m$ and implies four-fold disorder of the molecules, which themselves have no symmetry. However, because of severe texture and granularity problems with the flat-plate sample, which lead to large errors on the intensities of the diffraction peaks, attempts to complete the structure from this pattern were unsuccessful.

A new diffraction pattern was measured from a sample contained in a 2 mm diameter spinning capillary, at a wavelength of 1.40053 \AA , at 100 K, cooled by a stream of cold nitrogen from a Cryostream cooler. Data were collected in steps of $0.01^\circ 2\theta$ counting for 2 s per point. The pattern from the capillary specimen was much weaker, but appeared to be free of the problems experienced with the flat plate. The correct orientation for the camphor molecules was obtained by a grid search of molecular orientations. Input files for the Rietveld refinement (16) program PROFIL (17) were generated for the orientation ranges 0° – 180° , in steps of 10° , about the three orthogonal directions of the unit cell, with the center of mass of the molecule located near $(0, 0.25, \frac{1}{4})$. In the refinements, the structure and the orientation of the molecule were fixed, but the center of mass of the molecule was allowed to move to the most favorable (x, y, z) position. This was accomplished by giving all the atoms the same set of three code words for the x , y , and z positional parameters. Each 5-cycle refinement over the angular range 10° – $50^\circ 2\theta$, with contributions from 87 Bragg reflections, lasted $\approx 7 \text{ s}$ (13.5 h for the complete range of orientations). Finer grid searches were performed around the configuration that gave the best fit. The most favorable arrangement having been identified, a final refinement was carried out, including an overall isotropic temperature factor, allowing complete freedom for the molecule to move, restrained by the bond lengths and angles assumed for the single-crystal X-ray diffraction study of the inclusion compound of camphor with deoxycholic acid (18). Bond-length restraints were weighted $\pm 0.001 \text{ \AA}$ and angles $\pm 0.1^\circ$.

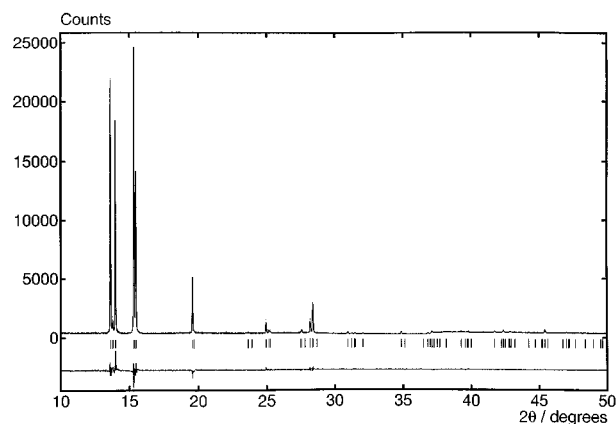


FIG. 1. Observed (\cdot), calculated ($-$), and difference plot of the final Rietveld refinement of RS-camphor. Reflection positions are shown as vertical lines.

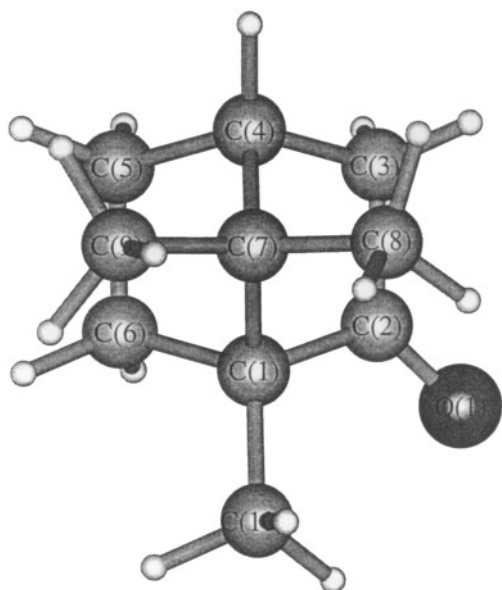


FIG. 2. Numbering of the C and O atoms.

The procedure was repeated with the subgroups of *Cmcm*. All produced significantly worse fits to the observed diffraction pattern. Hence it appears that the four-fold disordered model in *Cmcm* is the best description of the structure. The final *R*-factors, atomic parameters, and other structural information are given in Table 1. The observed and cal-

TABLE 2
Refined Bond Lengths (Å) and Angles (°)

C(1)–C(2)	1.52(1)	C(3)–C(4)	1.54(2)
C(1)–C(6)	1.56(1)	C(4)–C(5)	1.51(2)
C(1)–C(7)	1.56(1)	C(4)–C(7)	1.54(1)
C(1)–C(10)	1.49(2)	C(5)–C(6)	1.55(2)
C(2)–C(3)	1.51(2)	C(7)–C(8)	1.56(2)
C(2)–O(1)	1.18(1)	C(7)–C(9)	1.55(1)
C(2)–C(1)–C(6)	103.7(7)	C(3)–C(4)–C(5)	107.7(8)
C(2)–C(1)–C(7)	99.9(7)	C(3)–C(4)–C(7)	103.5(8)
C(2)–C(1)–C(10)	115.7(8)	C(5)–C(4)–C(7)	103.0(9)
C(6)–C(1)–C(7)	100.7(6)	C(4)–C(5)–C(6)	102.5(7)
C(6)–C(1)–C(10)	114.7(9)	C(1)–C(6)–C(5)	104.3(9)
C(7)–C(1)–C(10)	119.6(8)	C(1)–C(7)–C(4)	93.6(7)
C(1)–C(2)–C(3)	108.0(6)	C(1)–C(7)–C(8)	112.4(7)
C(1)–C(2)–O(1)	123.1(1.5)	C(1)–C(7)–C(9)	114.1(8)
C(3)–C(2)–O(1)	128.7(1.5)	C(4)–C(7)–C(8)	113.7(8)
C(2)–C(3)–C(4)	100.7(1.0)	C(4)–C(7)–C(9)	114.1(6)
		C(8)–C(7)–C(9)	108.5(8)

culated profiles are shown in Fig. 1. Refined bond distances and angles are given in Table 2. (Numbering of the C and O atoms is as in Fig. 2.) Even with restraints, the final distances and angles differ slightly from the values assumed.

DISCUSSION

Figure 3 shows a view of the structure displaying (for clarity) only one of the four possible orientations for each

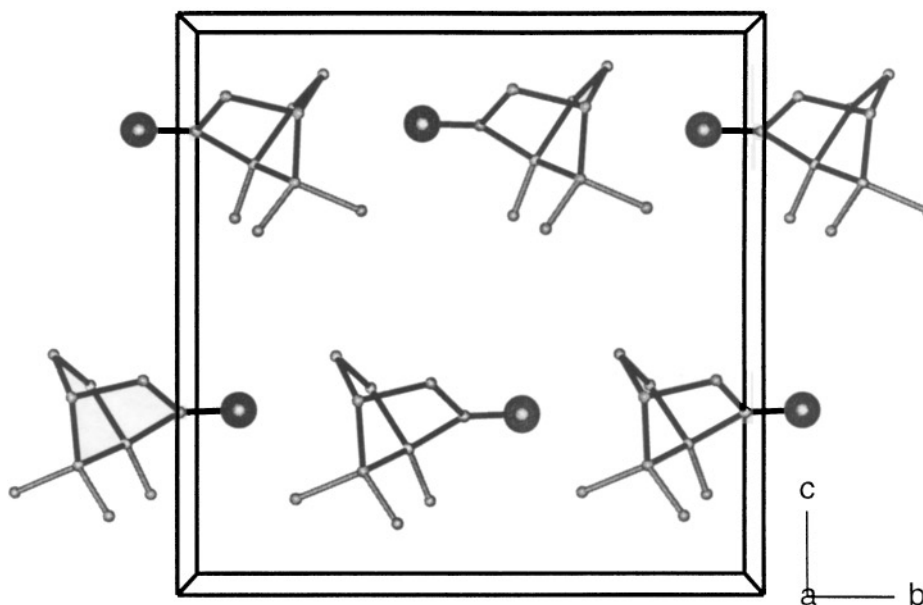


FIG. 3. A view down [100] of the structure of RS-camphor. The bicyclic rings are shown with dark bonds, the methyl groups with lighter bonds, and the oxygen atoms as shaded circles. The molecules are aligned with the carbonyl bond approximately parallel with the crystallographic *b*-axis. For clarity, only one of the four possible orientations of each molecule is shown. Molecules of opposite chirality are generated by the mirror planes at $x = 0$ and $z = \frac{1}{4}$, and rotational disorder is generated by the twofold axis along $(0, y, \frac{1}{4})$ (which corresponds to the intersection of the mirror planes). The oxygen atom is at distances of 0.15 and 0.71 Å from the mirror planes at $x = 0$ and $z = \frac{1}{4}$, respectively.

molecule. The structure shows an antiferroelectric ordering of the molecular dipole moments. Disorder in the chirality of the molecules is generated by the mirror planes at $x = 0$ and $z = \frac{1}{4}$. Their intersection, the twofold rotational axis along $(0, y, \frac{1}{4})$, generates additional twofold disorder. None of these symmetry operations alters significantly the alignment of the carbonyl bond or dipole moment, which is approximately parallel with the b -axis. For the long-range crystal structure therefore, left-handed and right-handed molecules are situated on the same crystallographic site, with an additional twofold rotational disorder of the molecules. Thus the disordered nature of phase III of normally cooled RS-camphor is confirmed by this study.

The view shown in Fig. 3 is in fact fully ordered, with left-handed and right-handed molecules related by the c -glide plane, as if the true space group were Cc . It is possible that the structure might transform to an arrangement like this during the extended annealing that is reported to produce further ordering of the structure (3).

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