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The Crystal and Molecular Structure of *meso*-*(2S, 4s, 6R)-2,4,6-Heptanetriol*

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The crystal structure of *meso*-(2*S*,4*s*,6*R*)-2,4,6-heptanetriol has been determined by means of X-ray methods. The crystal belongs to monoclinic system (space group Ic), with four molecules in a unit cell with dimensions of a=8.133, b=9.374, c=11.248 Å, and β=93.24°. The structure was solved by three-dimensional Patterson and trial-and-error methods. The final R factor was 0.076. The molecule has the GTTḠ conformation, and all of the OH groups are linked together by intermolecular hydrogen bonds.

The crystal and molecular structures of stereoregular vinyl polymers are of great interest. The structure of stereoregular polyvinyl alcohol has been proposed on the basis of the IR and NMR spectra and X-ray diffractions.[1–9] The configurations and conformations of 2,4,6-heptanetriol as a model compound have been studied by NMR and IR spectroscopy.[10–14] The present paper will report on the crystal and molecular structure of *meso*-(2*S*,4*s*,6*R*)-heptanetriol as a model compound of isotactic polyvinyl alcohol.

Experimental

The sample was prepared by the method reported by Fujii.[15] This compound was a highly viscous liquid, but it crystallized gradually upon standing in cold storage overnight. The specimens suitable for X-ray analysis were crystallized from a dioxane solution. They were colorless and needle-like elongated along the c axes or of a lozenge shape. Since the sample was very hygroscopic, it was enclosed in a glass capillary during exposure to X-rays.

The dimensions of the unit cell were determined by using a Syntex, on-line-controlled, four-circle diffractometer.

The density of the crystal, measured by the flotation method, was about 1.15 g cm^{-3}; this is in good agreement with the calculated value.

The probable space group is Ic or I2/c; the former was chosen, as the molecule can be placed neither on the center of symmetry nor on the two-fold axis. The crystallographic data are listed in Table 1.

Table 1. Crystallographic data

$C_7H_{16}O_3$	Systematic absences
a=8.133(2) Å	of the reflections
b=9.374(2)	hkl for $h+k+l=2n+1$
c=11.248(3)	$0k0$ for $k=2n+1$
β=93.24(2)°	D_x=1.149 g/cm^3
Mol. wt. 148.2	D_m=1.15
V=856.3(4) Å^3	mp 67°C
Z=4	
Space group Ic	

Multiple-film equi-inclination Weissenberg methods were applied to the layer lines from 0 to 8 and from 0 to 6 about the c and a axes respectively, using Ni filtered Cu$K\alpha$ radiation. The diffracted intensities were estimated visually by comparison with the standard scale. A total of 874 non-zero independent reflections were observed by these procedures. The corrections for Lorentz polarization and the spot-shape factors were made in the usual way, but no correction was made for absorption or extinction.

Structure Determination

From the three-dimensional Patterson function, it was deduced that the molecular axis made an angle of about 55° with the c axis and that the zigzag plane was nearly perpendicular to the b axis. From the consideration of the interatomic distances and internal rotation angles about the C–C–C–C–C bonds, it was deduced that five molecular models having different sequences of T, G, and/or Ḡ must be taken into account; they were (i) TTTT, (ii) GTTT, (iii) GTTḠ, (iv) TTGT, and (v) GTGT. We rotated each molecular model at an interval of 6° in Eulerian angles, fixing the middle carbon atom at x=0, and z=0, so that the lower-order calculated structure factors, $|F(h0l)|$'s, agreed relatively well with the observed $|F(h0l)|$'s. As a good agreement was obtained for the third model, we terminated these procedures without examining TTGT or GTGT.

The y parameters for all the atoms were introduced on the assumption that the y coordinate of the molecule is very close to 0, as the 020 is much stronger than the other $0k0$ reflections. With these parameters, the block-diagonal least-squares methods with isotropic temperature factors were applied on the TOSBAC 3400-41 using a program, HBLS IV, written by T. Ashida. After ten cycles of iterations, the discrepancy factor, R, for all the observed reflections decreased to 0.14. Further refinements were carried out with anisotropic temperature factors. After six cycles of iterations, the R factor decreased to 0.098. All of the hydrogen atoms were found in the difference Fourier map calculated at this stage, but their coordinates were thought not to be reliable. All of thier positions except for those bonded to oxygen were, therefore, determined assuming C–H bond lengths of 1.09 Å and bond angles of 109.5°. Fixing the calculated coordinates of the hydrogen atoms, six cycles of least-squares refinements were carried out. The R reduced to 0.076. The function to be minimized was $\sum w\Delta^2$, where:

$$w = (20.0/|F_0|) \quad \text{for } |F_0| > 20.0$$

$$w = 1 \quad \text{for } 20.0 \geq |F_0| \geq 5.0, \text{ and}$$

$$w = 0.3 \quad \text{for } |F_0| < 5.0$$

The final atomic coordinates and temperature factors, with their standard deviations, are listed in Tables 2 and 3. A list of observed and calculated

Table 2. THE FINAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS

Atom	x/a	y/b	z/c
C(1)	0.3071(8)	0.1395(7)	0.1079(6)
C(2)	0.2517(5)	−0.0038(5)	0.1529(4)
C(3)	0.0671(5)	−0.0320(6)	0.1278(4)
C(4)	0.0000(5)	−0.0210(4)	0.0000(3)
C(5)	−0.1847(6)	−0.0565(5)	−0.0067(4)
C(6)	−0.2710(5)	−0.0392(5)	−0.1302(4)
C(7)	−0.2891(7)	0.1145(5)	−0.1695(5)
O(1)	0.2773(4)	−0.0153(4)	0.2777(3)
O(2)	0.0825(4)	−0.1211(3)	−0.0734(3)
O(3)	−0.4354(4)	−0.0951(4)	−0.1286(3)
H(14)	0.372(9)	0.015(7)	0.294(6)
H(15)	0.155(10)	−0.076(7)	−0.125(6)
H(16)	−0.438(9)	−0.170(7)	−0.076(6)

Table 3. THE ANISOTROPIC TEMPERATURE FACTORS OF NONHYDROGEN ATOMS IN THE FORM $\exp\{-10^{-4}\times(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$. Their estimated standard deviations are given in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	190(11)	150(8)	89(5)	−71(7)	−32(6)	27(5)
C (2)	68(5)	112(5)	46(3)	−7(4)	−13(3)	3(3)
C (3)	83(6)	130(7)	62(4)	−13(5)	−18(4)	3(4)
C (4)	91(5)	81(4)	48(3)	−1(4)	−8(3)	−9(3)
C (5)	94(6)	112(6)	55(3)	−7(4)	−24(3)	11(3)
C (6)	93(6)	93(5)	50(3)	−2(4)	−21(3)	2(3)
C (7)	176(9)	100(6)	71(4)	4(6)	−30(5)	18(4)
O (1)	85(4)	145(5)	56(2)	−20(4)	−15(2)	7(3)
O (2)	119(4)	101(4)	65(2)	6(3)	1(2)	−18(2)
O (3)	95(4)	110(4)	108(4)	−18(3)	−56(3)	23(3)

structure factors is given in Table 4.*

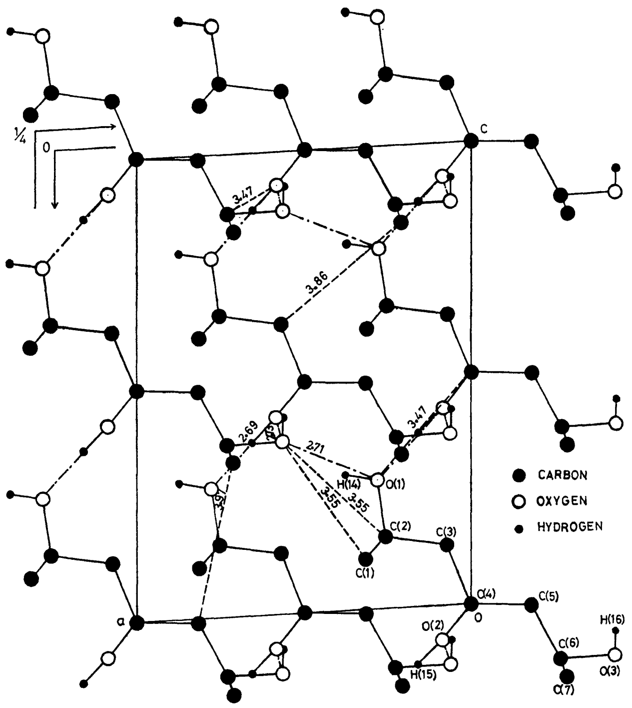

Fig. 1. The crystal structure viewed along the b axis. Only the hydrogen atoms attached to oxygen are indicated. The van der Waals distances shorter than 4.0 Å for C-----C and 3.6 Å for C-----O are shown by broken lines. The hydrogen bonds are also shown by chain lines.

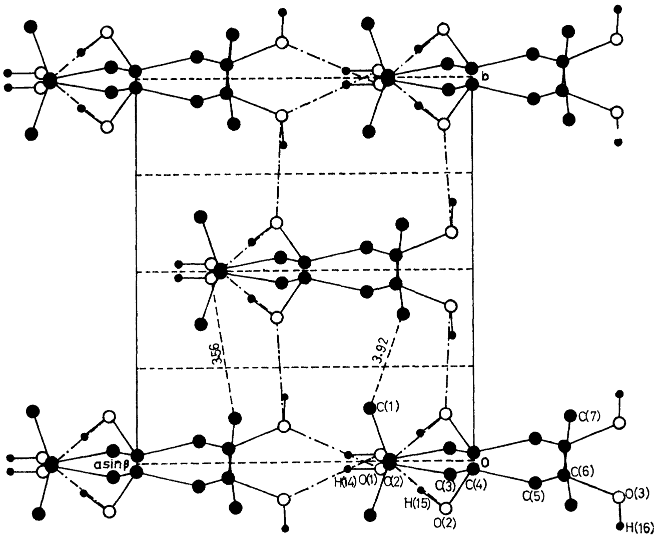

Fig. 2. The crystal structure viewed along the c axis. The hydrogen bonds are shown by chain lines.

Results and Discussion

The crystal structure projected along the b and c axes are shown in Figs. 1 and 2 respectively. The molecular structure is schematically shown in Fig. 3. As may clearly be seen from this figure, the molecule has a GTT$\bar{\text{G}}$ conformation, all of the hydroxyl groups are linked together by intermolecular hydrogen bonds, and their mean distances is 2.71 Å. The shortest van der Waals contact is 3.86 Å for C···C and 3.47 Å for C···O. The torsional angles about the C–C bonds are listed in Table 5. The best plane, composed of C(2) C(3), C(4), C(5), C(6), O(1), and O(3), is expressed by the equation:

$$-0.2495x + 0.9529y + 01856z + 0.1630 = 0$$

where x, y, and z are in Å units with respect to the crystallographic axes. The deviations from this plane are listed in Table 6.

The C–C and C–O bond lengths and the C–C–C

Table 5. TORSIONAL ANGLES

	Torsional angles (°)
C(1)-C(2)-C(3)-C(4)	55.2
C(2)-C(3)-C(4)-C(5)	178.5
C(3)-C(4)-C(5)-C(6)	175.9
C(4)-C(5)-C(6)-C(7)	−70.3
O(1)-C(2)-C(3)-C(4)	177.5
O(3)-C(6)-C(5)-C(4)	171.6
C(2)-C(3)-C(4)-O(2)	59.4
C(6)-C(5)-C(4)-O(2)	−63.8

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* Table 4 has been deposited with the Chemical Society of Japan (Document No. 7403)

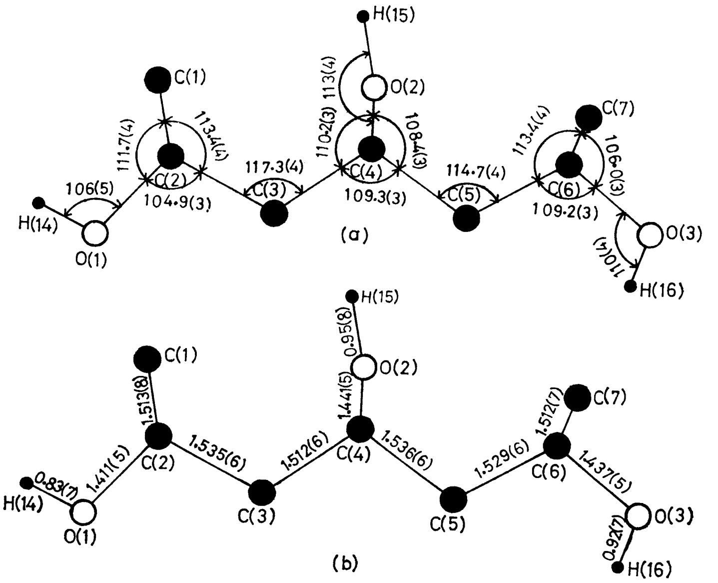

Fig. 3. Bond angles (degree) (a) and lengths (Å) (b). Hydrogen atoms attached to carbon are omitted.

TABLE 6. DEVIATION OF EACH ATOM FROM THE BEST PLANE

Atom	Deviation (Å)
C(2)	−0.063
C(3)	0.007
C(4)	−0.024
C(5)	0.018
C(6)	0.090
O(1)	0.042
O(3)	−0.071

and C–C–O bond angles agree well with those observed in ordinary aliphatic compounds, except for C(2)–C(3)–C(4), which is remarkably large.

It is thought to be unwize to discuss these results in comparison with those obtained by NMR or IR spectroscopy in solution,[10–14] as the solvents and thermal effects may affect the conformations and hydrogen bondings of the molecule. The structure of isotactic polyvinyl alcohol has a TTT sequence, and all of the hydroxyl groups are linked together by intermolecular hydrogen bonds,[1–3] which is quite different from the present trimer structure. There might be some metastable states or polymorphism. We expect to elucidate these points by future studies.

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