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NOTES

Refinement of the Crystal Structure of Pentaerythritol Tetracetate

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Synopsis. The crystal structure of the title compound has been refined to a final R value of 0.041 (weighted R=0.032), with 380 reflection data measured on a four-circle X-ray diffractometer. The overall structural features show no significant differences from those in the original determimation, while the structural parameters have been improved in precision.

A differential scanning calorimetry within the temperature range of 153 to 383 K suggested that the crystals of $C(CH_2OCOCH_3)_4$ undergo a reversible solid-phase transition at 209 K and melt at 358 K. The X-ray diffraction patterns of the low-temperature phase showed superstructural reflections at positions indicating a doubled c-period, while those of the room-temperature phase showed remarkable diffuse steaks parallel to the c^*-axis. In order to increase the precision of the structural parameters for a study of the phase transition, a reinvestigation of the crystal structure by the X-ray diffraction method was carried out.

Experimental

The compound was prepared as described by Tollens and Wigand.[1] Colorless single crystals were obtained by slow evaporation of an ethanol solution. The crystal used for the X-ray work was rectangular with dimensions of 0.21×0.22×0.27 mm^3. The unit-cell parameters and intensity data were measured on a Syntex $P\bar{1}$ automated four-circle diffractometer with monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The unit-cell parameters were refined by a least-squares fit of the setting angles of 25 reflections within a range of $14<2\theta<25°$. The density was measured by flotation in an aqueous solution of $C(CH_2OCOCH_3)_4$ and KI. The crystal data are given in Table 1.

The intensities of the reflections within a range of $2\theta<45°$ were measured by the θ–2θ scan technique with a variable scan rate of 4.0 to 24.0° min^{-1} at 293 K. Those of high-order reflections seemed to be practically non-significant; all 383 independent reflections with $2\theta<40°$ were used in subsequent calculations. The intensity data were corrected for Lp effects, but no corrections for absorption and extinction were applied due to the low absorption coefficient and the small size of the crystal. A refinement was carried out by a block-diagonal least-squares method; it was started with the atomic coordinates reported by Goodwin and Hardy,[2] together with the average temperature factor obtained by the Wilson statistics. The methylene H atoms were located in a difference Fourier synthesis, while the methyl H atoms were placed at calculated disordered positions with the half occupancy factor. The three intense reflections (110, 310, 011) were rejected because these seemed to suffer from extinction. Refinement with weights of $1/\sigma(F_o)$ was terminated when all shift/esd for the non-H atoms became less than 0.15. The final discrepancy index, R, was 0.041 (weighted R=0.032) for 380 reflections and 0.063 for all of 383 reflections. The final difference Fourier synthesis showed no significant features in the undulations within ±0.08 eA^{-3}. The atomic scattering factors used for C and O were taken from International Tables for X-ray Crystallography,[3] while those for H were adopted from the table of Stewart, Davidson, and Simpson.[4] All calculations were carried out in the Computer Center of Kyushu University of using locally modified versions of the UNICS-III program.[5,6] The final atomic parameters are listed in Table 2.[7] The drawings were made by using the *ORTEP* program.[9]

Table 1. Crystal Data[a)]

Molecular formula	$C_{13}H_{20}O_8$
Molecular weight	304.30
Space group	$P4_2/n$
a=12.136(2) Å	D_m=1.244 g cm^{-3} (at 298 K)
c=5.506(1) Å	D_x=1.246 g cm^{-3}
V=810.9(3) Å^3	μ=0.97 cm^{-1} (for Mo $K\alpha$)
Z=2	

a) The numbers in parentheses, here and elsewhere in this paper, are the esd's in the last significant digits.

Table 2. Fractional Atomic Coordinates and Isotropic Thermal Parameters[a)]

Atom	x	y	z	B/Å^2
C(1)	0	0	0	6.13(13)
C(2)	0.0926(2)	0.0375(2)	0.1667(4)	6.99(9)
O(1)	0.1835(1)	0.0710(1)	0.0164(3)	7.59(6)
C(3)	0.2720(2)	0.1107(2)	0.1314(5)	7.65(9)
O(2)	0.2752(2)	0.1191(2)	0.3463(3)	9.82(6)
C(4)	0.3599(2)	0.1403(3)	−0.0422(6)	10.29(9)
H(21)	0.068(1)	0.104(1)	0.264(4)	7.0(5)
H(22)	0.116(2)	−0.025(2)	0.271(4)	8.0(5)
H(41)	0.428(3)	0.167(3)	0.048(7)	8(1)
H(42)	0.379(3)	0.062(3)	−0.114(7)	10(1)
H(43)	0.321(4)	0.201(4)	−0.161(8)	11(1)
H(41′)	0.424(4)	0.100(4)	−0.002(10)	12(1)
H(42′)	0.369(4)	0.215(5)	−0.022(11)	15(2)
H(43′)	0.343(3)	0.123(3)	−0.220(8)	10(1)

a) The B's of the non-H atoms are the equivalent values of the anisotropic thermal parameters following the definition given by Hamilton.[8] The H atoms are labelled in terms of the C atom to which they are attached.

Results and Discussion

A steroscopic view of the molecule is shown in Fig. 1. The crystal structure projected along the c-axis is shown in Fig. 2, together with the atom numbering scheme. The bond distances, the valence angles, and the short intermolecular contacts are listed in Table 3. The molecule consists of four $-CH_2OCOCH_3$ groups attached to the C atom with four-fold alternating symmetry. This group has a planar zigzag configuration and lies approximately in the $(2\,\bar{5}\,0)$ or $(5\,2\,0)$ plane; the carbonyl bond is approximately parallel to the c-axis.

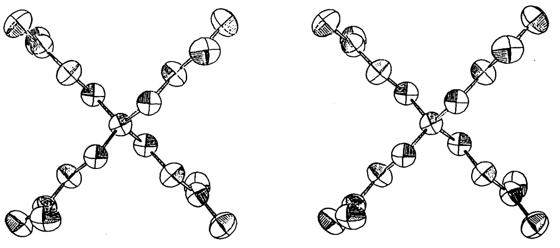

Fig. 1. Stereoscopic view of the molecule. The thermal motion ellipsoids are scaled to enclose 30% probability. The H atoms have been omitted for clarity.

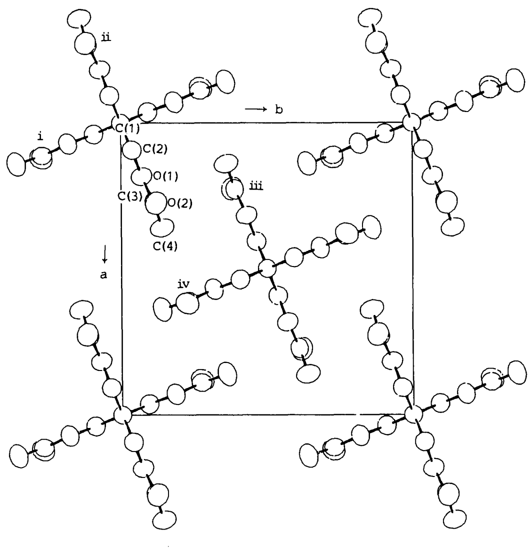

Fig. 2. Projection of the crystal structure along the c-axis, together with the atom numbering scheme. The thermal motion ellipsoids are scaled to enclose 30% probability. The H atoms have been omitted for clarity.

The C(3)-O(2) distance of 1.188(3) Å is shorter than the usual value for a carbonyl group. The O(1)-carbonyl-C(4) moiety is almost perfectly planar within the uncertainties in the atomic coordinates. This moiety may be considered to form a π-conjugation system. The deformation of the valence angles around C(3) may be ascribed to a steric repulsion between the methyl group and the carbonyl O atom in the adjacent molecule (C(4)$\cdots$O(2^{iv})=3.365(4) Å). There are short intermolecular contacts between the centrosymmetrically related carbonyl groups (O$\cdots$C=3.331(3), O$\cdots$O=3.405(3) Å). Each molecule is held together with four adjacent molecules by interactions between these dipoles parallel to the c-axis. The structure is very similar to that of pentaerythritol where, each molecule is held together by hydrogen bonds of the O-H$\cdots$O type.[10–12]

Table 3. Bond Distances (l), Valence Angles (θ), and Short Intermolecular Contacts (l)[a]

(a) Bond distance (l/Å)		(b) Valence angle (θ/°)	
C(1)-C(2)	1.521(2)	C(2)-C(1)-C(2^{i})	111.4(1)
C(2)-O(1)	1.438(3)	C(2)-C(1)-C(2^{ii})	105.8(1)
O(1)-C(3)	1.337(3)	C(1)-C(2)-O(1)	107.7(2)
C(3)-C(4)	1.477(4)	C(2)-O(1)-C(3)	116.5(2)
C(3)-O(2)	1.188(3)	O(1)-C(3)-O(2)	121.9(2)
		O(2)-C(3)-C(4)	126.9(3)
		O(1)-C(3)-C(4)	111.2(2)

(c) Molecular contact (l/Å)	
O(2)$\cdots$C(3^{iii})	3.331(1)
O(2)$\cdots$O(2^{iii})	3.405(3)
C(4)$\cdots$O(2^{iv})	3.365(4)

a) The superscripts refer to the following equivalent positions; none) x, y, z: i) $y, -x, -z$: ii) $-x, -y, z$: iii) $1/2-x, 1/2-y, 1/2-z$: iv) $1/2+y, 1/2-x, -1/2+z$.

The overall structural features show no significant differences from those in the original determination,[2] while the structural parameters have been improved in precision.

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