sheet perpendicular to the *c* axis. Three of the intermolecular hydrogen bonds are unique. They connect the *N*-hydroxyl of the hydroxamate groups with the peptide carbonyl of a neighboring molecule. All three bonds are very strong, $O(11)\cdots O'(13) = 2{\cdot}595$, $O(21)\cdots O'(23) = 2{\cdot}579$, and $O(31)\cdots O'(33) = 2{\cdot}563$ Å (Fig. 6). Fig. 5 also shows the nature of the pseudosymmetry ($R3$) in the crystal structure of deferriferrioxamine E. Along the *c* axis, the molecules stack on top of each other forming infinite cylinders. Within each cylinder, a molecule is linked to its nearest neighbors by hydrogen bonds *via* the water molecules.

All six water molecules in the asymmetric unit lie inside the macrocyclic ring of the deferriferrioxamine E molecule and are involved in extensive hydrogen bonding. The water molecules fall into two distinct groups: inner and outer. The three outer molecules [$W(1)$, $W(2)$, and $W(3)$] have a trigonal environment. Each of these forms three hydrogen bonds, two to the deferriferrioxamine E molecule and one to a water molecule belonging to the inner group. The three water molecules connect the peptide amino group of one molecule to the hydroxamate carbonyl of an adjacent molecule in the stack. The three inner water molecules [$W(4)$, $W(5)$ and $W(6)$] each form four hydrogen bonds in a tetrahedral environment: one to the deferriferrioxamine E molecule and three to other water molecules. The three inner water molecules are hydrogen bonded to each other in such a fashion that they form an infinite spiral along the *c* axis. The six water molecules are related to each other by a pseudo threefold screw axis at the center of the deferriferrioxamine E molecule. The hydrogen bonding, therefore, is quite efficient and involves all the O atoms, the peptide N atoms and water molecules.

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Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. VII.* Structure and Twinning of 2-(Hydroxymethyl)-2-methyl-1,3-propanediol

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Abstract

Crystals of the title compound, $CH_3C(CH_2OH)_3$, grown from solution or by sublimation, exhibit fourfold twinning thereby forming a pseudo-body-centered-tetragonal unit cell (cell II) in which the (*eee*) reflections have an average intensity 76 times greater than the other observed reflection types. Each of the fourlings contributes to the (*eee*) reflections, but only one fourling contributes to each of the other reflections. The structure reported here is an averaged, disordered structure determined from the (*eee*) reflections only.

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* Part VI: Sake Gowda & Rudman (1982).

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This structure (cell I) is isostructural with pentaerythritol, and is in the tetragonal space group, $I\bar{4}$, with $a = 6{\cdot}054$ (2), $c = 8{\cdot}866$ (3) Å, $V = 324{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}228$, $D_m = 1{\cdot}21$ Mg m^{-3}, and μ(Cu $K\alpha$) = 0·85 mm^{-1} at 294 K. Data were collected using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54051$ Å) and were refined to $R = 0{\cdot}039$ for 108 observed reflections. The distances and angles are normal, with the methyl group evenly distributed over the four possible sites. The relationships between cell (I), cell (II), and cell (III) (the true unit cell) are discussed.

Introduction

The structure of the title compound HO–CH_2–C(–CH_2OH)$_2$–CH_3, designated hereafter as RCH_3 [where R represents –C(CH_2OH)$_3$], was studied as part of our continuing investigation of hydrogen-bonded pseudo-spherical poly(hydroxymethyl) compounds known to undergo solid–solid transitions between ordered and orientationally dynamically disordered (plastic) phases. Doshi, Furman & Rudman (1973) reported that, on warming, RCH_3 undergoes a phase transition to an orientationally disordered face-centered cubic lattice (phase I) with $a \sim 8{\cdot}9$ Å, at 351·3 K. This paper describes the crystal and molecular structures of RCH_3 at room temperature (phase II). All the crystals of this compound that we examined were multiply twinned. The results reported here are for a statically disordered phase (II) which is isostructural with the closely related compound, pentaerythritol, C(CH_2OH)$_4$, or RCH_2OH (Eilerman & Rudman, 1979).

Twinning

Crystals grown from an ethyl acetate solution of RCH_3, obtained from Eastman Organic Chemicals, were pyramidal in shape and, when examined between crossed polaroids, were obviously twinned. Examination of these crystals on the diffractometer gave results compatible with those reported here. Crystals grown by vacuum sublimation were rectangular platelets. These crystals were examined with a polarizing microscope, particularly along the direction perpendicular to the face of the platelet, *i.e.* along the c axis of the pseudo-tetragonal cell. Although they initially appear to be isotropic along this direction, careful examination reveals very slight changes in shading and color as they are rotated on the microscope stage. This, together with the X-ray evidence discussed below, indicates the presence of twinning in the crystals. Over 15 crystals were examined by means of X-ray diffraction and all exhibited the same effects.

Three types of cells are involved in this discussion, as defined in Table 1. The initial examination of RCH_3, using a precession camera, indicated the presence of cell (I) which is isostructural with pentaerythritol. However, a more detailed systematic examination on the diffractometer revealed very weak reflections midway between the lattice points of cell (I), resulting in cell (II) in which each of the unit-cell dimensions of cell (I) is doubled.

Although the body-centered condition is retained (systematic absences for $h + k + l = 2n + 1$), cell (II) is only pseudo-body-centered-tetragonal, since equivalent reflections do not have equal intensities. Furthermore, the intensity data for cell (II) also showed that not even all the symmetry-allowed reflections are present. Reflections of the type (*ooe*) are completely absent (*o*: odd, *e*: even); (*eee*) reflections are present (and strong) only if ($h + k + l$, mod 4) = 0; while (*oeo*) and (*eoo*) are present but weak.

The (*eee*) reflections in cell (II) (which are the complete data set of cell I) have an average intensity which is 76 times that of the (*oeo*) and (*eoo*) reflections. It was also noted that, in cell (II), the ratios of the intensities of the strong reflections remained constant from crystal to crystal, while the ratios of the intensities of the weak reflections varied from crystal to crystal. These observations suggest that the crystals of RCH_3 are twinned.

The true cell was determined as follows: a list of the 25 'most intense' weak reflections was prepared. The Syntex Autoindexing routine was used to find a unit cell starting with eight strong reflections and one of these weak reflections. The unit cell they obtained is the monoclinic C-centered cell (III) in Table 1. All reflections in the list of 25 weak reflections corresponding to this monoclinic cell were identified. Then the process was repeated, using one of the remaining unidentified weak reflections and another cell was obtained. After four iterations, all 25 weak reflections could be accounted for by the four monoclinic cells in Table 1. They have identical cell parameters, but different orientations.

Table 1. *Unit cells encountered in the study of* RCH_3

This table is for identification purposes only, so approximate lattice constants are given. The transformation matrices from cell (I) are also given.

Cell designation	Lattice type	Unit-cell parameters
(I)	Tetragonal I	$a = 6{\cdot}05$, $c = 8{\cdot}87$ Å, $Z = 2$
(II)	Pseudo-tetragonal I	$a = 12{\cdot}1$, $c = 17{\cdot}7$ Å, $Z = 8$ (2,0,0/0,2,0/0,0,2)
(III)	Monoclinic C	$a = 10{\cdot}7$, $b = 6{\cdot}05$, $c = 12{\cdot}1$ Å, $\beta = 124{\cdot}3°$, $Z = 4$
	Cell (III)A	($\bar{1}$,0,$\bar{1}$/0,1,0/2,0,0)
	Cell (III)B	(1,0,$\bar{1}$/0,$\bar{1}$,0/$\bar{2}$,0,0)
	Cell (III)C	(0,$\bar{1}$,1/1,0,0/0,2,0)
	Cell (III)D	(0,1,1/$\bar{1}$,0,0/0,$\bar{2}$,0)

The findings are consistent with the non-systematic absences described for cell (II), since these unobserved reflections would give indices that were either fractional or not allowed by the monoclinic *C*-centered condition. Therefore we conclude that cell (III) represents the true cell, but is not easily obtainable as a single crystal. Since the only systematic absences found in cell (III) correspond to the *C*-centering condition, the space group of cell (III) is *Cm*, *C*2 or *C*2/*m*. We note that the presence of the other cells in the fourling results in measurable intensities for some reflections of symmetry-required systematic absences. Unfortunately, the superposition of lattice points in the fourling prevented us from solving the structure of the true cell. Consequently, we solved the structure of the averaged cell from cell (I).

Experimental

The density was measured by flotation in a carbon tetrachloride–xylene mixture. Crystal data for cell (I) have been given in the *Abstract*. Corresponding data for the other cells can be calculated using the transformation matrices found in Table 1. A crystal 0·15 × 0·11 × 0·09 mm was mounted on a Syntex $P2_1$-F diffractometer. Accurate lattice parameters were obtained by a least-squares refinement of 15 carefully centered reflections. An ω-scan showed a FWHM of 0·3°. The systematic absences ($h + k + l = 2n$) are consistent with several tetragonal space groups, but because of the similarity of $R\mathrm{CH_3}$ to $R\mathrm{CH_2OH}$, it was refined in $I\bar{4}$.

Intensity data were collected using the $\theta/2\theta$ scan method over the range $0 < 2\theta < 133°$, with $h_{\max} = k_{\max} = 7$, $l_{\max} = 10$. Two standard reflections (020,022) were measured every 15 reflections and indicated a 10% decay in intensity during the course of data collection. After a decay correction was applied there was a 3% random variation in the intensities of the standard reflections. Of the total 292 reflections that were measured, there were 132 unique reflections, with an internal agreement factor of 4·5%. The 108 reflections with $I > 3\sigma(I)$ were used in the refinement; Lorentz–polarization corrections were applied.

The C and O positions of $R\mathrm{CH_2OH}$ (Eilerman & Rudman, 1979) were used as starting parameters, with the multiplicity factor of O fixed at 0·75. Least-squares analysis (on *F*) was used and H atoms were located from a difference Fourier map [H(O1)] and by calculation (methylene H atoms). In the last cycle, 34 parameters were varied (positional parameters for all atoms, anisotropic thermal parameters for C and O, isotropic thermal parameters for H, a scale factor, and an extinction coefficient). The maximum shift-to-error ratio in this cycle was 0·027, with an average value of 0·009. The *R* and R_w values (defined in Eilerman & Rudman, 1979) were 0·039 and 0·045, with $S = 2{\cdot}68$ and $w^{-1} = \sigma(F)^2 + (0{\cdot}04F_o)^2$, where $\sigma(F) = \sigma(F^2)/(2F)^2$ and $\sigma(F^2)$ is based on counting statistics. The final Fourier difference map is featureless with a maximum height of 0·06 e Å^{-3}. The extinction coefficient is 0·064 (29), with a maximum correction of 0·785 to the 002 reflection; *F*(000) is 132. The sources of the programs and atomic scattering factors are described in Eilerman & Rudman (1979). The final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 2.* The multiplicities used in the refinement of the H atoms were 0·75. Thus, this model represents the central C atom [C(*C*)], three hydroxymethyl groups {—C(1) [H(11),H(12)]—O(1)—H(O1)}, and the methyl C atom [with the assumption that this atom is in the same position as C(1)]. The H atoms on the methyl group have not been accounted for.

Table 2. *Fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters for* $R\mathrm{CH_3}$ *in cell* (I) *at room temperature*

	x	*y*	*z*	B_{eq}*/ B_{iso} (Å^2)	Multiplicity
C(*C*)	0	0	0	2·73	0·25
C(1)	1276 (8)	1588 (8)	1012 (5)	4·05	1·00
O(1)	2445 (7)	3182 (6)	222 (7)	5·14	0·75
H(11)	229 (10)	81 (11)	169 (5)	3·3 (10)	0·75
H(12)	23 (10)	231 (10)	166 (6)	3·0 (9)	0·75
H(O1)	357 (10)	271 (10)	8 (9)	3·6 (14)	0·75

* $B_{\mathrm{eq}} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

Discussion

The distances and angles observed in $R\mathrm{CH_3}$ (Table 3) fall within the normal range observed in similar compounds (*e.g.* $R\mathrm{CH_2OH}$, Eilerman & Rudman, 1979), except for the C(1)—O(1) distance which is shorter than the value of 1·422 (2) Å found in $R\mathrm{CH_2OH}$, but is not significantly different from 1·405 (6) Å found in $R\mathrm{NO_2}$ (Sake Gowda & Rudman, 1982). The hydrogen-bonding scheme in $R\mathrm{CH_3}$ is similar to that found in $R\mathrm{CH_2OH}$ except that one 'link' is open.

The structural relationships between the orientationally disordered and ordered phases are of interest. Cell (I) requires the presence of a statically disordered molecule since the required site symmetry, $\bar{4}$, is not present in the $R\mathrm{CH_3}$ molecule as it is in $R\mathrm{CH_2OH}$.

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* Lists of structure factors, anisotropic thermal parameters and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38260 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* RCH$_3$ *in cell* (I)

	Uncorrected	Corrected*
C(*C*)–C(1)	1·525 (4)	1·539 (4)
C(1)–O(1)	1·386 (6)	1·405 (7)
O(1)···O(1$^{\mathrm{i}}$)†	2·714 (5)	
C(1)–H(11)	0·98 (6)	
C(1)–H(12)	0·96 (6)	
O(1)–H(O1)	0·75 (6)	
H(O1)···O(1$^{\mathrm{i}}$)†	1·99 (6)	
		Symmetry-related angles
C(1)–C(*C*)–C(1$^{\mathrm{ii}}$)	107·9 (4)	C(1$^{\mathrm{iii}}$)–C(*C*)–C(1$^{\mathrm{iv}}$)
C(1)–C(*C*)–C(1$^{\mathrm{iii}}$)	110·2 (2)	C(1)–C(*C*)–C(1$^{\mathrm{iv}}$); C(1)–C(*C*)–C(1$^{\mathrm{iii}}$); C(1$^{\mathrm{ii}}$)–C(*C*)–C(1$^{\mathrm{iv}}$)
C(*C*)–C(1)–O(1)	113·6 (4)	
O(1)–H(O1)···O(1$^{\mathrm{i}}$)†	162 (6)	

Symmetry code: (i) $y, 1-x, -z$; (ii) $-x,-y,z$; (iii) $y,-x,-z$; (iv) $-y,x,-z$.

* Riding correction (Busing & Levy, 1964).

† Hydrogen-bonded distance.

The relationship between the high-temperature f.c.c. cell of phase (I) ($a \sim 8\cdot9$ Å) and cell (I) of phase (II) is $a = b \approx (\sqrt{2}/2)\, a_{\mathrm{f.c.c.}}$ and $c \approx a_{\mathrm{f.c.c.}}$. Cell (II), with eight times the volume of cell (I) and the same systematic absences, would not require a disordered molecule. However, as mentioned above, it is not the true cell. The monoclinic cell (III), which appears to be the true unit cell of RCH$_3$, is related to the phase (I) f.c.c. cell in a manner similar to that found in phases (I) and (II) of CCl$_4$ and CBr$_4$ (Rudman, 1979; Powers & Rudman, 1980). It has been shown that in the f.c.c. cell, a vector from an origin lattice point to an adjacent face-centered lattice point is perpendicular to a (110) plane. The vector forms the **b** direction of the monoclinic cell and the (110) plane is the *ac* plane. In an f.c.c. cell there are 12 such vectors, leading to 12 possible orientations of the ordered crystal. However, in RCH$_3$ where the contractions of the lattice result in a pseudo-tetragonal cell, there are only four possible orientations: $\pm a$ and $\pm b$, as shown in Table 1. The lattice points from these four cells (with $Z = 4$) superimpose thereby giving rise to an average cell corresponding to a statically disordered molecule.

Each of the weak reflections was identified as belonging to only one of the four cells and a comparison of the intensity of five sets of similar reflections from each of the four cells resulted in the following percentages for the crystal from which data were collected: cell (III)*A*, 38·6; (III)*B*, 34·6; (III)*C*, 24·0; (III)*D*, 2·8%. No attempt has been made to refine the structure in cell (III).

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Molecular Conformation and Electronic Structure. VII.* The Structure of the Isomorphic System *p*-Chloro-*N*-(*p*-methylbenzylidene)aniline and *p*-Methyl-*N*-(*p*-chlorobenzylidene)aniline

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Abstract

The isomorphous crystal structures of two hetero *para* disubstituted derivatives of benzylideneaniline, BA, have been determined. Both *p*-chloro-*N*-(*p*-methylbenzylidene)aniline, MeCl, and *p*-methyl-*N*-(*p*-chlorobenzylidene)aniline, ClMe, (C$_{14}$H$_{12}$ClN, $M_r = 229\cdot6$) crystallize in space group $P2_1/a$ with $Z = 2$. For MeCl $a = 5\cdot960\,(1)$, $b = 7\cdot410\,(1)$, $c = 13\cdot693\,(3)$ Å, $\beta = 99\cdot20\,(2)^\circ$, $V = 597\cdot0$ Å^3, $D_m = 1\cdot28$, $D_x = 1\cdot28$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 2\cdot45$ mm^{-1}, $F(000) = 240$. For ClMe $a = 5\cdot969\,(2)$, $b = 7\cdot412\,(2)$,

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* Part VI: Bar & Bernstein (1982*a*).

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