

length was observed only for nitron oxygen being involved in strong hydrogen bonding. The presented nitron, as well as all other conjugated nitrones of 1,4-diazabutadiene systems, fulfil to a high extent all discovered relationships.

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High-Pressure X-ray Diffraction Study of Pentaerythritol

BY ANDRZEJ KATRUSIAK

Department of Crystal Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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Abstract

Pentaerythritol [2,2-bis(hydroxymethyl)-1,3-propanediol], $C(CH_2OH)_4$, tetragonal, $I\bar{4}$, $Z = 2$, $a = 6.0752$ (8), $c = 8.733$ (2) Å at $T = 291$ K and 0.1 MPa, has been studied at high pressures by X-ray diffraction. The pressure dependence of the unit-cell dimensions has been measured to 1.15 GPa, and the crystal structure has been

determined at 1.15 GPa: $a = 6.017$ (1), $c = 8.267$ (3) Å; final $R = 0.043$ for 185 observed reflections; the C and O atoms were refined with anisotropic thermal parameters, and H atoms located in a ΔF map and refined with isotropic thermal parameters. The compressibility of van der Waals contacts between the sheets of the hydrogen-bonded molecules is several times larger than along the sheets, and above 280 MPa the distances between the

centres of near molecules of neighbouring sheets become shorter than the distances between the centres of the hydrogen-bonded molecules; at ambient pressure these distances become equal when the structure transforms to the plastic phase at 453 K. Small changes in molecular dimensions are consistent with transformations of the crystal structure. The OH...O hydrogen bond is compressed to 98% of its ambient pressure length.

Introduction

Pentaerythritol is a model structure in the studies of polyhydroxymethyl compounds and has been investigated by various physical and chemical methods (e.g. Nitta, 1926; Pauling, 1960; Westrum, 1961; Smith, 1969; Marzocchi & Castellucci, 1971; Bärnighausen, 1978). At 452.7 K the crystal transforms from the ordered body-centred tetragonal structure to the plastic face-centred cubic phase, with the molecules orientationally disordered about their centres of inertia (Nitta & Watanabé, 1937, 1938). The X-ray crystal structure determination of pentaerythritol was carried out by Llewellyn, Cox & Goodwin [1937 (excluding the H atoms)], and redetermined by several other authors (Wyckoff, 1966; Ladd, 1979; Eilerman & Rudman, 1979; Hope & Nichols, 1981). A neutron diffraction study based on *hk0* and *00l* reflections was performed by Hvorslef (1958) and most recently, based on full three-dimensional data, by Semmingsen (1988). Owing to its relatively simple structure, pentaerythritol is a model compound for studying the properties of hydrogen bonds and transformations to the plastic phases of cyclic and acyclic alcohols, as well as of other structures in which hydrogen bonds between molecules are broken above transition temperatures. Several high-pressure studies of pentaerythritol were reported. Frolov, Vereshchagin & Rodionov (1962) measured, by X-ray powder diffraction, the unit-cell dimensions as a function of pressure to 883 MPa; the discontinuities observed in the compression of *a* and *c* between 410 and 550 MPa were interpreted as a first-order phase transition in that pressure range. The magnitudes of the discontinuities in *a* and *c* were approximately four times the combined e.s.d.'s of the measurements; the maximum compression reported in the study by Frolov, Vereshchagin & Rodionov (1962) at 883 MPa was *ca* 8 combined e.s.d.'s for *a* and 18 for *c*. The high-pressure phase was reported to be metastable for *ca* 30 days after releasing the pressure, although the authors also suggested that the ambient- and high-pressure phases had the same structure. This was contradicted by Zhorin, Maksimychev, Kushnerev, Shashkin & Enikolopyan (1979), who mentioned their observation of additional reflections in their high-pressure X-ray powder diffraction measurements. The pressure-induced phase transition seemed confirmed by the pressure dependence of the electric conduction of pentaerythritol (Zhorin, Maksimychev, Ponomarenko

Table 1. *Pressure-dependence of the unit-cell dimensions of pentaerythritol tetragonal crystals*

l is the distance between the centres of close molecules of the neighbouring sheets. The high pressures are calibrated with a precision of 50 MPa.

Pressure (MPa)	<i>a</i> (Å)	<i>c</i> (Å)	<i>l</i> (Å)	<i>V</i> (Å ³)
0.1	6.0752 (8)	8.733 (2)	6.114 (1)	322.3 (1)
110	6.0687 (10)	8.660 (3)	6.096 (2)	318.9 (2)
550	6.0490 (12)	8.464 (2)	6.017 (2)	309.7 (1)
1150	6.0173 (10)	8.267 (3)	5.932 (2)	299.3 (2)

& Enikolopyan, 1979), and its IR spectra (Hamann & Linton, 1976). Besides these indications, no evidence of the pressure-induced phase transition in pentaerythritol was reported.

This high-pressure study of pentaerythritol was undertaken to analyse external and internal strains of the crystal (Catti, 1989; Born & Huang, 1954) in relation to its structure, which is built of sheets of hydrogen-bonded molecules, the compressibility of the hydrogen bonds and van der Waals contacts between the molecules, to verify the information regarding the pressure-induced phase transition, and to identify the factors which destabilize the ambient-pressure structure and which may play an important role in destabilizing the orientation of the molecules at the phase transition to the plastic phase at 453 K. It was also intended to test the performance of high-pressure data collection and data reduction procedures being prepared for a KUMA diffractometer. The accuracy of high-pressure X-ray measurements on organic crystals is often insufficient to locate H atoms, or to draw conclusions concerning any changes in bond lengths or valency angles induced in molecules by elevated pressures (Katrusiak, 1991a). This, in turn, limits applications of otherwise potentially effective high-pressure structural studies on organic crystals in relation to their chemical and physical properties. The main experimental task of this work was to obtain results accurate enough for a conclusive comparison of the molecular dimensions at ambient and high pressures.

Experimental

Single-crystal tetragonal pyramids of pentaerythritol were obtained by slow evaporation of saturated aqueous solution. The crystal mounted in a high-pressure diamond-anvil cell (Merrill & Bassett, 1974) was a pyramid approximately 0.20 mm along each side of its square base, with its vertex truncated at a height of *ca* 0.07 mm; the crystals have a cleavage plane perpendicular to *z*. The sample crystal was glued to the diamond culet with a dab of silicone vacuum grease and an Inconel gasket was used (0.2 mm thick, initial hole diameter 0.45 mm); a 4:1 mixture of methanol and ethanol was applied as hydrostatic fluid (Hazen & Finger, 1982). A KUMA diffractometer and

graphite-monochromated $\text{Mo } K\alpha$ radiation was used. The measurements were carried out at $T=291\text{ K}$. An internal NaCl crystal standard was applied to calibrate the pressure with an accuracy of *ca* 50 MPa (Bassett & Takahashi, 1974). The unit-cell dimensions (Table 1) were determined to 1.15 GPa by a least-squares fit to the diffractometer angles of 18–25 reflections ($11 < 2\theta < 28^\circ$). The unit-cell dimensions redetermined at ambient pressure for the crystal mounted in the high-pressure cell are slightly shorter than those previously reported for bare pentaerythritol samples at room temperature (Eilerman & Rudman, 1979), and insignificantly shorter than the unit-cell dimensions determined at $T=294\text{ K}$ by Semmingsen (1988): $a=6.079(3)$, $b=8.745(4)\text{ \AA}$. Several attempts to increase pressure above 1.5 GPa resulted in damaging the samples. This could be caused by collisions of the sample with the anvils or mechanical strains, but it is also possible that at high pressures pentaerythritol undergoes a phase transition which damages the single crystals (see the *Introduction* and *Discussion*). The data collection at 1.15 GPa was performed with the ω -scan method; the setting angles of reflections with the $\varphi = 0^\circ$ condition (Finger & King, 1978), scan speed dependent on reflection intensity ($0.4\text{--}25.0^\circ\text{ min}^{-1}$) and stationary background measurement were employed. A hemisphere of accessible reflections ($2\theta \leq 50^\circ$), for which both the primary and reflected beams lay within 40° from the high-pressure cell axis, was collected. The intensity-data reduction procedure accounted for the absorption of the Merrill–Bassett cell and Lp effects. The ambient-pressure structure (Eilerman & Rudman, 1979) was used as a starting model for the full-matrix least-squares refinement. After the C and O atoms were refined with anisotropic temperature factors, the positions of all H atoms were located in a ΔF map, where they appeared as the strongest peaks. The H atoms were included in the refinement with isotropic temperature factors. The experimental details are summarized in Table 2, the final atomic parameters are listed in Table 3.*

The absorption of the Merrill–Bassett cell was calculated and applied by an *ad hoc* program: for each reflection, the angles between the axis of the radial symmetry of the cell and either of the incident and reflected beams (Finger & King, 1978), and then the combined attenuation, of the incident and reflected beams separately, from the pre-measured absorption of the diamond–anvil and the beryllium support disc were calculated. The program *SHELX76* (Sheldrick, 1976) was used for structure refinement and *PLUTO* (Motherwell, 1976) for plotting crystal structures.

*A list of structure factors has been deposited with the IUCr (Reference: HR0019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected crystallographic data, and details of the data collection and refinement of the pentaerythritol structure at 1.15 GPa

M_r	136.15
$F(000)$ (e)	148
D_x (1150 MPa) (g cm^{-3})	1.511 (1)
$\mu(\text{Mo } K\alpha)$ (cm^{-1})	0.84
$\lambda(\text{Mo } K\alpha)$ (\AA)	0.71069
Max. h, k, l	10, 10, 3
No of reflections: total	420
unique	185
Max. check reflection fluctuations	0.015
No. of refined parameters	33
R_{int}	0.018
R	0.043
wR [$w = \sigma^{-2}(F_o)$]	0.032
S	1.01
Max. shift/e.s.d.	0.001
Final ΔF map (e \AA^{-3}):	
maximum	0.22
minimum	−0.20

Table 3. Fractional coordinates, U_{eq} and U_{iso} (\AA^2) for pentaerythritol at 1.15 GPa/292 K

The anisotropic temperature factors U_{11} , U_{22} , U_{33} , U_{32} , U_{31} and U_{21} are: C(1) 0.018 (1), 0.018 (1), 0.046 (20), 0, 0, 0; C(2) 0.026 (1), 0.023 (1), 0.026 (9), 0.002 (2), 0.007 (2), −0.003 (1); O(1) 0.022 (1), 0.023 (1), 0.035 (6), −0.007 (2), −0.001 (1), −0.003 \AA^2 , respectively. The ambient-pressure atomic positions (Eilerman & Rudman, 1979) are also given for comparison.

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
0.1 MPa				
C(1)	0	0	0	0.025 (1)
C(2)	0.1584 (2)	0.1257 (2)	−0.1034 (1)	0.035 (1)
O(1)	0.3181 (1)	0.2461 (2)	−0.0194 (1)	0.048 (1)
H(1)	0.233 (3)	0.027 (3)	−0.170 (2)	0.0423 (8)
H(2)	0.074 (4)	0.229 (3)	−0.167 (2)	0.0504 (9)
H(3)	0.272 (3)	0.360 (4)	−0.007 (2)	0.0432 (9)
1.15 GPa				
C(1)	0	0	0	0.027 (12)
C(2)	0.1600 (4)	0.1265 (4)	−0.1111 (6)	0.025 (5)
O(1)	0.3219 (2)	0.2460 (2)	−0.0198 (4)	0.027 (4)
H(1)	0.219 (5)	0.026 (4)	−0.179 (8)	0.03 (1)
H(2)	0.063 (4)	0.234 (5)	−0.182 (7)	0.03 (1)
H(3)	0.277 (3)	0.368 (4)	0.012 (10)	0.02 (1)

Atomic scattering factors incorporated in *SHELX76* and an IBM-386SX computer were used.

Ambient-pressure structure

At ambient pressure and room temperature, the hydroxymethyl chains of a pentaerythritol molecule (see Fig. 1) are S_4 -symmetry related; the conformation of the chains is not otherwise constrained. When isolated, the molecule of pentaerythritol is relatively flexible and its fragments can rotate about the C—C or C—O single bonds; the rotations are only restricted by intramolecular steric hindrance of the O and H atoms. According to *ab initio* calculations (Ladd, 1979), the C(1)—C(2)—O(1)—H(3) torsion angle of $92(2)^\circ$ (Table 4) observed in the crystal is the least stable

position for the free molecule. In the light of these results, the conformation assumed by the pentaerythritol molecule in the tetragonal crystal (see Fig. 1) is mainly due to intermolecular forces, the strongest of which are the hydrogen bonds linking the molecules into sheets along the xy planes. Each hydroxyl group is involved in two moderately strong hydrogen bonds of 2.710 (1) Å (Eilerman & Rudman, 1979), and eight symmetry-equivalent hydrogen bonds link one molecule with four neighbouring molecules, two molecules at $x \pm 1$ and two at $y \pm 1$ (Fig. 2). The cohesion forces between the sheets can be classified as mainly weak van der Waals-type interactions. Although the intermolecular forces along z are much weaker than the hydrogen bonds along the sheets parallel to xy , the arrangement of the centres of the molecules, *i.e.* of atoms C(1), in the structure closely approximates a cubic F lattice, to which it transforms at 452.7 K. The transformation to the F lattice is defined by the matrix

$$M(I \rightarrow F) = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The parameter $a_F = a(2)^{1/2}$ of the *pseudo-cubic* F unit cell lies within the hydrogen-bonded sheet, and $c_F = c$ is perpendicular to the sheet. In the closely-packed cubic F lattice of the plastic phase, the molecules are cubo-octahedrally coordinated by 12 molecules, and distances between the centres of the nearest molecules are equal. At ambient pressure and 291 K, $a_F = 8.592(1)$ Å and is shorter than c by only 0.141 (2) Å; the distances from a molecule centre to four molecules within the sheet are shorter by a mere 0.039 (1) Å than the distances from the molecule centre to four near molecules below and to four near molecules above the sheet, l (Table 1).

Molecular strain

The molecular dimensions involving heavy atoms, measured by X-rays (Eilerman & Rudman, 1979) and by neutron diffraction (Semmingsen, 1988), are in very good agreement, however, the bonds to H atoms determined by X-rays, as expected, are shorter

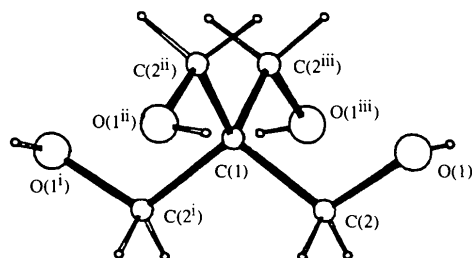


Fig. 1. Pentaerythritol molecule in the conformation present in the crystal structure. H atoms are represented as small circles, the symmetry codes are given in Table 4.

Table 4. Molecular dimensions of pentaerythritol (Å, °) at 1.15 GPa (this study) and 0.1 MPa (Eilerman & Rudman, 1979)

As the molecule is centred on the site of S_4 symmetry, several valency and torsion angles in this table involve symmetry-related atoms (see Fig. 4). The values in square brackets are the distances corrected for the rigid-body motion (Schomaker & Trueblood, 1968).

	1.15 GPa	0.1 MPa
C(1)—C(2)	1.533 (3)	1.527 (1)
	[1.534]	[1.548]
C(2)—O(1)	1.427 (4)	1.422 (2)
	[1.432]	[1.441]
C(2)—H(1)	0.90 (4)	0.95 (2)
C(2)—H(2)	1.05 (4)	0.99 (2)
O(1)—H(3)	0.82 (4)	0.75 (2)
C(1)—C(2)—O(1)	111.2 (3)	112.51 (9)
C(2)—C(1)—C(2')	106.4 (2)	107.33 (9)
C(2)—C(1)—C(2'')	111.05 (13)	110.55 (5)
C(1)—C(2)—H(1)	106.6 (16)	110.6 (9)
C(1)—C(2)—H(2)	106.9 (14)	109.2 (12)
H(1)—C(2)—H(2)	106 (4)	107.6 (14)
C(2)—O(1)—H(3)	113.4 (15)	107.0 (12)
O(1)—C(2)—C(1)—C(2')	-178.3 (2)	-178.68 (9)
O(1)—C(2)—C(1)—C(2'')	-57.3 (3)	-58.04 (11)
O(1)—C(2)—C(1)—C(2''')	60.8 (3)	60.67 (11)
H(3)—O(1)—C(2)—C(1)	-83 (4)	-92.0 (16)

Symmetry codes: (i) $-x, -y, z$; (ii) $y, -x, -z$; (iii) $-y, x, -z$.

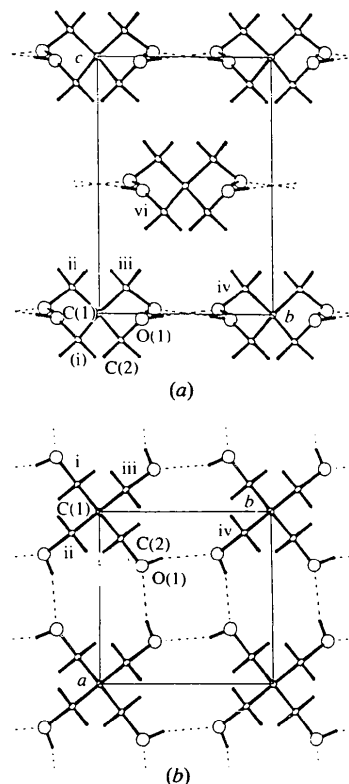


Fig. 2. Molecular arrangement in the pentaerythritol structure: (a) projection down [001]; (b) one sheet of the hydrogen-bonded molecules at $z = 0$ viewed down [001]. Hydrogen bonds are represented as dashed lines. The Roman numerals label the symmetry-equivalent molecular fragments and refer to the symmetry codes given in Tables 4, 5 and 6.

and less precise than those determined by neutron diffraction: 1.070 (6), 1.081 (6) and 0.933 (6) Å for H(1), H(2) and H(3), respectively (Semmingen, 1988). The neutron-diffraction measurement also showed that the thermal vibrations of the heavy atoms are considerably less anisotropic than those established in the X-ray diffraction experiment, which would imply that the corrections of the bond lengths for the rigid-body motion calculated by Eilerman & Rudman (1979) should be smaller. To minimize any possible systematic errors, the comparisons below are mainly based on the X-ray results not corrected for the rigid-body motion. Both the corrected and uncorrected bond lengths are listed in Table 4.

Several of the molecular dimensions, given in Table 4, markedly change their values between 0.1 and 1150 MPa. All the bond lengths, including those involving the H atoms, agree with the ambient pressure values within 2 e.s.d.'s (Table 4). Small, but highly statistically significant and systematic changes can be noted in the valency angles. The valency angles about the central C(1) atom indicate that the C(2) atoms do not form an ideal tetrahedron around C(1), but that it is slightly elongated along *z* (Eilerman & Rudman, 1979; Semmingen, 1988). This elongation becomes even larger at 1.15 GPa, which is consistent with the direction of strong intermolecular interactions within the sheets. The relatively rigid hydrogen bonds transmit the thrust of high pressures to the molecules along the *xy* plane, while the thrust between the molecules of neighbouring sheets is transmitted along cell-diagonal directions [111], $[\bar{1}11]$ etc, because in the *I* Bravais cell, the globular molecules of near sheets lie above and below the eight-membered rings of four hydrogen-bonded hydroxyl groups (see Fig. 2). This distribution of stress enforces a further elongation of the molecule along *z*, by a decreasing valency angle C(2)—C(1)—C(2ⁱ) and increasing angle C(2)—C(1)—C(2ⁱⁱ) (see Figs. 1 and 2 and Table 4). A small decrease in the C(1)—C(2)—O(1) angle is consistent with the above argument: the plane defined by the C(1)—C(2)—O(1) group is almost perpendicular to the *xy* plane, and the line through O(1)··C(1) is at 86.24° to the *z* axis (see Fig. 2). It can also be noted that the valency angles about C(1) are closer to the ideal angle of 109.5° at ambient pressure than at 1.15 GPa. No significant differences in torsion angles are observed for the pentaerythritol molecule between 0.1 and 1150 MPa (Table 4).

Crystal structure-strain relation

The pressure dependence of the unit-cell dimensions is plotted in Fig. 3. The compressibility of the crystal along *z*, perpendicular to the hydrogen-bonded sheets, is almost six times larger than along *x* and *y*: $\beta_c = 1/c_o(\partial c/\partial P) = 4.64 \times 10^{-2}$ and $\beta_a = 0.83 \times$

10^{-2} GPa^{-1} . The compressibility of the unit-cell dimensions along [001] is clearly non-linear, which is characteristic of molecular crystals and weak interplanar van der Waals contacts (Katrusiak, 1991a), while this effect is not observed along the hydrogen bonds. A similar anisotropic compressibility was also observed for the structure of squaric acid, built of sheets of hydrogen-bonded molecules (Katrusiak & Nelmes, 1986a). The magnitudes of compressibility of pentaerythritol given above are calculated from the unit-cell dimensions measured at 0.1 and 1150 MPa. The β_c compressibilities calculated for 0.1–110–550–1150 MPa pressure intervals are 7.60×10^{-2} , 5.14×10^{-2} and $3.28 \times 10^{-2} \text{ GPa}^{-1}$, respectively. Compressibility of the pentaerythritol crystal measured by ultrasonic methods (Nomura, Higuchi, Kato & Miyahara, 1972) is similar for the [001] direction, $\beta_c = 6.48 \times 10^{-2} \text{ GPa}^{-1}$, but considerably smaller along [100]: $\beta_a = 0.48 \times 10^{-2} \text{ GPa}^{-1}$. The pressure dependence of the unit-cell dimensions measured by Frolov, Vereshchagin & Rodionov (1962) is considerably different. The compressibilities obtained from the data reported in their work for 0.1 and 883 MPa are also different: $\beta_a = 2.04 \times 10^{-2}$ and $\beta_c = 3.50 \times 10^{-2} \text{ GPa}^{-1}$. Compressibility of the hydrogen bonds between the hydroxyl groups equals $1.604 \times 10^{-2} \text{ GPa}^{-1}$, and is somewhat larger than the compressibility of shorter —OH··O= hydrogen bonds in the cyclic β -diketoalkane structures of 1,3-cyclohexanedione or 2-methyl-1,3-cyclopentanedione (Katrusiak, 1990, 1991b), and much larger than in inorganic crystals of KH_2PO_4 and PbHPO_4 (Katrusiak, 1989). The dimensions of the hydrogen bond in pentaerythritol are shown in Table 5. Statistically

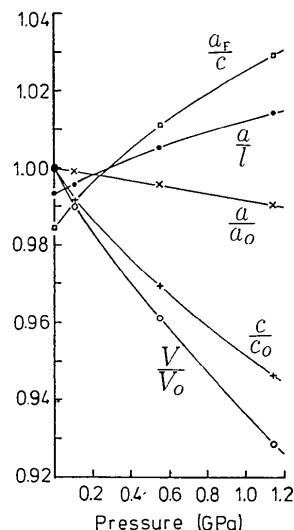


Fig. 3. Relative changes of the unit-cell dimensions with pressure and the pressure dependence of the ratios a/t and a_F/c , where $t = 0.5(2a^2 + c^2)^{1/2}$ is the distance between the centres of near molecules of neighbouring sheets, and a_F is the dimension of the tetragonal face-centred unit cell (see text).

Table 5. Hydrogen-bond geometry in pentaerythritol at 1.15 GPa (*this study*) and ambient pressure (Eilerman & Rudman, 1979)

	1.15 GPa	0.1 MPa
O(1)···O(1 ^{iv}) (Å)	2.660 (2)	2.710 (1)
H(3)···O(1 ^{iv}) (Å)	1.88 (2)	1.98 (2)
O(1)—H(3)···O(1 ^{iv}) (°)	158 (3)	163 (2)

Symmetry code: (iv) $y, 1 - x, -z$.

Table 6. Selected short intermolecular distances in the pentaerythritol crystal at 1.15 GPa (*this study*) and 0.1 MPa (Eilerman & Rudman, 1979)

	1.15 GPa	0.1 MPa
O(1)···C(2 ^v)	3.529 (3)	3.5923 (16)
O(1)···C(2 ^{vi})	3.466 (6)	3.728 (2)
O(1)···C(2 ^{vii})	3.604 (5)	3.842 (2)
H(3)···H(3 ^{iv})	2.21 (3)	2.31 (3)
O(1)···H(3 ^{iv})	2.88 (2)	2.95 (2)

Symmetry codes: (iv) $y, 1 - x, -z$; (v) $1 - y, x, -z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} + y, \frac{1}{2} - x, -\frac{1}{2} - z$.

significant changes are observed in the O···O and O···H distances, while no significant changes have been found in the O—H bond length and in the O···H—O angle (Tables 4 and 5). There are no effects, within experimental error, of the compressed O···H distance on the C—O bond lengths in the hydroxyl groups. Squeezing of C—OH···O=C hydrogen bonds caused an elongation of the O=C bonds (Katrusiak, 1991a).

Owing to the strong compressibility of weak van der Waals contacts between the sheets of hydrogen-bonded pentaerythritol molecules (see Table 6), and the relatively rigid structure of the sheets, at 280 MPa the l distance between the centres of the molecules from near sheets becomes shorter than the distance between the centres of the hydrogen-bonded molecules (see Fig. 3). This can also be observed from the changes in dimensions of the pseudo-cubic *fcc* unit-cell dimensions a_F (within the sheets) and c (perpendicular to the sheets). High pressures can destabilize the tetragonal structure by changing the balance of intermolecular interactions and intramolecular strains. High pressures increase the intermolecular interactions of the molecule, the shape of which is incompatible with the pseudo-symmetry of its site in the structure approximating a close-packing cubic arrangement of the plastic phase. The increased energy of the interactions diminish the role of the hydrogen bonds. The hydrogen bonds, in turn, stabilize the energetically unfavourable conformation of the hydroxyl groups, and the arrangement of the molecules in the ambient-pressure structure in which internal strains in the molecules increase with pressure. It appears that due to these factors above 280 MPa the pentaerythritol structure can become metastable, and that a structural phase transition could be responsible for damaging the samples, when attempts were made to increase pressures above 1.5 GPa. Pressure-induced

phase transitions are often observed in the ordered phases of other cyclic and acyclic alcohols, also exhibiting plastic phases at high temperatures (Würlfing, 1991, 1993). In the ordered phases of these materials an arrangement of the molecules determined by a motif of hydrogen bonds can be competitive to other intermolecular interactions or to conformations of the molecules. In such hydrogen-bonded molecular crystals the competitive interactions and molecular strains can facilitate breaking of even relatively strong hydrogen bonds at higher temperatures, and the globular molecules become orientationally disordered. Elevated pressures, in turn, by favouring certain competing factors can induce a transformation to an ordered phase with another motif of hydrogen bonds.

Vibrational parameters

Measurements of vibrational parameters at high pressures have been analysed by several authors (Finger & King, 1978; Katrusiak & Nelmes, 1986b; Katrusiak, 1991a,b). It was determined that in harder ionic crystals the vibrations decrease linearly in accordance with the harmonic model. The 'softer' molecular crystals exhibit strong and clearly non-linear compressibility in the pressures between 0.1 and 1000 MPa, which levels out and becomes more linear at still higher pressures (Katrusiak, 1991b). This effect is more pronounced in 'softer' materials, such as 1,3-cyclohexanedione or 2-methyl-1,3-cyclohexanedione, than for 'harder' molecular crystals, such as squaric acid.

A strong compression of the vibrational parameters in pentaerythritol is observed only for C(2), O(1) and the H atoms, while no significant changes have been noted for C(1). It was found by Eilerman & Rudman (1979) that at 0.1 MPa the molecules exhibit strong librational vibrations, with r.m.s. amplitudes of 7.65° about x and y , and 3.90° about z . Comparison of these X-ray data with the present results indicates that librations of the molecules are almost completely reduced at 1.15 GPa, while the translational component of the vibrations changes only insignificantly. As already noted, the vibrational parameters determined at ambient pressure by neutron diffraction are somewhat larger and more isotropic (Semmingsen, 1988), which would indicate that the pressure-induced changes have a larger contribution of translational components.

Concluding remarks

In this high-pressure X-ray diffraction study of the organic crystals of pentaerythritol, a relatively high accuracy of the structural results has been obtained: C and O atoms have been refined anisotropically and the H atoms have been located from a ΔF map and refined with isotropic temperature factors. The pressure-induced changes in molecular geometry

are statistically significant and consistent with the directions of intermolecular forces in the crystal lattice at high pressures. Although the high symmetry of the pentaerythritol crystal facilitated the experimental procedure and structure refinement, it is hoped that a similar accuracy will also be obtained for other organic molecules, and that it will widen the scope of problems in crystal chemistry solved by applying high-pressure methods. The question concerning the pressure-induced phase transition in the pentaerythritol crystal still remains open. The presently obtained results cannot be easily reconciled with previous reports on the phase transition in the pentaerythritol crystals at *ca* 500 MPa. On the other hand, there are indications that elevated pressures may induce a phase transition in the pentaerythritol structure. It is possible that the differences in the experimental techniques may also have some bearing: the present study was carried out on a single crystal, while powder samples were used in the previous high-pressure investigations. It was shown for continuous phase transitions in perovskite ferroelectrics that crystal size can influence the Curie temperature (Wang, Zhong & Zhang, 1994; Ayyub, Palkar, Challopadyan & Multani, 1995), however, no such observations were reported for first-order phase transitions and molecular crystals, and the discrepancy in pressures seems too large to be accounted for by the crystal-size effect. Further high-pressure studies of the pentaerythritol crystals are clearly needed.

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