I thank the Science Research Council for a grant towards the purchase of the diffractometer.

References

Allinger, N. L. (1977). *J. Am. Chem. Soc.* **99**, 8127–8134.

Allinger, N. L., Tribble, M. T., Miller, M. A. & Wertz, D. H. (1971). *J. Am. Chem. Soc.* **94**, 1637–1648.

Bhattacharjee, S. K., Chacko, K. K. & Zand, R. (1979). *Acta Cryst.* B**35**, 399–401.

Bovill, M. J., Cox, P. J., Flitman, H. P., Guy, M. H. P., Hardy, A. D. U., McCabe, P. H., Macdonald, M. A., Sim, G. A. & White, D. N. J. (1979). *Acta Cryst.* B**35**, 669–675.

Brown, W. A. C., Eglinton, G., Martin, J., Parker, W. & Sim, G. A. (1964). *Proc. Chem. Soc. London*, pp. 57–58.

Brown, W. A. C., Martin, J. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 1844–1857.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Osawa, E., Aigami, K. & Inamoto, Y. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 172–180.

Osina, E. L., Mastryukov, V. S., Vilkov, L. V. & Belikova, N. A. (1976). *J. Chem. Soc. Chem. Commun.* pp. 12–13.

Peters, J. A., Baas, J. M. A., van de Graaf, B., van der Toorn, J. M. & van Bekkum, H. (1978). *Tetrahedron*, **34**, 3313–3323.

Sheldrick, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.

White, D. N. J. & Bovill, M. J. (1976). *J. Mol. Struct.* **33**, 273–277.

White, D. N. J. & Bovill, M. J. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1610–1623.

Acta Cryst. (1979). B**35**, 2458–2460

Refinement of Pentaerythritol*

By Donna Eilerman and Reuben Rudman

Department of Chemistry, Adelphi University, Garden City, New York 11530, *USA*

(*Received* 9 *October* 1978; *accepted* 23 *February* 1979)

Abstract. $C_5H_{12}O_4$, tetragonal, $I\bar{4}$, $a = 6\cdot087$ (1), $c = 8\cdot757$ (2) Å, $Z = 2$, $D_c = 1\cdot393$, $D_m = 1\cdot363$ Mg m^{-3} (in carbon tetrachloride and xylene). The final R was 0·023 for 274 reflections and a model in which the H-atom thermal parameters were varied isotropically. There is one unique O—H···O hydrogen bond, with distances of 0·75 (2), 1·98 (2), and 2·710 (2) Å for O—H, H···O, and O···O respectively. A rigid-body analysis revealed large root-mean-square amplitudes of libration, a condition not uncommon to plastic-crystal precursors.

Introduction. A series of poly(hydroxymethyl) compounds which undergo phase transitions between the ordered and orientationally disordered (plastic) states are currently under investigation in this laboratory (*e.g.* Rudman, Eilerman & LaPlaca, 1978). Nitta (1926) and Nitta & Watanabé (1937, 1938) reported that pentaerythritol transforms from an ordered body-centered tetragonal phase to a plastic face-centered cubic phase at 452·7 K. The crystal structure was redetermined and refined several times (Llewellyn, Cox & Goodwin, 1937; Shiono, Cruickshank & Cox, 1958), most recently by Hvoslef (1958) who located the H atoms on the basis of $hk0$ and $00l$ neutron diffraction data. However, the published H atom coordinates were incorrect (Smith, 1969).

Pentaerythritol is a model compound for the other members of this series and, as such, it has been the subject of several other studies including calorimetry (Westrum, 1961), NMR (Smith, 1969), infrared spectroscopy (Marzocchi & Castellucci, 1971), and X-ray diffuse scattering (Terauchi, Okamoto, Tasaka & Watanabé, 1971; Bärnighausen, 1978). It has also been used as a model for hydrogen bonding in polyhydric molecules in the computation of the conformational energy of peptides (Némethy & Scheraga, 1977).

Inasmuch as the proper interpretation of these data requires an accurate model and the structure has not been determined to the precision and accuracy that modern methods allow (*cf.* van der Lugt, Smit & Perdok, 1968; Smith, 1969) the crystal structure of the ordered tetragonal phase of pentaerythritol was redetermined.

Single crystals were grown from a saturated aqueous solution. The crystal used for data collection was a square pyramid, approximately 0·24 mm along each side of the base and 0·30 mm in height. The observed reflections and systematic absences ($h + k + l \neq 2n$) were in agreement with the previously reported body-

---

* Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. I.

0567-7408/79/102458-03$01.00

centered tetragonal lattice. The lattice parameters (see *Abstract*) were obtained from 20 carefully centered high-angle reflections showing α_1–α_2 splitting (122–133° 2θ, centered on the α_1 peak, $\lambda = 1{\cdot}54051$ Å). The results agreed (within 3σ) with those obtained for a group of 16 reflections between 18 and 83° 2θ in which α_1–α_2 splitting did not occur ($\lambda = 1{\cdot}54178$ Å).

Data were collected with $\theta/2\theta$ scans on a Syntex $P2_1$-F diffractometer using Ni-filtered Cu K radiation out to 135° 2θ. The scan range was 2° plus the α_1–α_2 separation, at a scan rate between 1 and 5° 2θ min^{-1}. Six check reflections distributed in intensity and reciprocal space were measured fourteen times during data collection. An analysis of their intensities as a function of time did not indicate any appreciable change. Since μ for Cu K radiation is 1·04 mm^{-1} and a maximum μR is approximately 0·1, neither decay nor absorption corrections were applied.

492 reflections were measured, including 168 sets of equivalent reflections and 98 additional Friedel-related reflections (measured below 100° 2θ). The agreement between the 168 sets of equivalent reflections (but not including any Friedel-related reflections) was 1·1%, as calculated from our averaging program *EQUIV* (a local modification of the program written by J. Ibers). 274 reflections (176 unique plus 98 Friedel-related reflections) were used in the refinement. Only one reflection in the accessible region between 0 and 135° 2θ had an intensity less than 3σ, based on counting statistics. The least-squares refinement program is a local version (*NUCLS*) of *ORFLS* (Busing, Martin & Levy, 1962) containing modifications by J. Ibers, W. C. Hamilton, and P. Coppens. The weighting scheme used was $w = 1/\sigma^2$, where $\sigma = 0{\cdot}5\sigma(F^2)/F$, $\sigma(F^2) = (\mathrm{Lp})^{-1}\sigma(I)$, $\sigma(I) = [\sigma(c)^2 + (0{\cdot}04I)^2]^{1/2}$, and $\sigma(c) =$ [total scan count + (sum of background counts)/(background-to-scan ratio)^2]$^{1/2}$ × scan rate. (I is the integrated intensity and F is the structure factor.)

The coordinates of the non-hydrogen atoms reported by Shiono *et al.* (1958) were used as starting parameters in the refinement. Methylene H-atom positions were calculated and the hydroxyl H atom was clearly located on a difference Fourier map. An isotropic extinction factor was included in the final model: six reflections had correction factors less than 0·90, with a factor of 0·54 observed for the 002 reflection (based on an estimated value of $\bar{t} = 0{\cdot}002$ mm). Anomalous-dispersion corrections for the C and O atomic scattering factors were also included in the final model. The scattering factors used in this refinement were obtained from *International Tables for X-ray Crystallography* (1974): f for C and O from Table 2.2A, f for H from Table 2.2C, and f' and f'' for C and O from Table 2.3.1. The standard error of an observation of unit weight was 2·19 for 34 parameters and 274 observations.

Table 1. *Positional parameters for pentaerythritol*

	x	y	z
C(C)	0	0	0
C(1)	0·15837 (23)	0·12569 (20)	−0·10337 (13)
O(1)	0·31806 (10)	0·24610 (16)	−0·01937 (14)
H(11)	0·2333 (28)	0·0277 (24)	−0·1700 (17)
H(12)	0·0744 (34)	0·2292 (28)	−0·1671 (19)
H(O1)	0·2723 (25)	0·3595 (37)	−0·0073 (23)

The final R value ($\sum \|F_o| - |F_c\|/\sum |F_o|$) was 0·0230 for the parameters listed in Table 1* and 0·0276 if the signs of the z atomic coordinates were reversed. According to the Hamilton (1965) R test, the data in Table 1 represent the correct molecular orientation in this non-enantiomorphous space group within a 99·5% confidence level. The weighted R factor was 0·0324.

The final parameters were subjected to a rigid-body analysis using the **TLS**-6 program of Schomaker & Trueblood (1968) as obtained from Brookhaven National Laboratory.

Discussion. The previously reported crystal structure of pentaerythritol has been confirmed by the present

Table 2. *Bond distances* (Å) *and angles* (°) *in pentaerythritol*

(*a*) Intramolecular distances

	Distance (uncorrected)	Distance (rigid-body model)*
C(C)–C(1)	1·527 (1)	1·548
C(1)–O(1)	1·422 (2)	1·441
C(1)–H(11)	0·951 (16)	
C(1)–H(12)	0·985 (20)	
O(1)–H(O1)	0·752 (23)	

(*b*) Intramolecular angles: C(1)^a–C(C)–C(1)^b

(*a*)–(*b*)		Symmetry-related angles
(i)–(ii)	107·33 (9)	(iii)–(iv)
(i)–(iii)	110·55 (5)	(i)–(iv); (ii)–(iii); (ii)–(iv)

Symmetry positions: (i) x,y,z; (ii) $-x,-y,z$; (iii) $y,-x,-z$; (iv) $-y,x,-z$

(*c*) Hydrogen-bonded distances (O–H···O) and angles

O···O	2·710 (1)
O–H	0·752 (23)
H···O	1·983 (23)
O–H···O	163

* Schomaker & Trueblood (1968).

---

* Tables of structure factors, anisotropic thermal parameters, rigid-body tensors, and bond angles for these coordinates and a complete set of data for refinement using anisotropic H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34380 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

investigation. Pentaerythritol is a tetrahedral molecule centered on a site with $\bar{4}$ symmetry. The asymmetric unit is one-quarter of the molecule, resulting in only one crystallographically unique set of C—C, C—O, and O···O interatomic distances and only two unique angles around the central C atom (Table 2). The molecules are arranged in sheets perpendicular to the **c** direction, with strong hydrogen bonding joining the molecules within these sheets. The shortest interlayer distances are 2·70 (3) Å between two H(11) atoms, thus implying that weak London forces are most likely present. The angles around the central C atom are not ideally tetrahedral. The molecule is slightly compressed within the sheets of hydrogen-bonded molecules and slightly elongated perpendicular to these sheets (along the **c** direction).

The present positional parameters for the non-hydrogen atoms are in general agreement with those reported by Shiono *et al.* (1958), but the estimated standard deviations are an order of magnitude smaller. The interatomic distances (Table 2) fall within 3σ of the earlier values. The H parameters are similar to those of Hvoslef (1958), as corrected by Smith (1969), with comparable e.s.d.'s. However, as is common in X-ray diffraction investigations, the interatomic distances involving H atoms are somewhat shorter than those obtained from the neutron diffraction data.

The **TLS** analysis of the present data indicated that the pentaerythritol molecule acts as a rigid body; corrected distances are in Table 2. The striking feature of this analysis is the large anisotropic librational motion. The root-mean-square amplitudes of libration are 7·65° about the *a* and *b* axes and 3·90° about the *c* axis. On the other hand, the root-mean-square amplitudes of translations are nearly isotropic: 0·15 Å about *a* and *b* and 0·18 Å about *c*. These observations are consistent with the strong intraplanar and weak interplanar hydrogen bonding found in crystals of pentaerythritol. These large amplitudes of libration have been observed in other plastic crystal precursors. For example, Evans, Hine & Richards (1977) report root-mean-square amplitudes of libration of 7·62 and 4·05° at room temperature for diamantane which forms a plastic phase at 443 K.

In conclusion, it is noted that it was possible to refine the present data using anisotropic temperature factors for all atoms, including H, with a final residual of 0·019. The resulting parameters and distances are not significantly different from those reported here.*

This research has been supported by the National Science Foundation under Grant DMR 76-20639. The authors thank one of the referees for helpful and constructive comments.

Note added in proof: As a result of newly discovering the errors in Hvoslef's published H-atom coordinates, Ladd (1979) refined Llewellyn, Cox & Goodwin's (1937) data; however, the H-atom coordinates which were found by Fourier methods could not be refined successfully using least-squares techniques. Although the gross features of these two refinements of pentaerythritol are similar, our least-squares refinement of *all* atoms resulted in e.s.d.'s an order of magnitude smaller than Ladd's and gave bond lengths and angles that agree more closely with those found in similar compounds; *e.g.* C—C (uncorrected for thermal motion) is 1·527(1) and 1·566(14) Å for this work and Ladd's, respectively. As a result of the improvement in data-collection techniques over the past few decades, it is quite clear that when a refinement of an old structure is called for, a new data set should be collected whenever possible.

References

BÄRNIGHAUSEN, E. (1978). *J. Appl. Cryst.* **11**, 221–228.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

EVANS, E. H. M., HINE, R. & RICHARDS, J. P. G. (1977). *J. Phys. C*, **10**, 369–374.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

HVOSLEF, J. (1958). *Acta Cryst.* **11**, 383–388.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LADD, M. F. C. (1979). *Acta Cryst.* B**35**, 2375–2377.

LLEWELLYN, F. J., COX, E. C. & GOODWIN, T. H. (1937). *J. Chem. Soc.* pp. 883–894.

LUGT, W. VAN DER, SMIT, W. & PERDOK, W. (1968). *Acta Cryst.* A**24**, 439–445.

MARZOCCHI, M. P. & CASTELLUCCI, E. (1971). *J. Mol. Struct.* **9**, 129–137.

NÉMETHY, G. & SCHERAGA, H. A. (1977). *J. Phys. Chem.* **81**, 928–931.

NITTA, I. (1926). *Bull. Chem. Soc. Jpn*, **1**, 62–63.

NITTA, I. & WATANABÉ, T. (1937). *Nature* (*London*), **140**, 365.

NITTA, I. & WATANABÉ, T. (1938). *Bull. Chem. Soc. Jpn*, **13**, 28–35.

NOMURA, H., HIGUCHI, K., KATO, S. & MIYAHARA, Y. (1972). *Jpn. J. Appl. Phys.* **11**, 304–308, 1048–1049.

RUDMAN, R., EILERMAN, D. & LAPLACA, S. J. (1978). *Science*, **200**, 531–533.

SCHOMAKER, V. & TRUEBLOOD, L. (1968). *Acta Cryst.* B**24**, 63–76.

SHIONO, R., CRUICKSHANK, D. W. J. & COX, E. G. (1958). *Acta Cryst.* **11**, 389–391.

SMITH, G. W. (1969). *J. Chem. Phys.* **50**, 3595–3605.

TERAUCHI, H., OKAMOTO, H., TASAKA, A. & WATANABÉ, T. (1971). *Acta Cryst.* A**27**, 678–679.

WESTRUM, E. F. (1961). *Pure Appl. Chem.* **2**, 241–249.

---

* See previous footnote.