

A Refinement of the Crystal Structure of Pentaerythritol

BY R. SHIONO*, D. W. J. CRUICKSHANK AND E. G. COX

School of Chemistry, The University, Leeds 2, England

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A refinement of the crystal structure of pentaerythritol has been carried out with the data of Llewellyn, Cox & Goodwin and with new experimental results. The previous z co-ordinates are altered appreciably. The revised bond lengths are: C-C 1.548 ± 0.011 Å, C-O 1.425 ± 0.014 Å; the bond angles are close to the regular tetrahedral value.

The structure of tetragonal pentaerythritol, $C(CH_2OH)_4$, was settled some years ago by the X-ray analyses of Llewellyn, Cox & Goodwin (1937) (hereafter abbreviated to LCG) and of Nitta & Watanabé (1937, 1938) (hereafter NW). In view of the considerable improvements made since then in the methods of accurate structure analysis, it has seemed desirable to extend the work, and in the present investigation a more accurate structure has been obtained by refinements based on both the LCG data and new experimental measurements.

The results obtained by LCG and NW were very similar. The results of LCG alone will now be summarised, since their data have been used in the present work. LCG confirmed the space group as $I4$, with two molecules in the unit cell, and gave the cell dimensions as $a = 6.10$, $c = 8.73$ Å. Their analysis was based on the measurement of 101 independent $\{hkl\}$ intensities obtained with Cu $K\alpha$ radiation and a further 19 $\{hk0\}$ intensities obtained with Mo $K\alpha$ radiation. These measurements were made photographically, some intensities being estimated by microphotometer and others visually. The intensities were placed on the absolute scale by a direct comparison of certain reflexions with the (400) rock-salt reflexion.

A single molecule of pentaerythritol has the configuration shown in Fig. 1. In the crystal the central

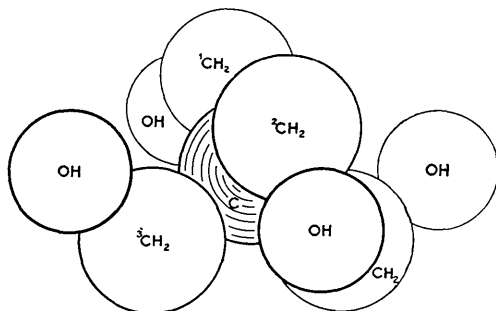


Fig. 1. Configuration of pentaerythritol.

* Present address: Department of Chemistry, University of Pittsburgh, Pittsburgh, U.S.A.

On leave from: The Faculty of Science, Osaka University, Osaka, Japan.

carbon atom occupies the special position (0, 0, 0). LCG determined the x and y co-ordinates of ^{12}C and O from the centrosymmetric (001) projection with both the Cu and Mo data. Approximate z co-ordinates obtained from three-dimensional Patterson line syntheses gave phase angles, $\alpha(hkl)$, for the $\{hkl\}$ F_o . Using these phases, LCG determined the z co-ordinates from three-dimensional electron-density line syntheses. The co-ordinates and molecular dimensions found by LCG and NW are shown in Tables 1 and 2. These

Table 1. Pentaerythritol fractional co-ordinates

	^{12}C			O		
	x	y	z	x	y	z
LCG	0.162	0.123	0.097	0.317	0.247	0.002
NW	0.160	0.128	0.100	0.312	0.248	0.002
Present refinement						
LCG data	0.1614	0.1219	0.1051	0.3179	0.2478	0.0200
New data	0.1628	0.1264	0.1059	0.3166	0.2475	0.0188
Weighted mean	0.1621	0.1242	0.1059	0.3172	0.2476	0.0188

Table 2. Molecular dimensions

	C- ^{12}C	^{12}C -O	^{12}C -C- ^{23}C	^{12}C -C- ^{33}C	C- ^{12}C -O
LCG	1.50 Å	1.46 Å	$111\frac{1}{2}^\circ$	$108\frac{1}{2}^\circ$	$111\frac{1}{2}^\circ$
NW	1.53 Å	1.45 Å	110°	109°	$108\frac{1}{2}^\circ$
Present refinement	1.548 Å	1.425 Å	$106^\circ 43'$	$110^\circ 52'$	$111^\circ 8'$
E.s.d.	0.011 Å	0.014 Å	$1^\circ 1'$	$0^\circ 31'$	$1^\circ 7'$

investigations established that the bond angles are all close to the regular tetrahedral value of $109\frac{1}{2}^\circ$, and showed the crystal to have a layer structure with neighbouring molecules linked by hydrogen bonds of 2.69 Å.

In new experimental work 188 independent $\{hkl\}$ intensities have been estimated visually from a - and c -axis Weissenberg photographs, obtained with Cu $K\alpha$ radiation. The crystals used were prepared by cutting, grinding, and rubbing with wet filter paper to give roughly circular rods, approximately 0.1 mm. in diameter. Each crystal was dipped in liquid air several

times (cf. LCG). The multiple-film technique was used and the intensities in each layer line were set approximately on the absolute scale by Wheatley's (1954) method, by means of the F_c 's computed in the first cycle with the LCG data as described below. The majority of the final intensities were averages of estimates made from a - and c -axis photographs. The cell dimensions were redetermined, by the Straumanis method, from the (2,2,10) and (554) reflexions, and were found to be

$$a = 6.083 \pm 0.002, \quad c = 8.726 \pm 0.002 \text{ \AA}.$$

The structure was refined by successive cycles consisting of structure-factor calculations followed by observed and calculated differential syntheses (Booth, 1946). The computations were carried out on the Manchester University electronic computer with programmes modified by us for the space group $I\bar{4}$ from routines for the non-centrosymmetric space group $P2_1$. The latter were developed by Mr R. K. Bullough from the centrosymmetric routines of Ahmed & Cruickshank (1953*b*).

The refinement was started from the co-ordinates given by LCG, with McWeeny (1951) scattering curves for carbon and oxygen and an assumed temperature factor $B = 2.0 \text{ \AA}^2$ for all atoms; throughout this work hydrogen has been omitted from consideration. After two cycles with the LCG data, two more cycles were made with the new data; the final co-ordinates from both the old and the new data are shown in the third and fourth lines of Table 1. The final values adopted for the temperature factors (B) and the n -shifts (Shoemaker, Donohue, Schomaker & Corey, 1950), and the agreement indices R were as follows:

	$B \text{ (\AA}^2\text{)}$			n		R (%)
	C	${}^1\text{C}$	O	x, y	z	
LCG data	1.4	1.6	2.2	1.2	3.0	22
New data	2.5	2.7	3.2	1.4	3.0	18.6

During the refinement the z co-ordinates changed considerably; none of the x and y shifts obtained after the second of each pair of cycles exceeded 0.01 \AA .

Two points of interest emerged from this refinement. One is that the temperature factors for the old and new data are very different. This can only be in part due to the differing proportions of $\{hk0\}$ and $\{hkl\}$ reflexions in the two sets of data, and must be partly due to differences in experimental methods and real differences between the crystals used in the two investigations.

The other interesting feature is that it was found necessary to adopt the value $n = 3$ for the z co-ordinate shifts, notwithstanding the fact that simple theory (Cruickshank, 1952) shows that the maximum possible value of n (when all the F 's determining the co-ordinate are complex, which is not the case here) is 2. Closer examination shows that higher values of

n are possible in special cases. In pentaerythritol the small z co-ordinate of O, together with the zero co-ordinate of C, cause an undue proportion of the $F(hkl)$ to have phases near 0 or π . In a least-squares or modified Fourier analysis (Cruickshank, 1952), both $\sin \alpha$ and $\partial A/\partial z_0$ would tend to be small so that

$$\frac{\partial |F_c|}{\partial z_0} = \frac{\partial A}{\partial z_0} \cos \alpha + \frac{\partial B}{\partial z_0} \sin \alpha$$

would tend to be small. In the full refinement equations this would result in the diagonal element corresponding to the oxygen z co-ordinate being unusually small, which in turn implies a high value of n in the ordinary Fourier method.

The estimated standard deviations (e.s.d.) of the co-ordinates derived from the new data, with Cruickshank's (1949) formula and the final values of n , are

$${}^1\text{C: } x, y, 0.010 \text{ \AA}; \quad z, 0.016 \text{ \AA}$$

$$\text{O: } x, y, 0.008 \text{ \AA}; \quad z, 0.013 \text{ \AA}$$

As the z co-ordinates from the LCG data were not fully refined, their e.s.d. have not been computed. The e.s.d. of the x and y co-ordinates derived from the LCG data are the same as those obtained with new data, so that the extra number of the new $\{hkl\}$ intensities has been balanced by the high order $\{hk0\}$ intensities obtained by LCG with Mo radiation.

The agreement of the co-ordinates, even of the z co-ordinates, derived from the two sets of data is satisfactory, the average discrepancy being 0.011 \AA and the maximum 0.027 \AA . In the fifth line of Table 1 weighted mean co-ordinates are given, the x and y co-ordinates being simple means of the two sets, and the z co-ordinates being those found with the new data; the z co-ordinates from the LCG data were rejected on account of the incomplete refinement.

Comparison of the final weighted mean co-ordinates with those given by LCG shows that the earlier x and y co-ordinates were extraordinarily good, the mean discrepancy being only 0.003 \AA . However the LCG z co-ordinates were seriously in error, ${}^1\text{C}$ by 0.078 \AA and O by 0.147 \AA . These comparisons indicate, on the one hand, the excellent results which can be obtained directly from well-resolved centrosymmetric projections of the *observed* electron density (as in oxalic acid dihydrate (Ahmed & Cruickshank, 1953*a*)), and, on the other hand, the misleading results which may be given by a single Fourier synthesis when the relevant coefficients have general phases. The inaccuracy of the LCG z co-ordinates was, of course, accentuated by the same factors that led to an increased n value for the z shifts. The z co-ordinates determined by NW are similarly in error.*

* We have recently learnt that Dr E. W. Hughes, who had started work on pentaerythritol in 1937 but had abandoned it on hearing of LCG's work, determined the z co-ordinates from six (00*l*) reflexions to be $0.107 \text{ (}{}^1\text{C)}$ and 0.022 (O) . His simple trial-and-error calculations thus achieved more satisfactory results than the uncorrected Fourier method.

The bond lengths and angles calculated from the weighted mean co-ordinates and the new cell dimensions are shown in Table 2, together with their e.s.d. and the results obtained by LCG and NW. The molecular dimensions have been altered rather less drastically than might have been expected from the large changes in the z co-ordinates. The effect of the latter has chiefly been to bend the four arms of the molecule upwards or downwards as wholes, so that the angle ${}^1\text{C}-\text{C}-{}^2\text{C}$ has changed by $4\frac{3}{4}^\circ$ from slightly more than the regular tetrahedral angle of $109^\circ 28'$ to slightly less, while ${}^1\text{C}-\text{C}-{}^3\text{C}$, which was formerly a little smaller than $109\frac{1}{2}^\circ$, is now a little larger.

The length of the C-C bond is now 1.548 Å, e.s.d. 0.011 Å, and is not significantly different from 1.544 Å, the C-C distance in diamond (Lonsdale, 1947). The C-O bond of 1.425 Å, e.s.d. 0.014 Å, agrees well with other values for a single bond between a tetrahedral carbon and a hydroxyl oxygen (1.424 Å, e.s.d. 0.011 Å, in threonine (Shoemaker *et al.*, 1950); 1.425 Å, e.s.d. 0.009 Å, in serine (Shoemaker, Barieu, Donohue & Lu, 1953); 1.434 Å, no e.s.d. quoted, in methanol (Ivash & Dennison, 1953; (microwave study)). The angle ${}^1\text{C}-\text{C}-{}^2\text{C}$ is $2^\circ 45'$ smaller than the regular tetrahedral value, while ${}^1\text{C}-\text{C}-{}^3\text{C}$ is $1^\circ 24'$ larger than the tetrahedral value. The fourfold inversion axis makes these angles interdependent and requires that small deviations from regularity should be in the ratio 2:1. The deviations given above may be real since they are 2.7 times the e.s.d., corresponding closely to the 1% significance level. $\text{C}-{}^1\text{C}-\text{O}$ is $1^\circ 40'$ larger than the tetrahedral angle, but the deviation is not significant.

The new values of the intermolecular distances, in the notation used by LCG, are shown in Table 3. The

Table 3. *Intermolecular distances*

O_0-O_3	2.70 Å	O_0-C_1 (lower)	3.69 Å	O_0-C_6	3.97 Å
O_0-O_4	2.70 Å	O_0-O_6	3.74 Å	O_0-C_2 (upper)	3.81 Å
O_0-C_3	3.61 Å	O_0-O_5	3.79 Å	C_0-C_2 (upper)	3.99 Å

important O-O hydrogen bond is altered little in length (from 2.69 to 2.70 Å), though the O-O line now makes an angle of about 7° with the (001) plane, instead of 0.7° .

The observed and calculated peak curvatures show that atoms ${}^1\text{C}$ and O have their largest amplitudes of vibration in the z direction, though the vibration of the carbon at the origin is approximately isotropic. In order to determine the effects of anisotropic motion on the co-ordinates, additional overall temperature factors of the form

$$\exp [-(A+B \cos^2 \varphi) (\sin \theta/\lambda)^2]$$

were applied to the calculated structure factors of the last cycle with the new data, φ being the angle be-

tween z axis and the reciprocal vector of the plane in question. The most satisfactory agreement with the observed structure factors was obtained with $A = -0.6$ and $B = 1.5 \text{ \AA}^2$; this gave $R = 17.8\%$. However the ρ_c back shifts, computed with these anisotropic F_c 's, differed by less than 0.001 \AA from those obtained in the isotropic refinement. The effect of this type of anisotropic thermal motion on the values found for the molecular dimensions is thus negligible.

The crystal structure analyses of pentaerythritol tetra-acetate (Goodwin & Hardy, 1938) and pentaerythritol tetranitrate (Booth & Llewellyn, 1947) may be more accurate than the LCG analysis of pentaerythritol, as the a - and c -projections in both are centrosymmetric and as at least two cycles of refinement with electron-density sections and lines were carried out for each. However, as both analyses were carried out before the discovery of the n -shift rule, it is perhaps unwise to use their results for detailed comparisons.

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