

Table 2. *Interatomic distances in PdF₂*

4 Pd-F	2.155 Å
2 Pd-F	2.171
8 F-F	3.060
2 F-F	2.664
2 F-F	3.389

perature. The spin-only value for two unpaired electrons is $2.83 \mu_B$. Since iron, cobalt and nickel difluorides are antiferromagnetic it is probable that the low value of the magnetic moment may arise from antiferromagnetic effects.

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making the magnetic measurement. They also thank Imperial Chemical Industries Limited, General Chemicals Division, Widnes for the use of the necessary fluorine cell. One of us (R. M.) is indebted to the United Kingdom Atomic Energy Authority for a maintenance grant.

References

- BARTLETT, N. & HEPWORTH, M. A. (1956). *Chem. and Ind.* 1425.
 EBERT, F. (1931). *Z. anorg. Chem.* **196**, 395.
 JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
 RUFF, O. & ASCHER, E. (1929). *Z. anorg. Chem.* **183**, 193.
 TAYLOR, A. (1951). *J. Sci. Instrum.* **28**, 200.

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Crystal and molecular structure of meso-erythritol. By AKIRA SHIMADA, *Department of Chemistry, Faculty of Science, Konan University, Motoyama, Kobe, Japan*

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From an X-ray crystal analysis of meso-erythritol,



which has 'asymmetric' carbon atoms (indicated by asterisks), interesting features of the structure were found.

The space group, $C_{2h}^2-I4_1/a$, previously assigned to meso-erythritol was confirmed (Burgers, 1926; Schoenfeldt, Hermann & Hassel, 1926). A redetermination of the unit-cell dimensions gave the following values

$$a = 12.81 \pm 0.03, \quad c = 6.81 \pm 0.02 \text{ \AA}.$$

There are eight molecules in the unit cell. In accordance with the conclusions given by Burgers (1926), and Schoenfeldt, Hermann & Hassel (1926), each molecule is found to be situated at the centre of symmetry.

An approximate electron-density projection on (001) was obtained with the aid of inequality and image-

seeking methods applied to (*hk*0) spectra. The approximate *x* and *y* parameters of the atoms were then successively refined by the syntheses of electron-density and

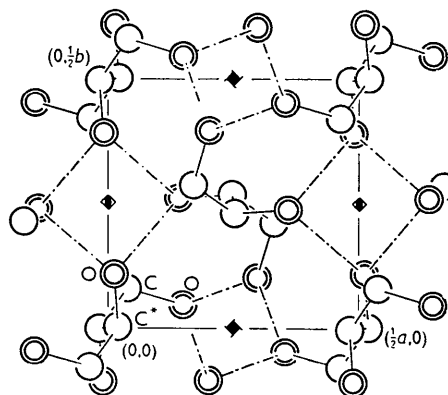


Fig. 2. The structure of meso-erythritol projected on (001), showing the hydrogen bonds by dot-dash lines. Single circles indicate carbon, and double circles oxygen atoms.

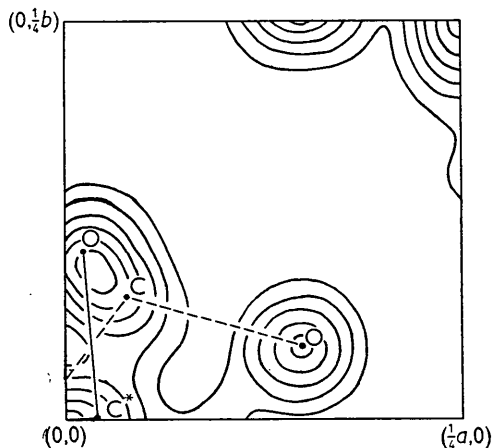


Fig. 1. The (001) electron-density projection; contours at arbitrary intervals.

difference electron-density. Using the *x* and *y* values for each atom obtained from the refined electron-density projection on (001), an effort was made to conform to a plausible molecular structure in the crystal so as to give an approximate value of *z* for each atom. Refinement of *z* parameters was done in the same way as *x* and *y* parameters. The electron density projected on (001) is shown in Fig. 1, and the structure is illustrated in Fig. 2. *R* factors are, at the present stage of refinement, 19.8 and 14.6% respectively for (*hk*0) and (*h*0*l*) spectra with an isotropic temperature factor $B = 2.2 \text{ \AA}^2$.

Bond distances for the outer and inner carbon-carbon bonds, C*-C and C*-C*, were computed to be 1.54 and 1.55 Å, and those for the outer and inner carbon-oxygen bonds, C-O and C*-O, to be 1.47 and 1.46 Å.

Since the molecule has a centre of symmetry and consequently corresponding atoms and groups in each half of the molecule are in trans-positions to each other with respect to the inner C*-C* bond, it is only necessary to give the relative orientation of the outer C-O bond with respect to the outer C*-C bond, in order to describe the configuration of the whole molecule. Thus the directions of the outer C-O bond and the C*-C* bond make a gauche-configuration with respect to the C*-C bond. The two hydroxyl-oxygen atoms are, too, in gauche-positions around the C*-C bond. Hence, it is highly probable that the oxygen atom in the outer hydroxyl group is in approximate trans-position to the hydrogen atom bonded to the asymmetric carbon atom. This relative configuration of the two hydroxyl groups with respect to the C-C* bond, agrees with that found in tartaric acid and tartrate ion (Beevers & Hughes, 1940, 1941; Stern & Beevers, 1950; Sadanaga, 1950; Parry, 1951; Bommel & Bijvoet, 1958). This configuration, moreover, can be compared with the molecular configurations reported for ethylene glycol and glycerol obtained from electron diffraction studies (Bastiansen, 1949).

Another interesting aspect of the structure is the hydrogen bond formation between adjoining molecules. The outer hydroxyl-oxygen atom is linked to two oxygen atoms of the outer hydroxyl groups of the neighboring molecules, above and below, with a distance 2.66 Å forming a spiral chain arrangement of hydrogen bonds along the *c*-axis. The inner hydroxyl-oxygen atom is, on the other hand, linked to two oxygen atoms of the

inner hydroxyl groups of the neighboring molecules. They form a square of 2.77 Å sides, with its diagonals on different planes, around the position given by the symmetry $\bar{4}$. They are making a lateral linkage, in a way, but at the same time they are uniting molecules within the same chain mentioned above. These two types of hydrogen bonds in this crystal link all the molecules firmly in a three-dimensional way, in agreement with the fact that this crystal has no cleavage.

The structure is now being refined and will be reported in detail at a later date.

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References

- BASTIANSEN, O. (1949). *Acta Chem. Scand.* **3**, 415.
 BEEVERS, C. A. & HUGHES, W. (1940). *Nature, Lond.* **146**, 96.
 BEEVERS, C. A. & HUGHES, W. (1941). *Proc. Roy. Soc. A*, **177**, 251.
 BOMMEL, A. J. VAN & BIJVOET, J. M. (1958). *Acta Cryst.* **11**, 61.
 BURGERS, W. G. (1926). *Phil. Mag.* (7), **1**, 289.
 PARRY, G. S. (1951). *Acta Cryst.* **4**, 131.
 SADANAGA, R. (1950). *Acta Cryst.* **3**, 416.
 SCHOENFELDT, N., HERMANN, K. & HASSEL, O. (1926). *Z. Phys. Chem. A*, **124**, 305.
 STERN, F. & BEEVERS, C. A. (1950). *Acta Cryst.* **3**, 341.

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The validity of the elliptic paraboloid approximation for peaks on electron density maps.

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The elliptic paraboloid approximation (Ladell & Katz, 1954)* has been subject to some criticisms recently concerning its validity under certain circumstances (Burns, 1958). Although this criticism is valid, the nature of the approximation is such as to indicate the range of its validity. It did not seem necessary in preparing the original short communication to list explicitly the limitations of this quadratic approximation. However, subsequent users of the method (Burns, 1955; Dickens, 1956) have indicated that they are unknowingly using the L.K. approximation either near or beyond its limitations. In order to establish quantitative limits for the effective use of the L.K. method, one of us has developed a set of criteria which determines the validity of the quadratic approximation (Katz, 1957).

If a function $f(x, y)$ is to have a maximum at (a, b) , then the necessary conditions that $f(a, b)$ be an extremum of $f(x, y)$ are:

$$\left. \frac{\partial f(x, y)}{\partial x} \right|_{\substack{x=a \\ y=b}} = 0; \quad \left. \frac{\partial f(x, y)}{\partial y} \right|_{\substack{x=a \\ y=b}} = 0. \quad (1)$$

That these conditions are not sufficient to ensure a

maximum or minimum can be readily seen by examining a saddle function, e.g. a hyperbolic paraboloid, at the saddle point.

An examination of the Taylor expansion of $f(x, y)$ leads to the well known sufficiency condition for an extremum, i.e.

$$\left(\frac{\partial^2 f}{\partial x \partial y} \bigg|_{\substack{x=a \\ y=b}} \right)^2 - \left(\frac{\partial^2 f}{\partial x^2} \bigg|_{\substack{x=a \\ y=b}} \right) \left(\frac{\partial^2 f}{\partial y^2} \bigg|_{\substack{x=a \\ y=b}} \right) < 0. \quad (2)$$

It is apparent that $\partial^2 f / \partial x^2$ and $\partial^2 f / \partial y^2$ must have the same sign to ensure a maximum or minimum in $f(x, y)$; a maximum when

$$\frac{\partial^2 f}{\partial x^2} \left(\text{or } \frac{\partial^2 f}{\partial y^2} \right) < 0$$

a minimum when

$$\frac{\partial^2 f}{\partial x^2} \left(\text{or } \frac{\partial^2 f}{\partial y^2} \right) > 0.$$

In the L.K. approximation

$$Z = f(x, y) = Ax^2 + By^2 + Cxy + Dx + Ey + F$$

so that equation (2) becomes $C^2 - 4AB$ which is exactly the denominator of the expressions for x_{\max} and y_{\max} in

* Henceforth abbreviated L.K.