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.

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

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* Henceforth abbreviated L.K.

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.

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

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

the approximation. It is this term $\Delta = C^2 - 4AB$ which determines both the quality of the shape of the peak and the accuracy with which the maximum position can be determined.

For $\Delta < 0$ the approximation is good and will yield accurate results provided $A < 0$, $B < 0$. If $\Delta < 0$, but $A > 0$ and $B > 0$ then the wrong point has been chosen as $Z(0, 0)$ and the peak obtained will be shifted from the true position by an amount proportional to the distortion in the elliptical paraboloid. This has been shown graphically by Dickens. As is correctly explained by Dickens, the maximum positions found using each of the points 616, 627, 634 in turn as $Z(0, 0)$ should not be expected to coincide. However, Dickens' use of these maximum positions as a measure of the accuracy of the L.K. approximation is invalid since the approximation only holds when the highest point, i.e. 645 is used as $Z(0, 0)$. Dickens' method of checking the accuracy of the L.K. method by choosing points other than the highest point on the map as $Z(0, 0)$ often will lead to substantially incorrect va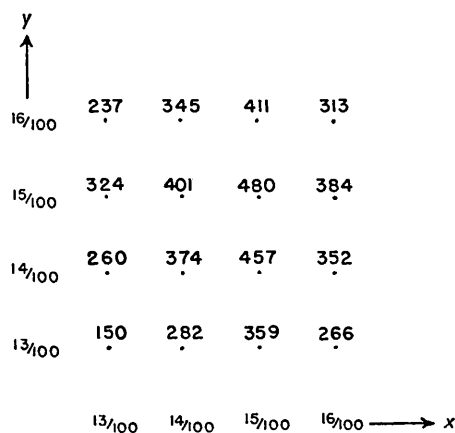lues. This can be shown by examining the following example (Fig. 1). In this case the highest mesh value is initially located at $x = y = 0.1500$.

When the L.K. method is used with $Z(0, 0) = 480$, $\Delta = -16{,}093$ and the peak position obtained is $x_m = 0.1495$, $y_m = 0.1475$, which checks quite closely with graphical results. If the method is applied using 401 as $Z(0, 0)$ (in order to check the accuracy as Dickens has done), $\Delta = +199$ and the calculation reduces to an absurdity, i.e. the peak position obtained is $x_m = -0.1834$, $y = 0.1711$, a shift of almost thirty three electron density intervals to the left in x, and two electron density intervals upwards in y. This effect is due to the marked deviation of the peak shape from a true elliptical paraboloid. It is this latter result which is also to be expected when the L.K. method is used on unresolved atoms. The shapes of these unresolved peaks deviate considerably from elliptic paraboloidal character in the neighborhood of the peak maximas; in fact the saddle point type distribution is most likely to be present. Thus it is to be expected that 'enormous' errors will be involved (see above example); indeed the L.K. approximation was never intended for use on unresolved atoms.

There are two simple criteria which must be obeyed if the L.K. approximation is to be used correctly: (1) Both A and B must be less than 0. This can be ensured by using the highest point on the map for $Z(0, 0)$; (2) $\Delta < 0$, i.e. the values of $x_{\max.}$ and $y_{\max.}$ obtained using the L.K. method must each be less than one.

Lastly, the claim that obliquity of the mesh could be neglected if only peak heights are required, was based on calculations where θ was close to 90°. It is to be expected that if θ deviates considerably from 90°, the more detailed calculations must be used in order to obtain accurate results.

Fig. 1. Set of hypothetical electron-density values on (001)

References

BURNS, D. M. (1955). *Acta Cryst.* **8**, 517.
BURNS, D. M. (1958). *Acta Cryst.* **11**, 88.
DICKENS, G. J. (1956). *Acta Cryst.* **9**, 201.
KATZ, J. L. (1957). Paper 33, 15th Annual Pittsburgh Diffraction Conference.
LADELL, J. & KATZ, J. L. (1954). *Acta Cryst.* **7**, 460.

The space groups of three isomers of acorone.
By E. J. GABE, *Viriamu Jones Laboratory, University College, Cardiff, Wales, England*

Acorone is a sesquiterpene ketone whose empirical formula is $C_{15}H_{24}O_2$. It occurs in three stereoisomeric forms: acorone, isoacorone and neoacorone (Sorm, Herout & Sykora, private communication), whose structures are of considerable stereochemical interest. The data presented below are the results of a preliminary X-ray investigation of these isomers.

The cell dimensions and space groups summarized in Table 1 were determined by oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. The accuracy of the values quoted is of the order of 1 %.

Acorone

Acorone itself forms poor crystals with ill-defined faces; the Laue symmetry is $2/m$. The only systematic absences are $0k0$ for k odd and, as the substance is optically active, the space group is uniquely determined as $P2_1$. Compar-

Tabel 1. *Crystallographic data*

Substance	a (Å)	b (Å)	c (Å)	β	Density g.cm.$^{-3}$ Obs.	Calc.	Z	Space group
Acorone	6·2	14·2	8·3	96°	1·09	1·08	2	$P2_1$
Isoacorone	6·2	9·6	23·7	—	1·12	1·11	4	$P2_12_12_1$
Neoacorone	6·4	13·7	32·4	—	1·12	1·11	8	$P2_12_12_1$