The SCNNC ring is of particular interest in this investigation. The atoms S(1), N(3), N(4) and C(5) lie within 0·02 Å of a plane whose equation is

$$1\cdot8422x-1\cdot8020y+11\cdot641z=1\cdot7113\ , \quad (5)$$

referred to the triclinic axes and where the quantity on the right hand side of the equation is the origin-to-plane distance in Å. Atom C(2), however, is 0·58 Å out of the plane. The puckering of the ring is similar to that found in saturated five-membered rings composed of all carbon atoms. The two adjacent nitrogen atoms in the ring are quite different from each other. The bonds to N(3) form tetrahedral angles whereas the bonds to N(4) lie in a plane. Furthermore, the bond distance C(2)–N(3) is 1·51 Å, a value near that found in saturated compounds while the C(5)–N(4) distance is much shorter, 1·35 Å. The latter value for C–N is characteristically found in compounds where C–N is adjacent to C=S as in thiourea (Kuncher & Truter, 1958) and its derivatives (Dias & Truter, 1964). Apparently the presence of the C=S has a profound effect not only on the neighboring nitrogen atom, N(4), but also on the neighboring sulfur atom, S(1). The two C–S distances in the ring are also considerably different from each other, 1·78 and 1·84 Å, with the lower value adjacent to the C=S. The C=S distance, 1·65 Å, is somewhat shorter than that found in thiourea derivatives, 1·72 Å (Dias & Truter, 1964).

The usual values have been obtained for the bond distances and angles in the benzyl and methoxyphenyl substituents. The equations for the least-squares planes through rings I, II, and III are, respectively,

$$7\cdot2663x-4\cdot3274y-\ 2\cdot1285z=\ \ 1\cdot2524 \quad (6)$$
$$-1\cdot8937x-3\cdot3007y+11\cdot835z=\ \ 0\cdot1323 \quad (7)$$
and
$$7\cdot4924x-4\cdot6072y-\ 0\cdot3992z=-1\cdot9598\ , \quad (8)$$

where the x, y and z values refer to coordinates in the triclinic system.

The thermal motion of the atoms in ring I is considerably greater than that of atoms in the other rings. The thermal parameters increase for atoms C(9), C(10), C(11), C(12) and C(13) as their distance from C(8) increases. The electron density map (Fig. 1) shows the effect of the thermal motion on these atoms.

The nearest intermolecular approaches are O(27)–C(17′) at 3·30 Å, O(27)–C(18′) at 3·66 Å, C(28)–C(20″) at 3·59 Å, and S(6)–C(20‴) at 3·62 Å.

We wish to express our appreciation to Mr Stephen Brenner, who performed all the high-speed machine calculations.

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Calculation of Exact Transmission Factors for Crystals with Constant Cross-Section

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Formulae for the calculation of exact transmission factors are derived by the block-mosaic method. The solutions of the integral for a cross-section are presented in a form which relates the area a_{qr} of a block to the paths of the X-rays diffracted at the corners of the a_{qr}. The use of the formulae is simplified if the a_{qr}'s are divided into triangles and parallelograms. The formulae are suitable for application to automatic computers.

Introduction

The intensities of the reflexions in X-ray diffraction patterns are affected by absorption. An exact evaluation of the absorption factor (or of the transmission factor) is needed to obtain good accuracy in structure determinations (Jeffery & Rose, 1964).

The transmission factor is usually defined as

$$A=\frac{1}{\tau}\int_{\tau}\exp\left(-\mu l\right)d\tau \quad (1)$$

in which l represents the length in cm of X-ray path in the crystal, μ is the absorption coefficient in cm^{-1} and τ can be either an area or a volume. The integral,

$$\tau_e = \int_\tau \exp(-\mu l) d\tau, \qquad (2)$$

can be considered as the equivalent diffracting area (*e.d.a.*) or the equivalent diffracting volume (*e.d.v.*).

Either the cross-section of the crystal or the whole crystal can be subdivided into a mosaic of blocks. In a cross-section each block is identified by the indices q, r whose meaning will be explained later.

Each block of the cross-section and its area are designated as a_{qr}, its equivalent diffracting area as $(e.d.a.)_{qr}$.

The integral (2) can be represented in the block-mosaic method (Ferrari, Braibanti & Tiripicchio, 1965) by

$$S_e = \Sigma_q \Sigma_r \int_{a_{qr}} \exp(-\mu l) da\,. \qquad (3)$$

This follows from the condition that the function to be integrated is continuous only within each block, a condition which is, strictly speaking, not satisfied by the method used by Busing & Levy (1957). They assume that the integrand function is approximately continuous over the whole crystal.

Approximate solutions of the integral (3) for special cases of highly absorbing crystals have been derived (Ferrari, Braibanti & Tiripicchio, 1961, 1965). An exact solution of it has now been found in a form which holds for every type of cross-section contour and all values of linear absorption coefficient. This solution is suitable for use on electronic computers.

Consider a crystal cross-section parallel to the plane formed by the incident and diffracted rays (Fig. 1). The corners P_j are numbered anticlockwise, the angles δ_j and the face vectors, $\mathbf{f}_j = \overrightarrow{P_{j-1} - P_j}$, are defined following the conventions assumed in a preceding paper (Ferrari, Braibanti and Tiripicchio, 1965). The angles ψ_j and φ_j (for example, ψ_4 and φ_4 in Fig. 1) give the orientation of the $\mathbf{f}_j$'s (or of the unitary vectors $\mathbf{t}_j$) with respect to the direction of the incident and diffracted rays, represented by the unitary vectors $\mathbf{i}$ and $\mathbf{d}$ respectively. The sides of the cross-section, *i.e.* the faces of the crystal, whose representative vectors $\mathbf{f}_j$ form with $\mathbf{i}$ an angle ψ_j such that $\pi < \psi_j < 2\pi$, can be numbered *anticlockwise* from $-\mathbf{i}$ to $\mathbf{i}$, and a set $r(r = 1,2,3,\ldots)$ is obtained; these faces are 'illumined' by the incident rays, *i.e.* the incident rays enter the crystal through these faces. The faces whose representative vectors form with $\mathbf{d}$ an angle φ_j for which $0 < \varphi_j < \pi$ are ordered in a *clockwise* set $q(q = 1,2,3,\ldots)$ from $-\mathbf{d}$ to $\mathbf{d}$; they are 'illumined' by the diffracted rays, *i.e.* the diffracted rays leave the crystal via these faces. The vectors of the two sets become $\mathbf{f}_j(q)$ and $\mathbf{f}_j(r)$, respectively.

The incident rays passing through the extreme points of faces r and the diffracted rays passing through the extreme points of faces q delimit the blocks of the mosaic. All the incident rays arriving at points of one block enter the crystal through the same side r and leave the crystal through the same side q, therefore the area of the block can be designated a_{qr}. Observe that q and r are interchanged with respect to the preceding paper (Ferrari, Braibanti & Tiripicchio, 1965).

For exact calculations the angles δ_j need to be calculated for each reflexion hkl because, when $l \neq 0$, the cross-section is differently inclined with respect to the edges of the crystal. It will be shown however that the components of the $\mathbf{f}_j$'s along the reference axes give the same information as the angles δ_j, ψ_j, and φ_j, provided the axes are properly chosen.

If the crystal cross-section is referred to a system of axes (Fig. 2), with the x axis having the same direction and sign as $\mathbf{i}$ and with the y axis having the same direction and sign as $\mathbf{d}$, the points P_j can be represented by vectors from the origin,

$$\mathbf{p}_j = x_j \mathbf{i} + y_j \mathbf{d}\,, \qquad (4)$$

where $\mathbf{i}$ and $\mathbf{d}$ are unit vectors. In order to find the components of $\mathbf{p}_j$, the coordinates of the edges and of the corners of the crystal must be referred at first to a standard system of axes; then rotations are applied to the axes to get the required final reference system.

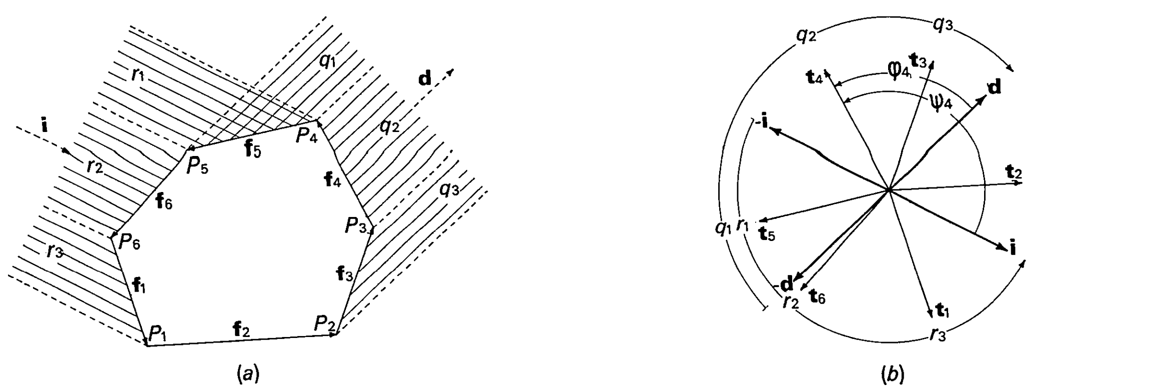

Fig. 1. Faces of the crystal cross-section 'illumined' by the incident rays (faces r) and faces 'illumined' by the diffracted rays (faces q).

(*a*) Cross-section contour represented by vectors $\mathbf{f}_j$.

(*b*) Vector fan formed by the unitary vectors $\mathbf{t}_j$ corresponding to the vectors $\mathbf{f}_j$.

The initial standard system and the rotations can be those used by Wells (1960), or others equivalent. It can be assumed here that the coordinates of P_j (*i.e.* the components of $\mathbf{p}_j$) are referred to the proper final system of axes.

The vectors $\mathbf{f}_j$ can be obtained by

$$\mathbf{f}_j = \mathbf{p}_j - \mathbf{p}_{j-1} = (x_j - x_{j-1})\mathbf{i} + (y_j - y_{j-1})\mathbf{d} \,, \tag{5}$$

and because they can be ordered into two sets $\mathbf{f}_j(q)$ and $\mathbf{f}_j(r)$, their extreme points also become $\mathbf{p}_j(q)$ or $\mathbf{p}_j(r)$. In other words, those $\mathbf{p}_j$'s which appear in each of the equations (5) defining the vectors $\mathbf{f}_j(q)$, and those which appear in the equations (5) defining the vectors $\mathbf{f}_j(r)$, can be ordered into two sets, one set, $[\mathbf{p}_j(q)]$, with the components x_j increasing, and the other, $[\mathbf{p}_j(r)]$, with the components y_j decreasing. Obviously the same sets hold for the coordinates of the P_j's. The same $\mathbf{p}_j$ can belong to both sets at the same time. The $\mathbf{p}_j(q)$ with the lowest x_j is $\mathbf{p}_j(q_0)$ and the $\mathbf{p}_j(r)$ with the highest y_j is $\mathbf{p}_j(r_0)$; the $\mathbf{f}_j(q)$'s and the $\mathbf{f}_j(r)$'s can be obtained by

$$\mathbf{f}_j(q) = \mathbf{p}_j(q-1) - \mathbf{p}_{j-1}(q) \tag{6}$$

and

$$\mathbf{f}_j(r) = \mathbf{p}_j(r) - \mathbf{p}_{j-1}(r-1), \tag{7}$$

and the numbering of the sets $\mathbf{f}_j(q)$ and $\mathbf{f}_j(r)$ is consistent with the numbering of the sets $\mathbf{p}_j(q)$ (clockwise) and $\mathbf{p}_j(r)$ (anticlockwise). It is worth noting that the sign of $\sin \psi_j$ changes with the sign of the component $f_{y_j} = (y_j - y_{j-1})$ of the $\mathbf{f}_j$'s and the sign of $\sin (\varphi_j - \pi)$ with the sign of the component $f_{x_j} = (x_j - x_{j-1})$. The assignment of the vectors $\mathbf{f}_j$ to the sets q and r can, therefore, be done directly by mean of the signs of their components.

Calculation of $(\mathbf{e.d.a.})_{qr}$

The path l of an X-ray in the crystal is expressible by the same function in the whole a_{qr} (see Appendix); so each $(e.d.a.)_{qr}$ can be calculated exactly.

Special cases arise only when one or more sides of the contour of the a_{qr} coincide with the *loci of constant path length.*

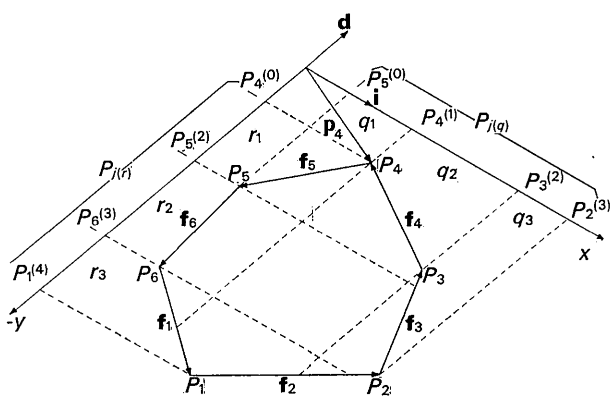

Fig. 2. Blocks a_{qr} of the mosaic in a crystal cross-section. Relation of vectors $\mathbf{f}_j(q)$ and $\mathbf{f}_j(r)$ to vectors $\mathbf{p}_j(q)$ and $\mathbf{p}_j(r)$ [and to points $P_j(q)$ and $P_j(r)$].

As a general rule, the $(e.d.a.)_{qr}$ is obtained as the sum of as many terms as there are corners of the a_{qr}. For any a_{qr} whose contours are not loci of constant path, each term is of the form: $(A/B) \exp(-C)$. For the nth corner,

A is the area of the parallelogram built on the two sides of a_{qr} adjacent to the corner.

B is the product $(l_n - l_{n+1})(l_n - l_{n-1})$ of the differences of X-ray path between the nth corner and the two adjacent corners.

C is μl_n, *i.e.* the path (multiplied by μ) of the X-ray path at the nth corner.

The general expression for each $(e.d.a.)_{qr}$ is therefore,

$$(e.d.a.)_{qr} = \frac{1}{\mu^2} \sum_1^n \frac{S_n \exp(-\mu l_n)}{\Pi_k (l_n - l_k)} \,, \tag{8}$$

where n indicates the corner and k the corners $n-1$ and $n+1$ adjacent to n; S_n is the area in square centimeters of the parallelogram built on the two sides, adjacent to n. The corners n are numbered consecutively either clockwise or anticlockwise. If a_{qr} is subdivided arbitrarily into smaller areas of whatever convex polygonal contour, the $(e.d.a)$ of each small area can be calculated by applying (8) in exactly the same way to its n vertices. The whole $(e.d.a.)_{qr}$ can then be obtained by summing the $(e.d.a.)$'s of all the small areas.

The path of the X-ray at any point A (Fig. 3) of the cross-section is given by the relation:

$$l_A = (x_A - x_{r-1}) - (x_r - x_{r-1}) \frac{(y_A - y_{r-1})}{(y_r - y_{r-1})} + (y_{q-1} - y_A) + \frac{(y_q - y_{q-1})(x_A - x_{q-1})}{(x_q - x_{q-1})} \,; \tag{9}$$

y_r and y_{r-1} [$y_r > y_A > y_{r-1}$ in the set $P_j(r)$] are coordinates of the extreme points of the entrance side; x_q and x_{q-1} [$x_q > x_A > x_{q-1}$ in the set $P_j(q)$] are coordinates of the extreme points of the exit side. The coordinates are intended to be referred to a system of axes with x having the direction and the sign of $\mathbf{i}$, and with y having the direction and opposite sign of $\mathbf{d}$.

If the area a_{qr} is subdivided into triangles and parallelograms, for example by means of straight lines parallel to x and y (Fig. 3), S_n is constant for each triangular zone ($t.z.$) or parallelogram zone ($p.z.$), and the expression (8) becomes for a triangular zone:

$$(e.d.a.)_{t.z.} = S_n \frac{1}{\mu^2} \sum_{n=1}^{n=3} \frac{\exp(-\mu l_n)}{\Pi_k (l_n - l_k)} \,; \tag{10}$$

and for a parallelogram zone:

$$(e.d.a.)_{p.z.} = S_n \frac{1}{\mu^2} \sum_{n=1}^{n=4} \frac{\exp(-\mu l_n)}{\Pi_k (l_n - l_k)} \tag{11}$$

The area S_n is given by:

$$S_n = |(x_n - x_{n-1})(y_{n+1} - y_n) - (x_{n+1} - x_n)(y_n - y_{n-1})| \sin 2\theta. \tag{12}$$

When a contour of the $t.z.$ or $p.z.$ coincides with a locus of constant path, the expressions (10) and (11) give rise to the following special cases:

(i) For a triangular zone:

if $l_{n-1}=l_{n+1}$,

$$(e.d.a.)_{t.z.}=S_n\left(\frac{\exp(-\mu l_{n+1})}{\mu(l_n-l_{n+1})}+\frac{\exp(-\mu l_n)-\exp(-\mu l_{n+1})}{\mu^2(l_n-l_{n+1})^2}\right); \quad (13)$$

if $l_n=l_{n+1}=l_{n-1}$,

$$(e.d.a.)_{t.z.}=S_n \exp(-\mu l_n)/2 \quad (14)$$

(ii) For a parallelogram zone:

if $l_n=l_{n+1}$ and $l_{n-1}=l_{n+2}$,

$$(e.d.a.)_{p.z.}=\frac{1}{\mu}S_n\frac{\exp(-\mu l_{n-1})-\exp(-\mu l_n)}{(l_n-l_{n-1})}; \quad (15)$$

if $l_n=l_{n+1}=l_{n-1}$,

$$(e.d.a.)_{p.z.}=S_n \exp(-\mu l_n) \quad (16)$$

The formulae found by Evans (1952) for some types of areas are equivalent to formulae (10), (11), (13). In fact, Evans's formula I corresponds to (11), his formulae III, IV and V to (10), and his formulae II, III*a*, III*b*, IV*a*, IV*b* to (13).

It can be demonstrated also that the formulae given in a preceding paper (Ferrari, Braibanti & Tiripicchio, 1965) are particular cases of the present formulae.

The formulae (13) and (14) for triangular zones and the formulae (15) and (16) for parallelogram zones give the $(e.d.a.)_{qr}$ when equalities arise between the paths of the X-rays at the corners of the zone. For path lengths nearly equal, formula (11) and formula (12) tend to indeterminate values. In order to overcome this difficulty we have searched for a special function capable of representing, at least in a given interval, all the three formulae for triangular zones; another function was sought for parallelogram zones. Such an expression for triangular zones is

$$(e.d.a.)_{t.z.}=S_n \exp(-\mu l_1+\alpha), \quad (17)$$

where

$$\alpha=-0{\cdot}69315+a_1X+a_2X^2+a_3Y+a_4Y^2+a_5XY+a_6X^2Y+a_7XY^2+a_8X^2Y^2 \quad (18)$$

and is a function of $X=\mu(l_2-l_1)$ and $Y=\mu(l_3-l_1)$; l_1 must be the shortest of the three paths and moreover $l_1\le l_2\le l_3$. $\exp\alpha=f(X,Y)$ can be considered as a *weighting function*. The expression (17) holds for triangular zones, provided that the corners are numbered clockwise or anticlockwise to comply the rules specified earlier.

For a parallelogram zone an analogous expression is obtained:

$$(e.d.a.)_{p.z.}=S_n \exp(-\mu l_1+\beta), \quad (19)$$

where

$$\beta=b_1X+b_2X^2+b_3Y+b_4Y^2+b_5XY+b_6X^2Y+b_7XY^2+b_8X^2Y^2 \quad (20)$$

and is a function of $X=\mu(l_4-l_1)=\mu(l_3-l_2)$ and $Y=\mu(l_2-l_1)=\mu(l_4-l_3)$. The *weighting function* is now $f(X,Y)=\exp\beta$. The relation is valid if $l_1\le l_2\le l_4\le l_3$ with corners numbered consecutively, clockwise or anticlockwise, to satisfy the required order of paths.

A program, where the formulae and principles of this paper have been applied, has been prepared for an Olivetti Elea 6001 computer, and it will be presented shortly in detail.

The extension of the procedure to crystals in three dimensions is not very different from the procedure for a cross-section.

We wish to thank Prof. A. Ferrari for constant encouragement and the Consiglio Nazionale delle Ricerche, Rome for financial aid.

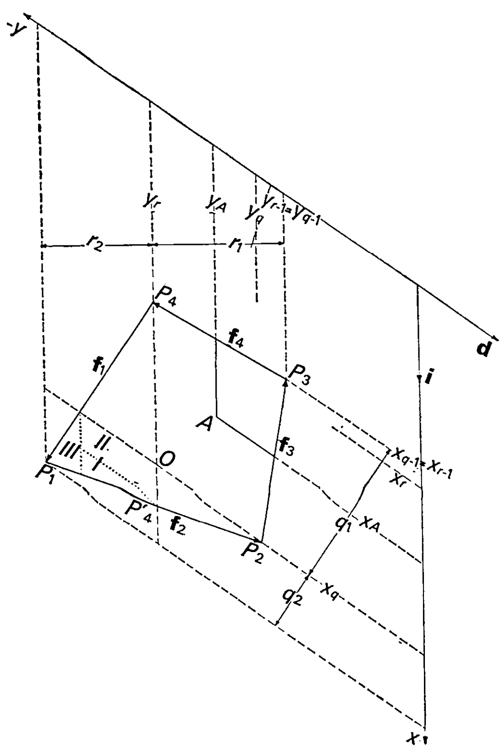

Fig. 3. X-ray path in the crystal at a point A. Subdivision of the block $a_{2,2}$ into triangular (I, III) and parallelogram zones (II).

APPENDIX

For the area DP_1IO (Fig. 4) the $(e.d.a.)_{2,2}$ can be calculated as follows:

The incident rays enter the crystal through P_4P_1 and the diffracted rays leave the crystal via P_1P_2; the reference system is assumed as in the figure.

The path of an X-ray in the crystal is (in cm)

$$l=a(x_{P_1}-x)+b(y_{P_1}-y), \quad (21)$$

where

$$a=\frac{-\sin\delta_1}{\sin(\delta_1-\psi_2)} \quad (22)$$

and

$$b=\frac{-\cos\delta_1}{\sin(\delta_1-\psi_2)}-\frac{1}{\sin\Phi_2}. \quad (23)$$

The value of the integral (2) for the area DP_1IO can be calculated and reduced to the form:

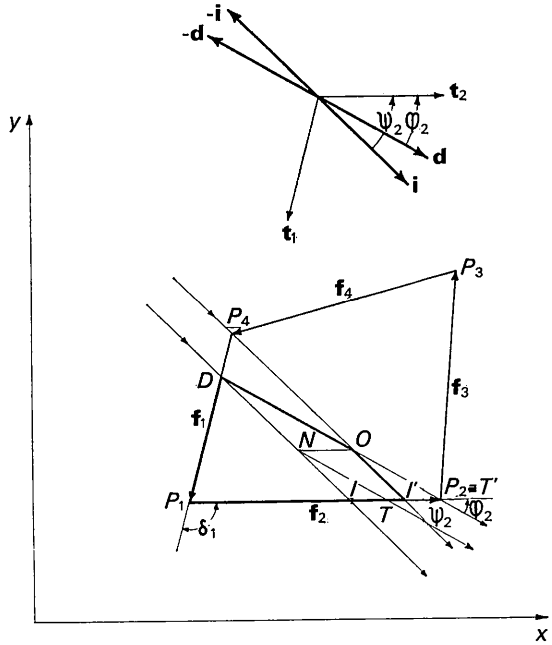

Fig. 4. Calculation of $(e.d.a.)_{DP_1IO}$. General case. $l_D = DN + NT$, $l_O = P_4O + OP_2$, $l_I = P_4I$, $l_{P_1} = 0$

$$
\begin{aligned}
&(e.d.a.)_{DP_1IO} \\
&= \frac{1}{\mu^2} \Big[OD \,.\, DP_1 \sin O\hat{D}P_1 \frac{\exp(-\mu l_D)}{(l_D - l_O)(l_D - l_{P_1})} \\
&+ DP_1 \,.\, P_1I \sin D\hat{P}_1I \frac{\exp(-\mu l_{P_1})}{(l_{P_1} - l_D)(l_{P_1} - l_I)} \\
&+ P_1I \,.\, IO \sin P_1\hat{I}O \frac{\exp(-\mu l_I)}{(l_I - l_{P_1})(l_I - l_O)} \\
&+ IO \,.\, OD \sin I\hat{O}D \frac{\exp(-\mu l_O)}{(l_O - l_I)(l_O - l_D)} \Big] ,
\end{aligned}
\tag{24}
$$

where l_D, l_{P_1}, l_I, l_O are path lengths at the corner of the area. Expression (24) is independent of the reference system and depends only on the contour of the area. The total $(e.d.a.)_{2,2}$ is of the form $(A/B) \exp(-C)$, each corner contributing one term to the sum.

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The Crystal Structure of Calcium 5-Keto-D-Gluconate (Calcium D-*xylo*-5-Hexulosonate)

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Crystals of calcium 5-keto-D-gluconate, $Ca(C_6H_9O_7)_2 \,.\, 2H_2O$ are monoclinic, space-group $A2$, with $a = 9{\cdot}39$, $b = 8{\cdot}03$, $c = 12{\cdot}37$ Å; $\beta = 107{\cdot}9°$; $Z = 2$.

The structure, determined by three-dimensional Fourier methods, exhibits a lactol arrangement of the 5-keto-D-gluconate ion, with eightfold coordination of the calcium atom (Ca – O, 2·46 Å; Ca – H_2O, 2·39 Å). The metal ion is chelated by two organic ions. The molecules form strongly bonded sheets, parallel to the (100) plane, held weakly together by hydrogen linkages. Ring closure occurs in the organic ion between C(2) and C(5), resulting in a (non-planar) furanoid ring with a new asymmetric centre at C(5), yielding a C(4),C(5) *cis* diol. The structure has been refined to an R index of 0·12 for the 1022 observed reflexions.

Cell dimensions are given also for calcium 2-keto-D-gluconate, (calcium D-*arabino*-hexulosonate), $Ca(C_6H_9O_7)_2 \,.\, 3H_2O$; $P2_12_12_1$; $a = 10{\cdot}43$, $b = 18{\cdot}33$, $c = 9{\cdot}50$ Å; $Z = 4$, and possible structural relationships between the two compounds are discussed.

Introduction

The sugar acids have been shown to be particularly effective as sequestrants for calcium ions from alkaline solution, their affinity for calcium being attributed to the formation, through coordinate and covalent bonds, of chelated rings between the metallic ions and the hydroxyl and carboxyl groups of the acid (Prescott, Shaw, Bilello & Cragwall, 1953; Mehltretter, Alexander & Rist, 1953). The identification of calcium 2-keto-gluconate in the growth products of micro-organisms

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