

representation of the dimeric units of  $K_2[Zr(SO_4)_3] \cdot 2H_2O$ . Examination of this structure shows that breaking and remaking one oxygen bridge in each dimeric ring of  $K_2[Zr(SO_4)_3] \cdot 2H_2O$  would result in the formation of infinite  $-Zr-O-S-O-Zr-$  chains similar to those found in  $Na_2[Zr(SO_4)_3] \cdot 3H_2O$  [Fig. 3(c)] and we see that in these two compounds we have an extension of the structural arrangements already found in the neutral hydrates of  $Zr(SO_4)_2$  and anhydrous  $\alpha-Zr(SO_4)_2$ .

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## The Determination of the Crystal Structure of *trans*-2,4-Dihydroxy-2,4-Dimethylcyclohexane-*trans*-1-Acetic Acid $\gamma$ -Lactone, $C_{10}H_{16}O_3$ , using Rotation and Translation Functions in Reciprocal Space.

BY ROGER M. BURNETT\* AND MICHAEL G. ROSSMANN

*Department of Biological Sciences, Purdue University, Lafayette, Indiana 47907, U.S.A.*

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Crystals of *trans*-2,4-dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid  $\gamma$ -lactone,  $C_{10}H_{16}O_3$ , have an orthorhombic unit cell with  $a = 10.09_6$ ,  $b = 14.02_8$ ,  $c = 7.03_9$  Å. The space group is  $P2_12_12_1$  and there are four molecules per unit cell. The structure was solved using a known grouping of atoms to calculate a search Patterson function. The rotation function of Rossmann & Blow was used to obtain the relative orientation of the known and unknown Patterson functions. The  $Q$ -functions of Tollin were used to obtain the translational parameters of the known group relative to the  $2_1$  axes present in the crystal structure. The 988 observed reflections, collected on a Picker four-circle automatic diffractometer were used to refine the structure to give a conventional  $R$  value of 0.068. The molecular structure consists of a lactone ring fused to a cyclohexane ring distorted by the closeness of the  $-CH_3$  and  $-OH$  groups attached to C(2) and C(4). The lactone ring is non-planar with one atom, C(1), lying 0.55 Å from the least-squares plane through the other four atoms. The C–O bond lengths in the lactone ring differ by 0.130 Å, the shorter bond being adjacent to the carbonyl group.

### Introduction

The rotation function (Rossmann & Blow, 1962) has been used to evaluate the degree of superposition of two sets of Patterson vectors when one set is rotated with respect to the other. A fuller account of this method has been given by Tollin (1970) and by Rossmann (1971). Tollin & Rossmann (1966) suggest the use of this method in the solution of the following problems:

(A) Determining the relative orientation of identical groups of atoms within the same crystallographic asymmetric unit.

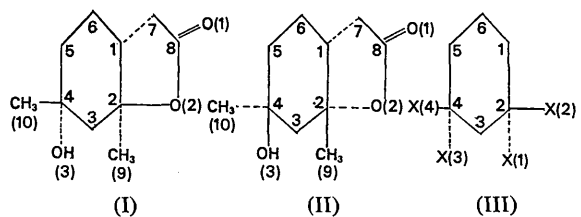
(B) Determining the absolute orientation of a rigid group with known chemical structure in a molecular crystal.

(C) Determining the relative orientations of identical groups in different crystal forms, when the chemical structure is unknown.

### References

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The method has been successful in the investigation of several protein structures; that of hemoglobin (Rossmann & Blow, 1962), insulin (Dodson, Harding, Hodgkin & Rossmann, 1966), and  $\alpha$ -chymotrypsin (Blow, Rossmann & Jeffery, 1964) illustrate problems of type (A) while the comparison of horse oxyhemoglobin with seal myoglobin (Lattman & Love, 1970) illustrates type (C) problems. We report here the solution of a small molecular crystal structure, for part of which the configuration was known, representing an application of the rotation function to a problem of type (B).



In a chemical study Wolinsky & Chan (1966) indicated the configuration of *trans*-2,4-dihydroxy-2,4-

\* Present address: Biophysics Research Division, Institute of Science and Technology, University of Michigan, Ann Arbor, Michigan 48104 U.S.A.

Table 1. Observed and calculated structure factors

Table with 12 columns and multiple rows, containing numerical data for structure factors. Each column is labeled with 'L FO FC A' and contains a list of values. The data is organized in a grid-like format with varying numbers of rows per column.

dimethylcyclohexane-*trans*-1-acetic acid  $\gamma$ -lactone (I) to be preferred to that of *trans*-2,4-dihydroxy-2,4-dimethylcyclohexane-*cis*-1-acetic acid  $\gamma$ -lactone (II). These two possible structures both have cyclohexane rings and two groups attached at both the C(2) and C(4) positions. The common atoms could be approximately represented by (III) which has mirror symmetry. The orientation of the vector set derived from this arrangement of atoms was determined with the rotation function. Subsequently, the position of the known fragment relative to the crystallographic symmetry elements was found using the  $Q$ -functions (Tollin, 1966). Our results have verified the assignment of Wolinsky & Chan.

### Experimental

#### Crystal data

Name: *trans*-2,4-Dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid  $\gamma$ -lactone.

Molecular formula:  $C_{10}H_{16}O_3$

Molecular weight: 184.2

Melting point:  $145.5 \pm 0.5^\circ C$

Growth solvent: Methylene chloride-diethyl ether

Crystal shape: Hexagonal prisms

System: Orthorhombic

Space group:  $P2_12_12_1$

Systematic absences:  $h00$  when  $h$  is odd;  $0k0$  when  $k$  is odd;  $00l$  when  $l$  is odd

Cell dimensions:  $a = 10.09_6$ ,  $b = 14.02_8$ ,  $c = 7.03_9$  Å  
 $\alpha = \beta = \gamma = 90^\circ$

Volume of unit cell:  $996.9$  Å<sup>3</sup>

Density, measured:  $1.25$  g.cm<sup>-3</sup> (Flotation in ammonium sulphate solution)

Density, calculated:  $1.23$  g.cm<sup>-3</sup>

Number of molecules per unit cell: 4

Linear absorption coefficient, calculated:  $7.4$  cm<sup>-1</sup>

$F_{000}$ : 400.

Preliminary investigations of Laue symmetry and systematic absences were made with a Buerger precession camera. A Picker four-circle diffractometer was used to collect all available reflections in the  $hkl$  and  $hkl$  octants from a single crystal at room temperature. The intensities were measured in blocks of 25 pairs of symmetry-related reflections. Two intense reference reflections (002 and 200) were measured after each block. A decay of 5.5% was observed in both intensities at the end of the 48 hours of exposure required for the total data collection. Errors were estimated entirely on the basis of counting statistics, and reflections with negative corrected intensities were assigned a value of zero. Other details of diffractometer technique were:

Radiation: Cu  $K\alpha$   
Crystal size: 0.4 mm long  $\times$  0.1 mm thick  
Mosaicity:  $0.1^\circ$

Crystal-counter distance: 200 mm

Crystal-source distance: 146 mm

Counter aperture: 2.5 mm high  $\times$  2.3 mm wide

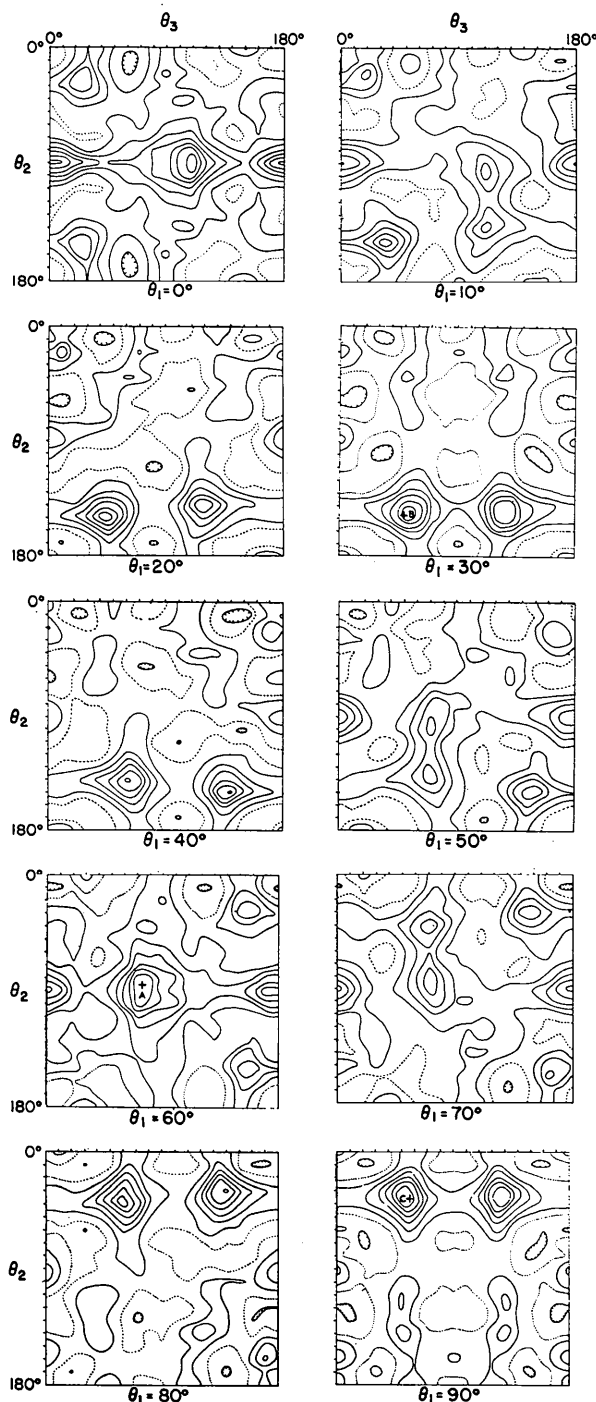


Fig. 1. The rotation function of the model structure against the unknown structure. The corresponding Pattersons were in space group  $P2_1/m$  and  $Pmmm$ , respectively, producing the Eulerian space group  $Pbab$ .

Take-off angle:	4°	factor found from the normalized plot of the reference
Attenuators:	not necessary owing to the	reflection intensities. The pairs of reflections were cor-
	small size of the crystal	rected for Lorentz and polarization effects but no cor-
Scan type:	moving-crystal,	rection was made for absorption. The pairs were then
	moving-counter (2θ scan)	averaged to give a set of 988 independent reflections
Scan limits:	2θ° - (0.55 + 0.4 tan θ)° to	(Table 1).
	2θ° + 0.55(1 + tan θ)°	A Wilson (1942) plot yielded an initial overall <i>B</i>
Scan rates:	30 sec per degree	value of 5.0 Å <sup>2</sup> , and allowed the data to be placed on an
Background:	10 sec at each end of the	approximately absolute scale. For the purposes of the
	range of 2θ	rotation and <i>Q</i> -functions, the data were sharpened to
		be representative of those obtained from point atoms,
		with an effective <i>B</i> value of 4.0 Å <sup>2</sup> to reduce series ter-
		mination effects.

An allowance was made for decay of the crystal due to X-ray damage by multiplying each reflection by a

Table 2. *Atomic positional coordinates and temperature parameters*

The estimated standard deviations in parentheses refer to the last decimal positions of the corresponding values. The temperature factor expression used was  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . The  $\beta_{ij}$  in the Table have been multiplied by 10<sup>4</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	0.2211 (4)	0.1701 (3)	0.3591 (5)	124 (5)	56 (2)	154 (7)	-3 (3)	3 (6)	12 (4)
C(2)	0.2762 (4)	0.2116 (3)	0.1750 (5)	97 (4)	56 (2)	147 (7)	3 (3)	-8 (5)	0 (4)
C(3)	0.2699 (4)	0.3193 (3)	0.1870 (5)	112 (5)	56 (2)	182 (8)	2 (3)	-13 (6)	10 (4)
C(4)	0.3426 (4)	0.3572 (3)	0.3654 (6)	108 (5)	60 (2)	194 (9)	3 (3)	0 (6)	-11 (4)
C(5)	0.3088 (5)	0.3018 (3)	0.5466 (6)	144 (6)	78 (3)	164 (8)	-9 (4)	9 (7)	-8 (4)
C(6)	0.3127 (5)	0.1925 (3)	0.5252 (5)	176 (6)	69 (3)	147 (8)	-18 (4)	-16 (7)	15 (4)
C(7)	0.1799 (4)	0.0702 (3)	0.2976 (6)	146 (5)	56 (2)	224 (10)	-4 (3)	-16 (7)	18 (4)
C(8)	0.1287 (4)	0.0918 (3)	0.1000 (6)	106 (5)	56 (2)	241 (10)	11 (3)	4 (6)	-7 (5)
C(9)	0.4094 (4)	0.1731 (3)	0.1103 (6)	97 (4)	80 (3)	252 (10)	7 (3)	25 (6)	-27 (5)
C(10)	0.3105 (5)	0.4634 (3)	0.3910 (7)	162 (6)	61 (2)	342 (13)	5 (3)	-15 (9)	-32 (5)
O(1)	0.0513 (3)	0.0463 (2)	0.0039 (4)	131 (3)	68 (2)	294 (8)	-7 (2)	-41 (5)	-17 (4)
O(2)	0.1781 (3)	0.1754 (2)	0.0360 (3)	113 (3)	62 (2)	179 (6)	-4 (2)	-33 (4)	2 (3)
O(3)	0.4839 (2)	0.3470 (2)	0.3431 (4)	98 (3)	80 (2)	208 (6)	-4 (2)	-12 (4)	0 (3)
<i>B</i>									
H(1)	0.129 (3)	0.203 (2)	0.391 (5)	2.2 (8)					
H(2)	0.103 (4)	0.036 (3)	0.383 (6)	4.5 (10)					
H(3)	0.249 (4)	0.023 (2)	0.289 (5)	2.3 (8)					
H(4)	0.414 (3)	0.097 (2)	0.105 (5)	3.1 (9)					
H(5)	0.436 (4)	0.188 (3)	0.998 (6)	3.6 (9)					
H(6)	0.484 (4)	0.199 (2)	0.188 (5)	3.3 (9)					
H(7)	0.308 (3)	0.347 (2)	0.075 (5)	2.7 (8)					
H(8)	0.171 (3)	0.343 (2)	0.193 (5)	2.5 (8)					
H(9)	0.502 (5)	0.382 (3)	0.257 (7)	5.4 (12)					
H(10)	0.344 (4)	0.508 (3)	0.269 (6)	6.2 (12)					
H(11)	0.359 (4)	0.483 (3)	0.509 (6)	3.9 (10)					
H(12)	0.207 (4)	0.471 (3)	0.395 (6)	5.3 (12)					
H(13)	0.379 (4)	0.324 (3)	0.647 (6)	4.1 (10)					
H(14)	0.210 (4)	0.321 (3)	0.598 (5)	3.3 (9)					
H(15)	0.271 (3)	0.163 (2)	0.640 (5)	3.4 (9)					
H(16)	0.416 (4)	0.166 (3)	0.503 (6)	3.8 (10)					

Table 3. *Distances in Å between the model atoms and their final refined positions*

	Results from rotation function		Results from rigid body refinement
	10° search (60°, 88°, 72°)	0.5° search (61.0°, 85.0°, 74.5°)	(57.70°, 78.59°, 77.68°)
C(1)	0.12	0.08	0.14
C(2)	0.04	0.07	0.06
C(3)	0.05	0.07	0.19
C(4)	0.08	0.08	0.03
C(5)	0.37	0.31	0.11
C(6)	0.36	0.27	0.07
X(1)-C(9)	0.43	0.39	0.29
X(2)-O(2)	0.32	0.26	0.15
X(3)-O(3)	0.33	0.26	0.24
X(4)-C(10)	0.40	0.33	0.16
Average distance	0.25 Å	0.21 Å	0.14 Å

### Structure determination

The search model (III), used in this determination, consisted of tetrahedral carbon atoms separated by bond lengths of 1.54 Å in the cyclohexane ring and by the mean, 1.47 Å, of a C-O and C-C bond elsewhere. This molecule was placed in a monoclinic unit cell of space group  $Pm$  and cell dimensions  $a=8.0$ ,  $b=12.0$ ,  $c=6.0$  Å,  $\alpha=\beta=\gamma=90^\circ$ . The local mirror plane, through atoms (6) and (3) (III), was made coincident with the mirror plane of the chosen space group, and the pseudo molecular  $\bar{3}$  axis was oriented parallel to  $c$ . The utilization in the model crystal structure of the search model's symmetry avoided the generation of nonlinear symmetry in the rotation function. Additionally, the unit cell was chosen to be of sufficient size to prevent the overlap of intramolecular vectors from adjacent origins (Tollin & Rossmann, 1966). Structure factors were calculated for this model at all reciprocal lattice points within the copper sphere and were sharpened in the same manner as the observed data.

In the large terms version of the rotation function program (Tollin & Rossmann, 1966), the largest structure factors are used to define one of the vector sets. Since a partial data set of given size will define the real structure more accurately than the model structure (due to the absence of electron density in a large proportion of the model cell), the one hundred largest observed reflections were chosen to define the vector set to be rotated.

The rotation function,  $R$ ,

$$R = \sum_{\mathbf{p}} |F_{\mathbf{p}}|^2 \sum_{\mathbf{h}} |F_{\mathbf{h}}|^2 G_{\mathbf{h}, \mathbf{h}'} \quad (\text{Rossmann \& Blow, 1962})$$

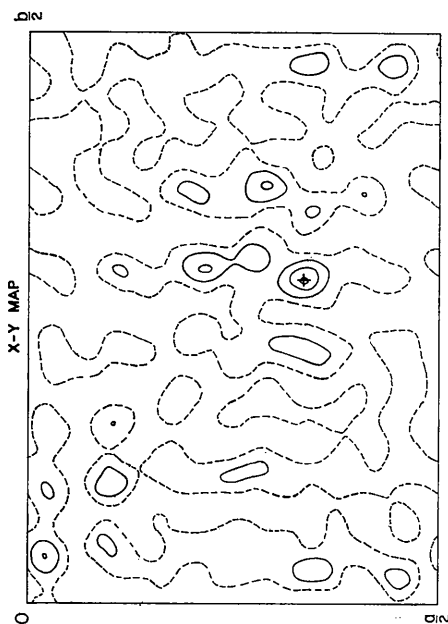


Fig. 2.  $Q$ -functions calculated parallel to the three mutually perpendicular  $2_1$  axes in the unknown structure, computed with sharpened  $|F|$  values.

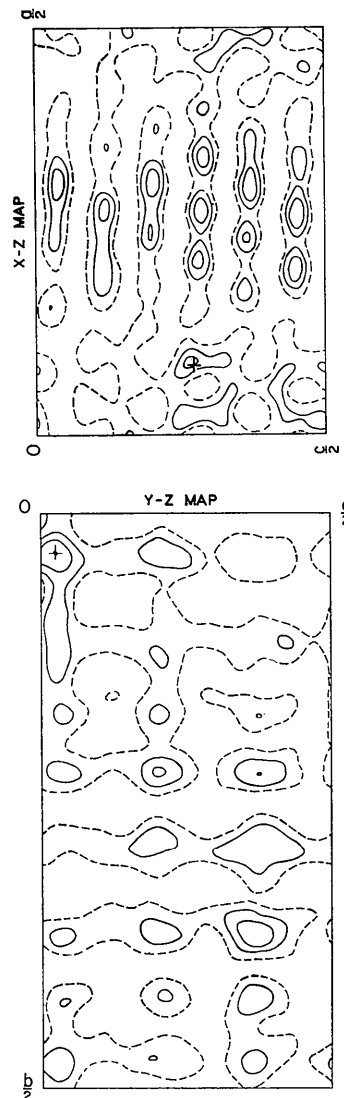


Fig. 2 (cont.)

is the result of a double summation. The summation over  $\mathbf{h}$  is around the non-integral lattice points  $\mathbf{h}'$  obtained by rotating the lattice points  $\mathbf{p}$  through a set of known angles. The function  $G_{\mathbf{h}, \mathbf{h}'}$  is determined by the distance,  $\mathbf{H}$ , between the points  $\mathbf{h}$  and  $\mathbf{h}'$  and the radius of integration,  $r$ , within which the two Patterson functions are to be compared. Since for a sphere

$$G_{\mathbf{h}, \mathbf{h}'} = \frac{3(\sin 2\pi Hr - 2\pi Hr \cos 2\pi Hr)}{(2\pi Hr)^3},$$

its value can be considered negligible when  $|Hr| > 1.0$  (Tollin & Rossmann, 1966). Therefore if we express  $\mathbf{H}$  as  $n/d$ , where  $n$  is an integer and  $d$  is the cell dimension in a particular direction,  $n$  need be no greater than  $\pm(d/r - 1)$  in that direction. In this investigation a sphere of radius of 5.5 Å was used, giving values of  $|n| \leq 1$  and a range of integration of  $-1 \leq n \leq +1$  along each axis.

The superposition of the  $Pmmm$  Patterson of the unknown structure on the  $P2/m$  symmetry of the model Patterson gives a rotation function of space group  $Pbab$  (Tollin, Main & Rossmann, 1966) with angles defined

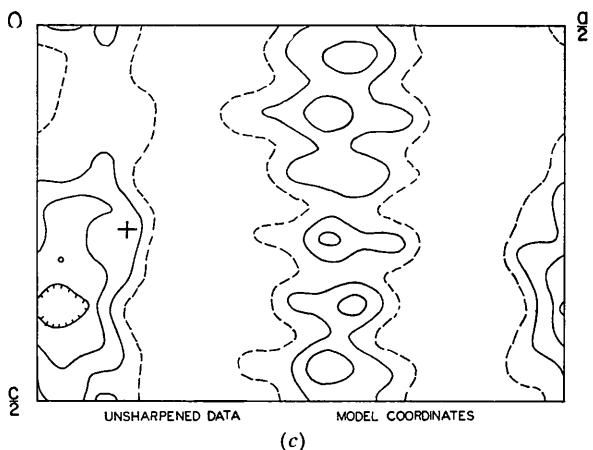
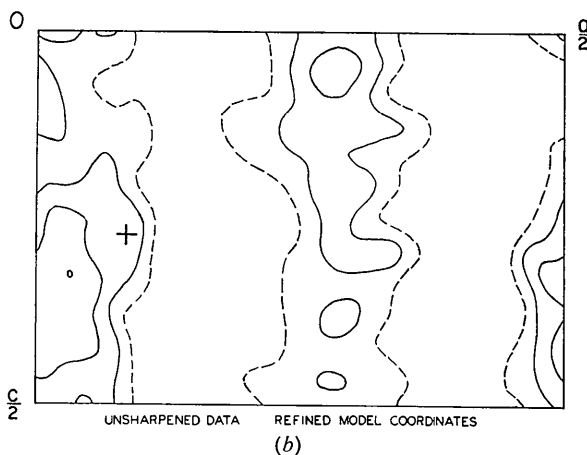
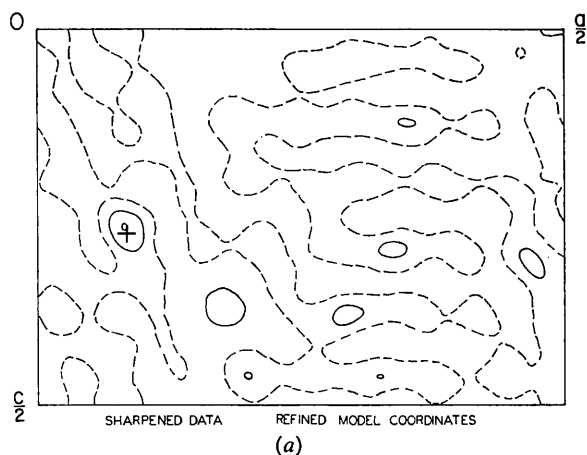


Fig. 3. The  $(x-z)$   $Q$ -function calculated using final refined and unsharpened coordinates for the model atoms with sharpened data (a, b), and the original model coordinates with unsharpened data (c).

according to the convention of Rossmann & Blow (1962). An asymmetric unit of this space group, defined by the limits  $(0 \leq \theta_1 \leq \pi/2, 0 \leq \theta_2 < \pi, 0 \leq \theta_3 < \pi)$ , was explored at  $10^\circ$  intervals of  $\theta_1, \theta_2, \theta_3$ .

The rotation function is shown in Fig. 1. The pseudo  $\bar{3}m$  symmetry of the cyclohexane ring in the known structure generates a corresponding higher pseudo-symmetry within the Eulerian space group. The three-fold axis parallel to  $c$  gives rise to the symmetry operation  $(\theta_1, \theta_2, \theta_3) \rightarrow (-2\pi/3 + \theta_1, \theta_2, \theta_3)$  which represents a complete repetition of the  $Pbab$  symmetry every  $120^\circ$  along  $\theta_1$ . Thus the twofold axes at levels  $\theta_1 = 0$  and  $\theta_1 = \pi/2$  will occur additionally at  $\theta_1 = \pm\pi/3$  and  $\theta_1 = \pm\pi/6$  respectively, giving rise to the pseudo twofold axes

$$(\theta_1, \theta_2, \theta_3) \rightarrow \frac{\pi}{3} - \theta_1, \quad \theta_2, \pi - \theta_3$$

and

$$(\theta_1, \theta_2, \theta_3) \rightarrow \frac{2\pi}{3} - \theta_1, \pi - \theta_2, \quad \theta_3$$

within the true asymmetric unit. The pseudo asymmetric unit is now contained within the limits  $0 \leq \theta_1 \leq \pi/6, 0 \leq \theta_2 < \pi, 0 \leq \theta_3 < \pi$ . These pseudo-symmetry operations are easily visible in Fig. 1, which shows the true asymmetric unit and illustrates the importance of placing even a pseudo-symmetry operation along, or normal to, a crystallographic axis. If this had not been done fortuitously in the present case, interpretation would have been more difficult. The rotation function was explored at  $0.5^\circ$  intervals around the three, pseudo-symmetry related, major peaks ( $A, B, C$  in Fig. 1). Each represented an orientation closely related to that given by the other two (*i.e.* the molecular framework was in a different orientation but the vector set had much in common with that from the other orientations of the model). The peak  $A$  ( $61.0^\circ, 85.0^\circ, 74.5^\circ$ ) giving the largest value was used to compute atomic coordinates relative to an arbitrary origin.

The position of a known group of atoms relative to a symmetry operation may be determined with the  $Q$ -functions (Tollin, 1966), which are multiple three-dimensional sum functions of the Patterson function on each of the atomic positions calculated from relative coordinates and arbitrary origin displacements. A  $Q$ -function was calculated for each of the three mutually perpendicular  $2_1$  axes and the resulting set of three maps (Fig. 2) should have given consistent translational parameters, noting the shift of origin by  $\frac{1}{4}$  of the unit cell from one map to the next. The  $x-y$  map, which explored the position of the model structure relative to the  $2_1$  axis parallel to  $z$ , gave the clearest results, with the  $y$  coordinate of its largest peak consistent with the  $y$  coordinate of the largest peak on the  $y-z$  map. This was in agreement with a minor peak on the  $x-z$  map.

Structure factors based on these rotational and translational parameters were used to phase an electron density map which not only revealed the positions of

the remaining three atoms, but also distinguished between the carbon and oxygen atoms. The conventional  $R$  value at this stage was 0.56.

A modified version of the Busing, Martin & Levy (1962) full-matrix least-squares program, *ORFLS*, was used to minimize the expression  $\sum \omega(|F_o| - |F_c|)^2$ ; the atomic form factors were taken from *International Tables for X-ray Crystallography* (1962). The initial weighting scheme was based on estimates of the stan-

dard deviations derived from the counting statistics of each intensity measurement. Refinement using isotropic temperature factors ceased at a residual of 0.16. No significant improvement, measured by the tests of Hamilton (1965), was obtained by introducing anisotropic temperature factors.

A plot of  $\sum \omega(|F_o| - |F_c|)^2$  for different ranges of  $F_o$  revealed a strong dependence on  $F_o$ , apparently due to underestimating the errors in the large intensities.

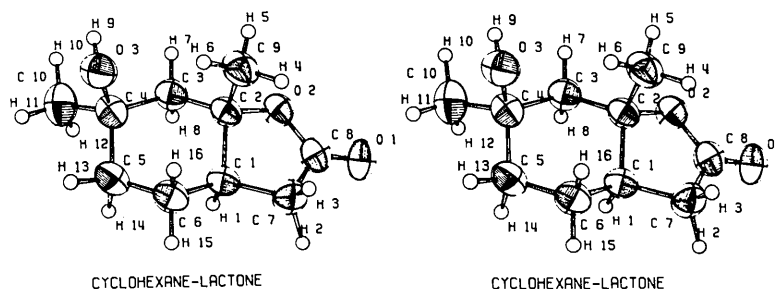


Fig. 4. Stereoscopic pair showing the cyclohexane lactone in an arbitrary orientation to illustrate the thermal ellipsoids of the atoms.

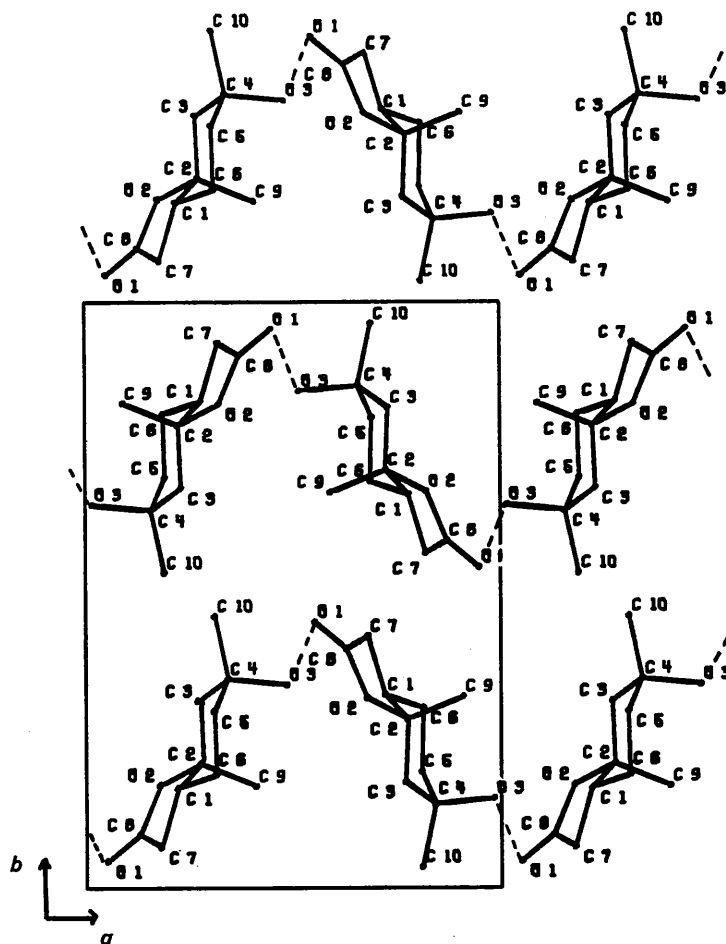


Fig. 5. View of part of the crystal structure, looking down the  $z$  axis, illustrating the packing arrangement of the molecule.

Unitary weights were then assigned to all but the weakest reflections and refinement then progressed with the introduction of anisotropic thermal parameters to a residual of 0.12. A difference map at this stage yielded the positions of 15 of the 16 hydrogen atoms and the refinement was continued with alternating blocks of nonhydrogen and hydrogen atom refinement due to the large number of variables. A further difference map gave three possible positions of the undetected hydrogen of the hydroxyl group. An occupancy of  $\frac{1}{3}$  was assigned to each position and a further cycle gave an occupancy-standard deviation ratio of less than one for two positions and greater than two for the third, thus establishing the position of the missing hydrogen. Refinement was then continued with all atoms present to give a final residual of 0.068, calculated for all intensities, and 0.054 without including the zero terms.

The final atomic positional and thermal parameters are shown in Table 2, and these were used to calculate the  $F_{calc}$  values and phase angles listed in Table 1.

#### Discussion of structure determination

Some difficulty was experienced in the solution of this structure because of the inconsistency of the translational parameters taken from the maps shown in Fig. 2. To determine the cause of this difficulty, the distance between the positions,  $\mathbf{x}_i$ , of each of the model atoms

and their final refined positions,  $\mathbf{x}'_i$ , was calculated for various orientations of the model. Table 3 shows these values for the peak positions found in the  $10^\circ$  search, and the  $0.5^\circ$  search. A rigid body refinement of the model against the final parameters was performed by varying the Eulerian angles and translational param-

eters in order to minimize the sum  $\sum_{i=1}^n (\mathbf{x}_i - \mathbf{x}'_i)^2$ . It can

be seen that each atom except X(1) was within 0.35 Å of its final position when the angles obtained from the  $0.5^\circ$  search were used. Comparing the results of the translation functions calculated from the final refined atomic positions showed that the  $Q$ -function maps can be sensitive to relatively small errors in the model [compare Fig. 3(a) and the corresponding map of Fig. 2].

Table 4.

	Refined model	Original model
Sharpened	Fig. 3(a)	Fig. 2
Unsharpened	Fig. 3(b)	Fig. 3(c)

The accurate location of the peak maximum in the rotation function may thus be useful. (*cf.* Table 3). The rotation function itself appears relatively insensitive to small errors of the search model.

$Q$ -functions have been computed for the four combinations of original and refined model parameters,

Table 5. Bond lengths (Å) and angles ( $^\circ$ ) for the non-hydrogen atoms

Lengths		Angles*	
C(1)–C(2)	1.525 (5)	C(2)–C(1)–C(6)	110.6°
C(1)–C(6)	1.523 (6)	C(1)–C(2)–C(3)	108.6
C(1)–C(7)	1.524 (6)	C(2)–C(3)–C(4)	111.6
C(2)–C(3)	1.514 (5)	C(3)–C(4)–C(5)	113.3
C(2)–C(9)	1.519 (5)	C(4)–C(5)–C(6)	114.7
C(3)–C(4)	1.549 (5)	C(1)–C(6)–C(5)	105.4
C(4)–C(5)	1.532 (6)		
C(4)–C(10)	1.535 (6)	(Average cyclohexane C–C–C)	110.7°
C(5)–C(6)	1.541 (6)		
C(7)–C(8)	1.515 (6)	C(2)–C(1)–C(7)	102.1
(Average C–C)	1.528° (6)	C(6)–C(1)–C(7)	125.0
C(2)–O(2)	1.482 (5)	C(1)–C(7)–C(8)	99.8
C(8)–O(2)	1.352 (5)	C(1)–C(2)–C(9)	116.2
C(4)–O(3)	1.443 (5)	C(3)–C(2)–C(9)	114.1
		C(3)–C(4)–C(10)	109.2
C(8)=O(1)	1.214 (5)	C(5)–C(4)–C(10)	110.4
		(Average C–C–C)	111.0°
		C(1)–C(2)–O(2)	100.8
		C(3)–C(2)–O(2)	110.5
		C(9)–C(2)–O(2)	105.8
		C(3)–C(4)–O(3)	110.3
		C(5)–C(4)–O(3)	105.1
		C(10)–C(4)–O(3)	108.5
		C(7)–C(8)–O(2)	110.7
		(Average C–C–O)	107.4°
		C(2)–O(2)–C(8)	108.9
		O(2)–C(8)=O(1)	120.5
		C(7)–C(8)=O(1)	128.8

\* The root mean square estimated standard deviation of the angles is  $0.3^\circ$ .



with sharpened and unsharpened data. A key to the four  $x$ - $z$  maps illustrated here (as this was the poorest section) is given in Table 4. These maps indicate the advantage to be gained from sharpening the data when an accurate model is available. Since the accuracy of the search model is not usually known at the outset of an investigation, a useful procedure could be to calculate  $Q$ -functions both with sharpened and unsharpened data. The correct position should be marked by a peak common to both maps.

Our experience with this structure has shown that of the rotational and translational problems, the latter is the more intractable. The major advantage of the vector space search employed by Nordman & Nakatsu (1963) is that the correctly orientated vector set may be refined to give the best fit with the observed Patterson function before proceeding with the translational search. The principal disadvantage of a vector space search is that the whole Patterson function must be stored in the computer. The ability to refine the vector set should therefore be set against the storage capacity of the available computing facilities.

### Discussion of the structure

At the end of the refinement the root mean square value for the ratio of shift to error for all parameters was less than 20%. Standard errors were then computed by

inversion of the least-squares matrix using the Busing, Martin & Levy program *ORFFE* (1964). The errors computed for the hydrogen atoms were necessarily low due to the separate refinement of the nonhydrogen and hydrogen atoms.

The principal axes of the thermal ellipsoids are illustrated in a stereoscopic pair drawing (Fig. 4) (Johnson, 1965). Tables 5 and 6 contain intramolecular bond lengths and angles.

The molecule consists of a slightly flattened cyclohexane ring fused to a lactone ring. The distortion of the cyclohexane ring is due to the overcrowding between the  $-\text{OH}$  and  $-\text{CH}_3$  groups at C(4) and C(2). The separation of O(3) and C(9) is 3.03 Å, which is somewhat shorter than the van der Waals separation of 3.4 Å for an oxygen atom and a methyl group. It is therefore of some interest that H(6) is inclined towards O(3) [the angle O(3)-H(6)-C(9) is  $125 \pm 3^\circ$ ] suggesting an interaction between H(6) and O(3). These two atoms are 2.34 Å apart.

Several planes were fitted to the atoms in the lactone group and ring using a program written by Pippy & Ahmed (1968) utilizing the least-squares procedure of Blow (1960). The best fit was obtained with a plane of equation  $0.7701X - 0.4936Y - 0.4041Z - 0.0693 = 0$  ( $X$ ,  $Y$ ,  $Z$  are coordinates in Å measured along the crystallographic axes and referred to the cell origin) passing through C(7), C(8), O(1) and O(2) of the lactone group.

Table 6. Bond lengths (Å) and angles ( $^\circ$ ) involving hydrogen atoms

Lengths		Angles*	
C(1)—H(1)	1.06 (3)	C(2)—C(1)—H(1)	109°
C(3)—H(7)	0.9 (4)	C(6)—C(1)—H(1)	106
C(3)—H(8)	1.06 (4)	C(7)—C(1)—H(1)	103
C(5)—H(13)	1.05 (4)	C(2)—C(3)—H(7)	110
C(5)—H(14)	1.10 (4)	C(4)—C(3)—H(7)	110
C(6)—H(15)	1.00 (4)	C(2)—C(3)—H(8)	110
C(6)—H(16)	1.12 (4)	C(4)—C(3)—H(8)	108
C(7)—H(2)	1.09 (4)	C(4)—C(5)—H(13)	105
C(7)—H(3)	0.96 (4)	C(6)—C(5)—H(13)	110
C(9)—H(4)	1.07 (4)	C(4)—C(5)—H(14)	111
C(9)—H(5)	0.86 (4)	C(6)—C(5)—H(14)	107
C(9)—H(6)	0.99 (4)	C(1)—C(6)—H(15)	106
C(10)—H(10)	1.11 (5)	C(5)—C(6)—H(15)	109
C(10)—H(11)	1.00 (5)	C(1)—C(6)—H(16)	113
C(10)—H(12)	1.05 (5)	C(5)—C(6)—H(16)	111
(Average C—H)	1.03 Å	C(1)—C(7)—H(2)	117
		C(8)—C(7)—H(2)	110
		C(1)—C(7)—H(3)	117
		C(8)—C(7)—H(3)	109
		C(2)—C(9)—H(4)	114
		C(2)—C(9)—H(5)	118
		C(2)—C(9)—H(6)	112
		C(4)—C(10)—H(10)	113
		C(4)—C(10)—H(11)	105
		C(4)—C(10)—H(12)	108
		(Average C—C—H)	110°)
		C(4)—O(3)—H(9)	105° (4)
Angles*			
H(13)—C(5)—H(14)	109°		
H(15)—C(6)—H(16)	112		
H(2)—C(7)—H(3)	104		
H(4)—C(9)—H(5)	101		
H(4)—C(9)—H(6)	110		
H(5)—C(9)—H(6)	100		
H(11)—C(10)—H(10)	110		
H(11)—C(10)—H(12)	115		
H(12)—C(10)—H(10)	106		
(Average H—C—H)	108°)		

\* The r.m.s. estimated standard deviations of the angles involving one, and two, hydrogen atoms are respectively  $2^\circ$  and  $3^\circ$ .

C(1) and C(2) are displaced by  $-0.55 \text{ \AA}$  and  $+0.12 \text{ \AA}$  from this plane; the average r.m.s. for the displacement of the remaining four atoms was  $0.006 \text{ \AA}$ . The bonds C(8)–O(2) and O(2)–C(2) are of interest since there is a difference of  $0.130 \text{ \AA}$  between them, the shorter bond being adjacent to the carbonyl group. This shortening is connected with the planarity of the lactone group. The average angle in the lactone ring is  $104.5 \pm 0.3^\circ$ . The displacement of one atom from the plane through the remaining atoms in the lactone ring, the shortening of the bond adjacent to the carbonyl group, and the average angle within the ring observed here are consistent with previous observations (Kim, Jeffrey, Rosenstein & Corfield, 1967; Jeffrey, Rosenstein & Vlasse, 1967).

The shortest intermolecular contact is  $2.154 \text{ \AA}$  between O(1) and H(9) and this is due to hydrogen bonding between the hydroxyl hydrogen and the oxygen of the carboxyl group. The angle C(8)=O(1)···H(9) is  $112^\circ$  and the angle O(3)–H(9)···O(1) is  $169^\circ$ . The hydrogen bond distance O(1)–O(3) is rather long at  $2.944 \text{ \AA}$  but since the hydrogen bonding is approximately collinear with the O(3)–H(9) bond some interaction would appear likely. Fig. 5 illustrates the packing arrangement of the molecules in the crystal structure from which it can be seen that the hydrogen bonding links chains of molecules along the direction of the crystallographic  $a$  axis.

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