

	Angle
C(7)—C(8)—C(11)	119
C(11)—C(8)—C(9)	107
C(8)—C(9)—C(10)	101
C(9)—C(10)—O(1)	108
C(10)—O(1)—C(11)	109
O(1)—C(11)—C(8)	112
O(1)—C(11)—O(2)	117
O(2)—C(11)—C(8)	131

The carbonyl group of the lactone ring is *trans* to the substituted phenyl group on C(7) of the exocyclic double bond (Fig. 2). The phenyl group is planar. In agreement with earlier reports (Mathieson & Taylor, 1961; Fridrichsons & Mathieson, 1962; Jeffrey & Kim, 1966) the C—C—O—C

||
O

group of the lactone is planar; the carbon atom C(9) of the lactone is 0.3 Å (~6 e.s.d.) above this plane. Least-squares refinement of the structure in space group *Pcam* (the 4 molecules on mirror planes) led to values for *R* of 0.066 (unweighted) and 0.069 (weighted), comparable with those from the *Pca*₂₁ refinement. However, temperature factors for atoms C(9), C(10), C(11), O(1), O(2) and O(3) rose by an average of more than 1.0 Å², so that although a disordered structure containing molecules of each hand cannot be ruled out, the ordered *Pca*₂₁ structure seems more probable. In any event, all bond lengths agree within one e.s.d. between the two refined structures, including the unreasonable C(3)—C(4) length of 1.29 Å.

The ester oxygen O(1) of one molecule is hydrogen-bonded to the phenolic oxygen O(3') of the molecule related to the first one by the *a*-glide plane normal to *b*. The O(1)—O(3') distance is 2.79 Å (e.s.d. 0.02 Å) and the angle of O(1)—O(3')—C(6') is about 144°. The hydrogen-bonded molecules form zigzag chains running along the *a* axis. Perpendicular to *c* and at *c*/2 apart, alternate sheets of parallel chains running in opposite directions are stacked with maximum overlapping of the phenolic rings.

The crystal structure confirms the hypothesis that the initial step in the formation of a coumarin from an α -(2-

hydroxybenzylidene)- γ -butyrolactone consists of a *trans, cis* isomerization (Zimmer, Haupter, Rothe, Schrof & Walter, 1963), and lends support to the chemical evidence that all α -arylidene-substituted five-membered lactones and lactams in Fig. 1 are *trans* isomers.

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The absolute structure of LiIO₃ crystals. By I. D. CAMPBELL and A. MCL. MATHIESON, *Division of Chemical Physics, CSIRO Chemical Research Laboratories, P.O. Box 160, Clayton, Victoria, Australia 3168* and M. F. MACKAY, *Chemistry Department, Melbourne University, Parkville, Victoria, Australia 3052*

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Rosenweig & Morosin (*Acta Cryst.* (1966) **20**, 758) concluded that the non-centrosymmetric structure of individual crystals of LiIO₃ could not be placed on an absolute basis by use of the anomalous dispersion of the iodine atoms because these particular atoms are related by a point of inversion. This conclusion is erroneous and its implication of such a restriction on the determination of absolute structure is misleading. Numerical evidence that the absolute chirality of individual LiIO₃ crystals is capable of experimental confirmation is presented.

Recent re-investigation of the crystal structure of LiIO₃ (Rosenweig & Morosin, 1966; Boer, Bolhuis, Olthof-Hazekamp & Vos, 1966), referred to subsequently as RM and BBOV respectively, has unambiguously established its space

group as *P6*₃. This space group is non-centrosymmetric, the structure consisting of discrete trigonal iodate groups and Li ions surrounded by six oxygen atoms in a distorted octahedral arrangement. The iodine atoms lie on trigonal

axes at $x = \frac{1}{3}, y = \frac{2}{3}, z = 0$ and $x = \frac{2}{3}, y = \frac{1}{3}, z = \frac{1}{2}$, sites which are related by a point of inversion. Because of this relationship, RM concluded – ‘It is unfortunate in a crystal whose space group is unambiguously established (as $P6_3$) that the iodine atoms are related to each other by a point of inversion, and hence one is not able to utilize their dispersion to resolve the absolute configuration of the packing.’

This conclusion is erroneous and it would be unfortunate if it led others to assume a limitation concerning the determination of absolute configuration which does not in fact exist. We wish to point out that it is the absence of a point of inversion in the whole structure *i.e.* the unit-cell contents, which is the essential feature for the application of this method. A non-space-group centrosymmetric relationship limited to specific atoms or even to atomic groups does not impose a corresponding condition on the whole structure.

That this is the case is made evident by reference to Patterson’s (1963) formulation of the relationship between the reduced intensities, F^2 , of mirror reflexions:

$$D = |F(hkl)^+|^2 - |F(hkl)^-|^2 \\ = -4(\Delta f_H''/f_H)(AB_H - A_H B).$$

This relates the difference, D , to the atomic scattering factor, f_H , of the anomalously scattering atom H , its imaginary component, $\Delta f_H''$, and the values A, B, A_H, B_H . A and B are the non-dispersive structure factor components for the whole structure ($F = A + iB$), whereas A_H and B_H are the corresponding non-dispersive contribution resulting from atom H . Either A_H or B_H may be zero depending on the choice of origin, but only if both are zero (corresponding to centrosymmetry of the whole structure) will the inequality disappear.

To illustrate this in the case of LiIO_3 , we have calculated the complete set of structure factors, $F(hkl)$ and $F(hk\bar{l})$, with anomalous dispersion corrections for iodine with $\text{Mo } K\alpha$ radiation applied. A few are shown in Table 1, together with the associated values $-(AB_1 - A_1B)$ where A, B refer to the non-dispersive structure factor components for the whole structure and A_1, B_1 to that for I alone. A guide to the practical magnitude of the differences in the present case, is given by the percentage difference, $\% \Delta F$. Corresponding intensity differences would range up to $\sim 10\%$.

In these calculations, temperature factor corrections for all atoms were as listed by RM. Scattering factors for Li^+ , O and I^- (approximated as Xe) and the dispersion corrections for I with $\text{Mo } K\alpha$ radiation ($\Delta f' = -0.5$; $\Delta f'' = 2.4$) were from *International Tables for X-ray Crystallography* (1962). Our F values differ slightly from the corresponding

Table 1. Selected calculated structure factors, $F(hkl), F(hk\bar{l})$, their percentage differences, $\% \Delta F$, and the associated values $(AB_1 - A_1B)$

A, B refer to non-dispersive structure factor components for the whole structure and A_1, B_1 to the corresponding components for the iodine atoms only.

hkl	$F(hkl)$	$F(hk\bar{l})$	$\% \Delta F$	$-(AB_1 - A_1B)$
2,0,1	60.8	62.5	2.7	-1090
5,0,1	34.2	35.3	3.2	-185
3,1,1	57.9	56.7	2.1	550
2,3,1	39.9	40.7	2.0	-260
2,4,1	36.7	36.1	1.7	70
0,0,2	73.5	70.4	4.3	2100
2,0,2	32.9	31.8	3.4	325
3,0,2	58.8	58.1	1.2	120
5,0,2	19.3	18.3	5.3	80
1,1,2	80.2	81.5	1.6	-815
2,1,2	30.2	29.0	4.0	225
3,1,2	24.9	23.8	4.5	190
1,3,2	32.9	34.0	3.3	-215
0,0,4	50.9	53.2	4.4	-870
3,0,4	43.6	44.7	2.5	-140
1,1,4	55.1	54.4	1.3	215
2,1,4	24.0	24.6	2.9	-50
5,2,4	24.1	25.2	4.4	-50
2,4,4	15.3	16.0	4.5	-15
5,0,5	23.6	22.6	4.3	75
6,1,5	19.1	19.8	3.6	-20
3,2,5	28.0	27.1	3.2	30
2,4,5	24.3	25.2	3.6	-50
0,0,8	23.0	22.2	3.5	100

ones listed by RM because of differences in scattering factors used. RM and BBOV report the inclusion of $\Delta f_i'$ and $\Delta f_i''$ in their refinement procedure but apparently used only experimental values corresponding to the non-equivalent reflexions. RM and BBOV appear to have utilized either experimental data derived from only one set of independent reflexions or to have averaged F^2 values from equivalent reflexions before structure analysis was carried out.

It is evident that in principle and in practice the absolute structure of any individual LiIO_3 crystal can be established by the X-ray method.

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