Fig. 4. Molecular model of furane-α,α'-dicarboxylic acid.

All the values are in good agreement with the values found for furoic acid (Goodwin & Thompson, 1954; Hudson, 1962).

In Fig. 4 the refined molecular model of furane-α,α'-dicarboxylic acid is shown.

The length of the bond C(1)–C(2) (1·475 Å) may indicate some conjugation between the carboxylic group and the furane ring. The distance C(3)$\cdots$O(2) (3·32 Å) appears to be rather short (Fig. 2). The rotation internal angle O(2)–C(1)–C(2)$\wedge$C(1)–C(2)C(3) is 175·6°. This means that the carboxylic group is slightly twisted out of the plane of the ring.

Table 5. *Intramolecular distances, angles and standard deviations*

Distances		
O(1)–C(1)	1·315 Å	0·007 Å
O(2)–C(1)	1·205	0·007
C(1)–C(2)	1·475	0·008
C(2)–O(r)	1·368	0·006
C(2)–C(3)	1·354	0·008
C(3)–C(3')	1·442	0·008
Angles		
O(1)–C(1)–O(2)	124·7°	0·5°
O(1)–C(1)–C(2)	111·7	0·5
O(2)–C(1)–C(2)	123·4	0·5
C(1)–C(2)–O(r)	116·9	0·5
C(1)–C(2)–C(3)	130·7	0·5
C(2)–C(3)–C(3')	105·4	0·5
C(2)–O(r)–C(2')	104·4	0·5
C(3)–C(2)–O(r)	112·3	0·5
O(2)–C(1)–C(2) $\wedge$ C(1)–C(2)–C(3)	175·6	0·5

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Refinement of the Crystal Structure of Lithium Diborate, Li₂O.2B₂O₃

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The crystal structure of anhydrous lithium diborate was determined by Krogh-Moe in 1962 from two-dimensional data only. The proposed structure has now been verified by a full-matrix, least-squares refinement based on three-dimensional data recorded with Cu $K\alpha$ radiation. The refinement (including anisotropic temperature factor parameters) resulted in a discrepancy index $R = 4·9\%$. The structure consists, as previously described, of two three-dimensional interlocking networks of the characteristic diborate groups. The lithium ions are coordinated by four close oxygen atoms with lithium–oxygen distances in the range from 1·97 to 2·14 Å. A fifth oxygen atom is separated from lithium by 2·63 Å, others being separated by 2·85 Å or more. Lengths of the boron–oxygen and lithium–oxygen bonds were determined with estimated standard deviations of 0·01 and 0·02 Å respectively.

Introduction

The crystal structure of lithium diborate, Li₂O.2B₂O₃, was determined by Krogh-Moe (1962) with two-dimensional data only. In particular it proved difficult to evaluate the lithium positions from the electron-density projections, and only rough estimates of the lithium parameters were given. It was therefore considered worth while to perform a complete three-dimensional refinement of the structure.

Experimental

The unit-cell dimensions were redetermined from a least-squares fit of powder diffraction data, with lead nitrate as internal standard. The following values were found:

$$a = b = 9.479 \pm 0.003 \text{ Å} \quad c = 10.280 \pm 0.004 \text{ Å}.$$

The space group is $I4_1cd$ with 8 formula units of Li$_2$O.2B$_2$O$_3$ in the cell.

Three-dimensional intensity data were collected with Cu $K\alpha$ radiation. Crystals were rotated about the a axis as well as the c axis. In both cases the crystals had a quadratic cross-section of 0·1 × 0·1 mm. The reflexions were recorded on integrated multiple film Weissenberg photographs and evaluated photometrically. The photometer data were processed in the usual manner, and the observed structure factors thus obtained were scaled together. No correction for absorption was introduced, but four strong reflexions were corrected for extinction.

The refinement

A modified version of the Busing, Martin & Levy (1962) full-matrix least-squares refinement program was used. The original parameters given by Krogh-Moe (1962) were used as a starting point. (The x and y parameters were exchanged, however.) Atomic form-factor curves for neutral boron and oxygen atoms and for the Li$^+$ ion were taken from *International Tables for X-ray Crystallography* (1962). The final parameters reported here are based on the use of a Hughes weighting scheme, with σ proportional to F_o when $F_o > 30$. Other weights were tried, however, without significant differences in the result.

The refinement was first performed with individual isotropic temperature factors. The refinement converged, giving a final R value of 5·9% (counting ob-

served structure factors only). The isotropic temperature factors and their standard deviations are given in the last two columns of Table 2.

The refinement was then continued with anisotropic temperature factors. R was now reduced to 4·9%. The positional parameters from the last cycle of the anisotropic refinement are given in Table 1 and the corresponding temperature factor parameters are found in Table 2.

The ratio of the R value for the isotropic to that for the anisotropic case is 5·94/4·85 = 1·22. According to the significance tests proposed by Hamilton (1965), this ratio would mean that the hypothesis: 'all atoms vibrate isotropically' is rejected on the 0·005 level. Using the weighted R values, the ratio becomes even larger, *viz.* 1·28, in favour of anisotropic vibrations.

The positional parameters do not change significantly on going from the isotropic to the anisotropic case. None of the position parameters are shifted more than twice their estimated standard deviations and only two of these parameters are shifted more than the standard deviation. The anisotropic temperature factor parameters from the final refinement cycle, given in Table 2, are positive definite only for the atoms O(2) and B(1), however, though the remaining atoms obey within the limits of error the requirement of having a positive definite set of temperature factor parameters.

Observed and calculated structure factors from the final anisotropic refinement cycle are given in Table 3.

Discussion

The final parameters do not differ greatly from those given previously by Krogh-Moe (1962). Hence the main features of the previous structure proposal are substantiated. For a description of the structure, the reader is referred to the earlier work. Here we shall briefly discuss only the lithium coordination, which was not

Table 1. *Atomic position parameters, with standard deviations*

The values are given as fractions, multiplied by 10^4, of the unit cell edge.

	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$
Li	1507	17	1679	16	8512	17
O(1)	2814	5	1371	5	2679	7
O(2)	0671	5	1778	5	1561	8
O(3)	1552	5	9420	5	1831	7
O(4)	0		0		0	
B(1)	1686	9	0860	9	2032	12
B(2)	9461	8	1118	8	0831	9

Table 2. *Thermal parameters from anisotropic refinement* ($\times 10^4$) *and from isotropic refinement* (*last two columns*)

Atom O(4) occupies a special position requiring that $\beta_{13} = \beta_{23} = 0$.

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ	B (isotropic)	σ
Li	51	18	43	16	81	18	63	13	−33	15	−55	16	1·84	0·26
O(1)	16	7	5	5	23	4	−9	4	−11	4	1	4	0·59	0·10
O(2)	14	5	23	5	10	5	10	5	−7	4	0	4	0·64	0·10
O(3)	15	5	14	5	20	5	6	4	−22	5	4	4	0·59	0·10
O(4)	25	7	12	7	4	6	18	7	(0)		(0)		0·57	0·12
B(1)	28	9	18	9	16	6	3	6	−4	7	−1	7	0·71	0·13
B(2)	5	7	14	7	10	6	8	7	8	6	−8	7	0·55	0·12

Table 3. *Observed and calculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	34.0	36.0	2	1	3	85.6	90.0	3	1	6	39.3	37.1
4	0	0	57.0	61.8	4	1	3	54.7	57.5	5	1	6	53.2	58.0
6	0	0	50.0	47.2	6	1	3	17.4	15.9	7	1	6	16.9	17.3
8	0	0	34.8	34.1	8	1	3	23.1	23.5	9	1	6	16.6	15.4
10	0	0	30.8	30.9	3	2	3	51.7	54.3	0	2	6	36.7	35.0
12	0	0	17.4	15.4	5	2	3	[illegible]	27.4	8	2	6	21.5	21.0
5	1	0	20.4	19.2	7	2	3	26.5	25.3	3	3	6	35.9	35.0
7	1	0	39.9	39.9	9	2	3	13.6	13.0	5	3	6	37.4	35.6
9	1	0	34.2	35.4	11	2	3	15.5	17.1	7	3	6	42.6	44.4
2	2	0	7.6	4.5	4	3	3	53.9	53.1	9	3	6	11.4	11.8
4	2	0	33.0	36.2	6	3	3	14.3	12.5	0	4	6	72.7	73.7
6	2	0	69.4	72.6	8	3	3	24.8	27.2	6	4	6	17.9	16.4
8	2	0	19.1	19.1	5	4	3	24.3	22.1	8	4	6	10.0	11.3
10	2	0	26.8	25.3	7	4	3	35.5	33.5	2	1	7	14.9	16.6
5	3	0	35.0	32.7	9	4	3	22.2	24.1	4	1	7	37.2	37.8
7	3	0	30.3	31.9	6	5	3	20.1	19.1	6	1	7	23.8	29.5
4	4	0	6.2	4.6	8	5	3	30.1	30.0	8	1	7	26.3	27.9
6	4	0	47.7	49.3	10	5	3	23.4	24.3	3	2	7	31.1	29.4
8	4	0	58.8	64.0	8	7	3	20.5	20.7	5	2	7	51.5	54.6
10	4	0	24.3	24.0	0	0	4	97.4	103.1	7	2	7	22.2	21.8
6	6	0	43.5	40.6	2	0	4	26.7	26.1	4	3	7	13.8	11.6
8	8	0	24.6	23.4	4	0	4	55.0	50.7	6	3	7	17.6	16.0
2	1	1	32.1	33.7	6	0	4	23.9	20.6	8	3	7	11.5	12.7
4	1	1	51.5	50.3	8	0	4	70.1	76.6	5	4	7	16.0	15.5
6	1	1	40.9	41.9	10	0	4	30.7	29.3	7	4	7	25.4	23.2
10	1	1	31.0	32.3	3	1	4	54.3	54.3	0	0	8	44.0	42.5
3	2	1	31.2	30.4	7	1	4	41.0	39.3	2	0	8	22.8	21.4
5	2	1	63.2	63.4	9	1	4	15.2	14.0	4	0	8	38.4	37.3
7	2	1	20.2	19.4	2	2	4	86.8	90.2	6	0	8	24.2	22.1
9	2	1	30.1	29.3	4	2	4	62.9	60.9	8	0	8	42.6	41.9
4	3	1	26.5	26.2	6	2	4	60.7	62.4	3	1	8	31.6	30.7
6	3	1	36.1	35.6	10	2	4	18.7	18.6	5	1	8	40.1	41.5
8	3	1	17.7	17.6	5	3	4	30.8	29.7	7	1	8	11.2	12.3
10	3	1	30.2	31.4	7	3	4	33.7	33.9	0	2	8	21.8	21.4
5	4	1	33.5	32.9	9	3	4	12.9	12.4	2	2	8	44.5	43.0
7	4	1	38.5	37.8	4	4	4	21.7	20.8	4	2	8	46.5	45.2
9	4	1	14.5	11.7	6	4	4	35.9	35.7	6	2	8	20.5	20.2
6	5	1	41.2	42.5	8	4	4	20.2	18.7	5	3	8	25.2	24.4
8	5	1	33.6	34.0	7	5	4	23.1	24.3	0	4	8	39.0	37.3
7	6	1	38.9	32.5	9	5	4	13.2	14.9	4	4	8	23.5	23.0
9	6	1	21.0	20.6	6	6	4	59.0	60.9	2	1	9	17.0	16.5
8	7	1	18.3	18.6	8	6	4	17.8	17.3	4	1	9	49.4	52.6
2	0	2	81.9	84.4	8	8	4	23.8	25.4	6	1	9	14.9	16.1
4	0	2	40.6	35.1	2	1	5	41.1	41.2	3	2	9	11.7	[illegible]
6	0	2	15.2	14.9	4	1	5	32.8	32.0	5	2	9	17.8	18.6
8	0	2	15.9	12.6	6	1	5	48.7	47.5	7	2	9	19.4	13.4
10	0	2	33.1	34.1	8	1	5	15.8	15.5	4	3	9	20.4	[illegible]
1	1	2	123.7	123.6	3	2	5	54.7	54.5	6	3	9	13.8	15.4
3	1	2	38.7	92.2	5	2	5	39.6	38.1	2	0	10	33.4	31.7
5	1	2	35.5	32.9	7	2	5	23.4	24.5	4	0	10	25.4	26.1
7	1	2	17.3	18.5	9	2	5	17.2	16.4	6	0	10	50.9	53.6
9	1	2	52.6	54.5	4	3	5	25.3	22.7	1	1	10	30.8	[illegible]
4	2	2	53.4	57.9	6	3	5	33.4	33.6	3	1	10	[illegible]	[illegible]
6	2	2	19.5	19.4	8	3	5	14.1	13.1	5	1	10	[illegible]	11.5
8	2	2	21.1	20.4	5	4	5	16.9	11.3	0	2	10	30.5	31.7
10	2	2	20.7	[illegible]	7	4	5	21.0	20.1	4	2	10	11.2	[illegible]
3	3	2	108.1	[illegible]	9	4	5	14.9	15.5	[illegible]	3	10	[illegible]	[illegible]
5	3	2	33.5	30.7	6	5	5	33.0	34.5	0	4	10	[illegible]	[illegible]
7	3	2	59.0	[illegible]	7	6	5	21.5	21.6	[illegible]	1	11	13.5	[illegible]
9	3	2	15.2	13.4	2	0	6	36.4	35.0	[illegible]	[illegible]	11	[illegible]	[illegible]
6	4	2	17.0	16.2	4	0	6	71.2	73.7	[illegible]	[illegible]	11	[illegible]	[illegible]
8	4	2	22.0	22.4	6	0	6	59.7	51.9	[illegible]	3	11	39.3	40.4
5	5	2	33.2	29.3	8	0	6	48.0	45.8	[illegible]	[illegible]	12	[illegible]	[illegible]
7	5	2	[illegible]	[illegible]	10	0	6	17.0	15.5	[illegible]	0	12	[illegible]	[illegible]
7	7	2	[illegible]	[illegible]	1	1	6	70.1	[illegible]	4	0	12	[illegible]	[illegible]

considered in the earlier paper, and the bond lengths.

Bond lengths and corresponding standard deviations are given in Table 4. The average value for the boron–oxygen bond is 1·373 Å for the threefold-coordinated boron atom B(1) and 1·477 Å for the fourfold-coordinated boron atom B(2). Similar values for threefold and fourfold-coordinated boron have been found in numerous other borate structures. The distances from boron to the oxygen atoms O(2) and O(3) seem to be longer than the corresponding distances to O(1) and O(4). In this connexion it may be noted that the shortest lithium–oxygen distances are those involving oxygen atoms O(2) and O(3). This is consistent with the assumption that the boron–oxygen interaction is reduced by a strong lithium–oxygen interaction.

Table 4. *Interatomic bond distances*

The boron–oxygen and lithium–oxygen distances have estimated standard deviations of 0·010 and 0·020 Å respectively. The atoms labelled with letters are symmetry-related to the x,y,z positions given in Table 1 as follows: a: $\bar{x},y,\frac{1}{2}+z$; b: $\bar{x},\bar{y},z$; c: $x,\bar{y},\frac{1}{2}+z$; d: $\bar{y},\frac{1}{2}-x,\frac{3}{4}+z$; e: $\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z$; f: $\frac{1}{2}-y,x,\frac{3}{4}+z$. (The addition or subtraction of unity is necessary in some cases.)

B(1)–O(1)	1·349 Å
B(1)–O(2)	1·384
B(1)–O(3)	1·386
B(2)–O(1*d*)	1·448
B(2)–O(2)	1·507
B(2)–O(3*b*)	1·497
B(2)–O(4)	1·454
Li—O(2*f*)	1·97
Li—O(3*c*)	2·02
Li—O(3*d*)	2·07
Li—O(1*e*)	2·14
Li—O(4)	2·63
Li—O(1*f*)	2·85
Li—O(2*a*)	2·88

The lithium atom is surrounded by four close oxygen atoms in an arrangement which may be regarded as a considerably distorted tetrahedron. The four lithium–oxygen distances lie in the range from 1·97 to 2·14 Å. Thereupon follows a fifth lithium–oxygen distance of 2·63 Å, the next distances being 2·83 Å and more. Hence the coordination around lithium cannot be said to be truly fourfold. The average lithium–oxygen distance for the four close oxygen atoms is 2·05 Å. In comparison *International Tables for X-ray Crystallography* (1962) quotes corresponding average values of 1·98 Å for fourfold-coordinated lithium and 2·16 Å for sixfold-coordinated lithium.

A distorted oxygen coordination tetrahedron around the cation is known from another diborate, $CdO.2B_2O_3$ (Ihara & Krogh-Moe, 1966). Also in the stable modification of lithium metaborate, studied by Zachariasen (1964), the lithium is coordinated in a manner reminiscent of that in lithium diborate. The lithium atom is surrounded by four close oxygen atoms in the range from 1·952 to 2·007 Å with a fifth oxygen atom at 2·473 Å. Actually the experience from a number of anhydrous borate structures shows that the anionic polyborate network generally does not provide the cations with highly symmetrical sites.

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