The Crystal and Molecular Structure of Furane-α,α'-Dicarboxylic Acid

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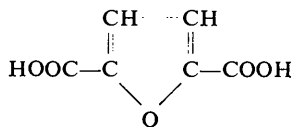Università di Napoli, Via Mezzocannone 4, Napoli, Italy*

Furane-α,α'-dicarboxylic acid crystallizes in the monoclinic system. The unit cell dimensions are $a=4\cdot97$, $b=16\cdot69$, $c=3\cdot66$ Å; $\beta=96°$. The space group is $P2_1/m$ with two molecules in the unit cell. The atomic parameters were refined by the differential synthesis method. The structure consists of hydrogen-bonded molecules, the bonds being between carboxylic groups of centrosymmetrically related molecules. The molecular rows are directed along the crystallographic b axis.

Introduction

The investigation of furane-α,α'-dicarboxylic acid has been undertaken as a part of a project for studying the crystal and molecular structure of a series of dicarboxylic acids for which there is a reasonable expectation that their molecules are associated in rows in the crystal lattice. When this is verified, and the direction of the row axis in the crystal lattice is found, the determination of the position of the asymmetric units in the unit cell is greatly simplified. In fact while in the general case six coordinates have to be determined (three translations and three Euler angles), in the actual case only one parameter, namely the rotation angle about the row axis, needs to be determined (Corradini, Diana, Ganis & Pedone, 1963; Ganis, Pedone & Temussi, 1964; Ganis & Martuscelli, 1966; Ganis, Martuscelli & Avitabile, 1966; Corradini, Avitabile, Ganis & Martuscelli, 1966).

Experimental

Furane-α,α'-dicarboyxlic acid:

$$\text{CH} - \text{CH}$$
$$\text{HOOC} - \text{C} \qquad \text{C} - \text{COOH}$$
$$\text{O}$$

($M=156$; m.p. 342°C) crystallizes in the monoclinic system.

The unit-cell dimensions, determined from Weissenberg photographs taken with Cu $K\alpha$ radiation, are:

$$a=4\cdot97\pm0\cdot01,\ b=16\cdot69\pm0\cdot02,$$
$$c=3\cdot66\pm0\cdot01\ \text{Å};\ \beta=96\pm1°\ .$$

From the systematic absence ($0k0$, $k=2n+1$) the space group is $P2_1$ or $P2_1/m$. On the basis of the hypothesis that the molecules are held by hydrogen bonds between carboxylic groups of centrosymmetrically related molecules, the space group was assumed to be $P2_1/m$ and this was confirmed later. The X-ray density is 1·74 g.cm⁻³ for two molecules per unit cell, in agreement

with the experimental value (1·74 g.cm⁻³). The molecule contains a crystallographic mirror plane.

Intensity data were collected with Cu $K\alpha$ radiation, multiple-film equi-inclination Weissenberg photographs being taken about the c axis for layer lines 0 to 2 and about the b axis for layer line 0. The number of independent reflexions observed was 356. The intensities were measured by eye-estimation with a set of standard strips, and corrected for change of spot shape on upper layer equi-inclination photographs by the Phillips (1954) method. No absorption corrections were applied; Lorentz and polarization corrections were applied in the usual way and the reflexions were put on a common scale by referring all of them to the $hk0$ layer.

Determination of the structure

For the determination of a preliminary model we followed the idea that the molecules are held together in rows by means of hydrogen bonds between carboxylic acid groups of symmetrically related molecules.

On the basis of this assumption and taking into account the unit cell of $P2_1/m$ symmetry, the row axis was uniquely determined as the crystallographic **b** direction. Then the problem of determinating a preliminary model of the structure was reduced to rotating the molecule around the b axis in order to achieve the best packing (Corradini, Avitabile, Ganis & Martuscelli, 1966).

For the preliminary model of the molecule, angles and bond lengths were chosen from data in the literature for similar compounds (Hudson, 1962). A trial model was obtained.

The first computation of the structure factors for all observed reflexions yielded an R value of 0·33. Refinement was carried out by the differential synthesis method. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C and O and McWeeny (1951) for H were used. After several cycles with the same isotropic temperature factor for all the atoms ($B=2\cdot0$ Å²) the R index, $R=\Sigma\ (|F_o|-|F_c|)/\Sigma\ |F_o|$, was 0·18.

Table 1. *Final fractional atomic coordinates and their standard deviations* (Å)

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O(1)	0·7097	0·0477	0·7437	0·0044	0·0040	0·0052
O(2)	0·0782	0·0950	0·0757	0·0041	0·0038	0·0044
C(1)	0·8710	0·1053	0·8790	0·0057	0·0057	0·0060
C(2)	0·7578	0·1852	0·7840	0·0052	0·0054	0·0060
C(3)	0·5240	0·2068	0·5850	0·0057	0·0061	0·0077
O(r)	0·9106	0·2500	0·9053	0·0034	0·0033	0·0039
H(1)	0·848	0·987	0·828			
H(3)	0·384	0·161	0·463			

Table 2. *Comparison between observed* (F_o)
and calculated (F_c) *structure factors of furane-α,α'-dicarboxylic acid*

At this stage, individual anisotropic temperature factors were assigned to the C and O atoms and after few cycles R decreased to 0·13.

The contribution of the hydrogen atoms was included assuming calculated positions with C–H and O–H lengths equal to 1·08 Å with the same isotropic temperature factor $(B=2·0 Å^2)$. The refinement was stopped when the average shift in the atomic coordinates in terms of their standard deviations was less than 0·5σ; the final R value was 0·125. Some discussion on the intensities of the reflexions is necessary. It is
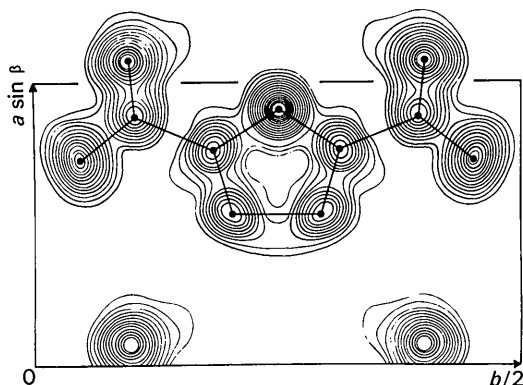

Fig. 1. Projection of the electron density of furane-α,α'-dicarboxylic acid on the (001) plane. Contours are drawn at intervals of 1 e.$Å^{-2}$ starting at zero.

found that in the $hk2$ layer very weak reflexions are present, and the values of the intensities are doubtful. The agreement between observed and calculated intensities is more satisfactory for the other layers.

The final atomic coordinates together with the corresponding standard deviations (Cruickshank, 1949) are reported in Table 1. In Table 2, observed and calculated structure factors are listed. In Table 3 the peak heights and curvatures of the electron density are compared at the points corresponding to the atomic positions.

The standard deviations of the electron density and of its first derivatives are:

$$\sigma(\varrho) = 0·16 \text{ e.}Å^{-3}$$
$$\sigma(A_h) = 0·44 \text{ e.}Å^{-4}$$
$$\sigma(A_k) = 0·47 \text{ e.}Å^{-4}$$
$$\sigma(A_l) = 0·30 \text{ e.}Å^{-4} .$$

An electron density projection on (001) is shown in Fig. 1. In Table 4 are shown the coefficients b_{ij} of the temperature factor in the form:

$$\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right] .$$

The molecular arrangement in the crystal is shown in Figs. 2 and 3, in which the most significant contact distances between molecular rows contained in the (001) plane and between molecular rows contained in the (100) plane are also reported. The structure con-

Table 3. *Peak heights and curvatures*

Values in parentheses are from F_c differential synthesis.

	ϱ (e.$Å^{-3}$) obs. (calc.)	$-A_{hh}$ (e.$Å^{-5}$) obs. (calc.)	$-A_{kk}$ (e.$Å^{-5}$) obs. (calc.)	$-A_{ll}$ (e.$Å^{-5}$) obs. (calc.)	A_{hk} (e.$Å^{-5}$) obs. (calc.)	A_{hl} (e.$Å^{-5}$) obs. (calc.)	A_{kl} (e.$Å^{-5}$) obs. (calc.)
O(1)	11·89 (12·25)	100·2 (104·2)	118·0 (123·5)	57·3 (60·9)	0·33 (0·53)	−0·09 (−0·06)	0·21 (0·15)
O(2)	12·32 (12·24)	106·8 (107·5)	124·0 (122·8)	68·1 (69·2)	0·59 (0·73)	−0·33 (0·20)	−0·06 (0·00)
C(1)	8·83 (8·82)	77·1 (80·5)	81·3 (79·8)	49·9 (49·8)	0·04 (0·42)	0·48 (0·87)	−0·16 (−0·11)
C(2)	9·22 (9·20)	84·2 (88·1)	86·2 (85·2)	49·8 (50·5)	−2·30 (−0·18)	0·87 (1·02)	−0·25 (−0·13)
C(3)	8·33 (8·67)	77·7 (81·7)	77·1 (78·8)	38·8 (41·0)	0·37 (0·35)	0·33 (0·38)	0·03 (0·18)
O(r)	14·06 (13·81)	129·3 (123·6)	141·3 (137·5)	77·0 (77·7)	0·00 (0·00)	0·79 (0·84)	0·00 (0·00)

Table 4. *Temperature parameters*

Temperature factors are given in the form: $\exp\left[-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)\right]$.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
O(1)	0·0340	$\overline{0·0070}$	$\overline{0·0050}$	0·0009	0·0000	0·0470
O(2)	0·0300	0·0000	0·0006	0·0008	0·0000	0·0420
C(1)	0·0217	$\overline{0·0005}$	0·0002	0·0015	0·0005	0·0377
C(2)	0·0225	0·0006	0·0000	0·0012	0·0005	0·0385
C(3)	0·0220	0·0005	0·0002	0·0016	$\overline{0·0005}$	0·0386
O(r)	0·0190	0·0000	0·0002	0·0007	$\overline{0·0005}$	0·0386

sists of hydrogen bonded molecules (O–H---O being 2·66 Å).

The equation of the least-square mean plane, passing through the seven atoms C(1), C(2), C(3), O(r), C(1')-C(2')C(3') calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), attributing a unitary weight factor to all atoms, is:

$$0 \cdot 98x - 1 \cdot 17z = 1 \, .$$

This equation is referred to the axes of the unit cell; x, y, z are fractional coordinates. The deviations of the seven atoms from the plane are:

$$C(1), C(1') + 0 \cdot 005$$
$$C(2), C(2') + 0 \cdot 006$$
$$C(3), C(3') - 0 \cdot 003$$
$$O(r) \qquad - 0 \cdot 017 \, .$$

We see that only the O(r) atom displacement is substantially greater than the standard deviation.

The equation of the least-square mean plane passing

through the atoms C(1)–C(2)$\overset{\displaystyle O(1)}{\underset{\displaystyle O(2)}{\big\langle}}$ is:

$$1 \cdot 00x - 2 \cdot 29y - 1 \cdot 11z = 1 \, ,$$

and the displacements of the atoms from the plane are

$$C(1) - 0 \cdot 021; \ C(2) + 0 \cdot 006; \ O(1) + 0 \cdot 007; \ O(2) + 0 \cdot 008 \, .$$

The observed bond angles and lengths are reported in Table 5 with the calculated values of their estimated standard deviations (Cruickshank & Robertson, 1953).
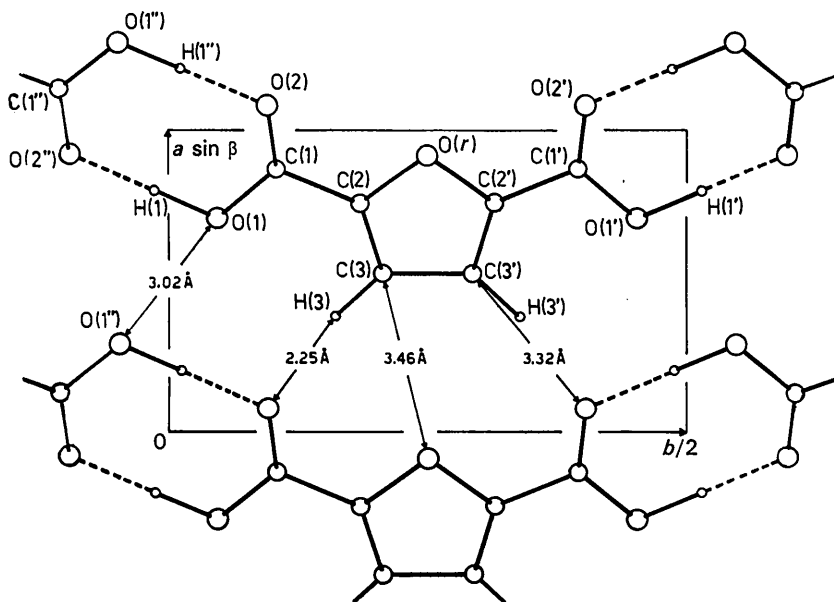

Fig. 2. Packing of furane-α,α'-dicarboxylic acid molecules. Projection along the [001] axis.
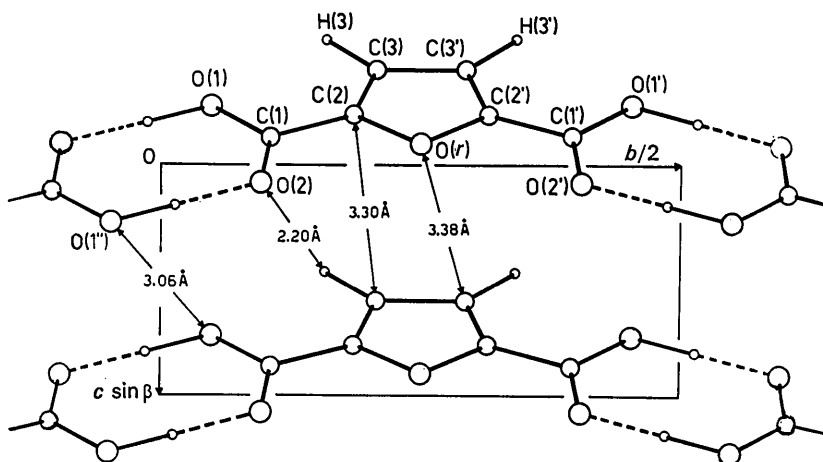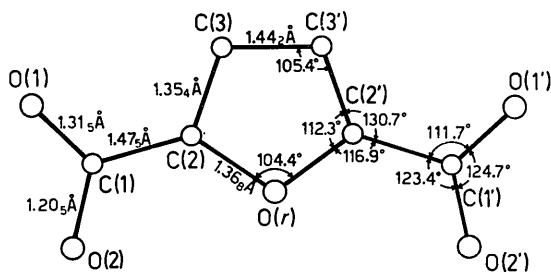

Fig. 3. Packing of furane-α,α'-dicarboxylic acid molecules. Projection along the [100] axis.

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

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) ∧ C(1)–C(2)–C(3)	175·6	0·5

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)···O(2) (3·32 Å) appears to be rather short (Fig. 2). The rotation internal angle O(2)–C(1)–C(2) ∧ 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.

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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.