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# Crystal Structures of Heterocyclic Compounds. I. Furoic Acid

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Furoic acid, furane α-carboxylic acid, crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. A quantitative X-ray investigation, based on visual intensity measurements of over 300 crystallographically different planes in the axial zones, has led to a complete determination of the structure and the results have been refined by double Fourier projections parallel to *b* and *c*. The discrepancies $R = 100.\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ are 11·2, 18·7 and 14·5 % in the (*hk*0), (*h*0*l*) and (0*kl*) zones respectively.

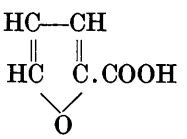
The bond lengths and valency angles are given; in particular, the C–O bonds of the carboxyl group are 1·16 and 1·26 Å long and those of the ring 1·30 and 1·31 Å, while the C–C bond between the ring and the carboxyl group is 1·47 Å. The molecule is planar, pairs of molecules being grouped about centres of symmetry by means of hydrogen bonds.

## 1. Introduction

Heterocyclic compounds are of special interest to chemists in view of their varying aromatic character; measurements of bond lengths and angles should permit correlation of this property not only among the heterocyclic substances themselves but also in relation to benzene derivatives on the one hand and to cyclic dienes on the other. A number of compounds containing furane, pyrazine and other heterocyclic rings are being examined in this department by X-ray methods and the present communication is Part I of the series of reports on these investigations.

## 2. Space group and cell dimensions

Furoic or pyromucic acid



of molecular weight 112·03, crystallizes in the triclinic system with

$a=10{\cdot}24\pm0{\cdot}02$ Å, $b=6{\cdot}80\pm0{\cdot}02$ Å, $c=3{\cdot}81\pm0{\cdot}02$ Å;
$\alpha = 92°\,57'$, $\beta = 94°\,16'$, $\gamma = 106°\,10'$,

giving reciprocal cell dimensions of

$a^* = 0{\cdot}1571$, $b^* = 0{\cdot}2361$, $c^* = 0{\cdot}4063$;
$\alpha^* = 85°\,41'$, $\beta^* = 84°\,42'$, $\gamma^* = 73°\,27'$

for Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54$ Å). Volume of the unit cell 253·3 Å$^3$; observed density 1·483 g.ml.$^{-1}$, calculated density 1·469 g.ml.$^{-1}$ for two molecules of $C_5H_4O_3$. There are no systematic halvings and the space group is therefore either $P1(C_1^1)$, in which there are no symmetry elements, or $P\bar{1}(C_i^1)$, in which there is a centre of symmetry. Attempts to distinguish between these space groups were made by use of both pyroelectric and piezoelectric tests. (We are indebted to Dr Maria Przybylska of the Canadian National Research Laboratory, Ottawa, for carrying out the piezoelectric tests.) No such effects could be detected in any crystallographic direction, suggesting that the space group $P\bar{1}$ is almost certainly, but not definitely, correct, since either of these effects might be present but too feeble to be observed. Experience leads one to expect a centre of symmetry to be present, for carboxyl groups (like hydroxyl and amino groups) always link up about centres of symmetry, either in pairs, as, for example, in β-succinic acid (Morrison & Robertson, 1949*a*), or in spirals, as, for example, in oxalic acid dihydrate where the water molecules are part of the spiral (Robertson & Woodward, 1936). Finally, as will be seen later, since conclusive evidence of the centre of symmetry could not be obtained, at least as much effort was expended on trying to find an asymmetric structure as on testing a centrosymmetrical one, and failed consistently. Some time after the projection along [001] had been completed, Wilson's (1949) statistical criterion for the existence of a centre of symmetry became available, and showed that the (*h*0*l*) projection was centrosymmetric. We therefore concluded that the space group is $P\bar{1}$.

The absorption coefficient for Cu $K\alpha$ radiation is 12·63 cm.$^{-1}$ and the number of electrons per unit cell, $F(000)$, is 116.

The crystals used were thin colourless laths, m.p. 133° C., often occurring as aggregates, though singly crystalline fragments were easily selected under the microscope. They were tabular on {100} and elongated parallel to *c*. End and side faces were rather variable, but striations often crossed the laths in a direction nearly coincident with the good cleavage parallel to

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{011} at 63° to the *c* axis. The optical extinction direction is at 61° to the *c* axis, and two refractive indices were measured for light travelling perpendicular to the crystal plate; that for light vibrating nearly parallel to the cleavage was $n_2 = 1{\cdot}688 \pm 0{\cdot}004$ and that for light vibrating at right angles thereto was $n_1 = 1{\cdot}384 \pm 0{\cdot}004$. The plates were too thin to permit measurement of other indices for light travelling along the plate. Nevertheless, the birefringence is very high, being at least 0·304.

### 3. Analysis of the structure

For the centrosymmetrical space group $P\bar{1}$ the asymmetric unit consists of one molecule containing five carbon, three oxygen and four hydrogen atoms; for the space group $P1$ it is two molecules. As usual, the light hydrogen atoms were neglected at the beginning, and, indeed, no evidence for their position was forthcoming at any time.

As a basis for the trial-and-error method of structure determination the following bond lengths and angles were assumed (nomenclature as in Fig. 3):

$O_1$–$C_1$ = 1·24 Å, $O_2$–$C_1$ = 1·29 Å, $C_1$–$C_2$ = 1·46 Å, $C_2$–$C_3$ = 1·35 Å, $C_3$–$C_4$ = 1·46 Å, $C_4$–$C_5$ = 1·35 Å, $C_5$–$O_r$ = 1·41 Å, $O_r$–$C_2$ = 1·41 Å; $O_1$–$C_1$–$O_2$ = 123°, $O_1$–$C_1$–$C_2$ = 118½°, $C_1$–$C_2$–$C_3$ = 125½°, $C_2$–$C_3$–$C_4$ = $C_3$–$C_4$–$C_5$ = 107°, $O_r$–$C_2$–$C_3$ = $O_r$–$C_5$–$C_4$ = 109°, $C_2$–$O_r$–$C_5$ = 107°. Initially the whole molecule was supposed to be planar but, later, non-planar models were also considered in the {*h*0*l*} and {0*kl*} zones. The above figures were based (i) on those of Schomaker & Pauling (1939) and of Beach (1941) relating to the examination of furane by electron diffraction, (ii) on the investigation of various hydrated and anhydrous dicarboxylic acids by Robertson and others (Robertson & Dunitz, 1947*a*, *b*, *c*; Morrison & Robertson, 1949*a*, *b*, *c*, *d*) and of the dimers of formic and acetic acids by Karle & Brockway (1944), and (iii), for the extracyclic C–C bond, on the C–C bond in oxalic acid (Robertson & Dunitz, 1947*a*) since orbital overlap of $\pi$ electrons on $C_1$ and $C_2$ was expected to shorten this formal single bond.

*(a) Projection along c axis*

Since the *c* axis is 3·81 Å in length, it seemed probable that the molecules would lie in a plane inclined at about 65° to this axis. There is a high refractive index for light vibrating along a direction approximating to that of the [0$\bar{1}$1] axis (at 63° to the *c* axis) and also a good cleavage in this direction. It therefore seemed reasonable to suppose that the molecules lay in a plane approximately parallel to (011).

In view of the initial uncertainty as to the space group, both asymmetric and centrosymmetrical arrangements were studied extensively in trying to find the molecular disposition giving the best agreement between observed and calculated structure factors. However, no asymmetric model gave such satisfactory results as the centrosymmetrical one which was finally adopted. Using the signs of the calculated *F*'s for the space group $P\bar{1}$ with the observed *F*'s, a Fourier projection along [001] was carried out. The structure was refined twice more by successive Fourier syntheses; the final Fourier projection is shown in Fig. 1.

The atomic co-ordinates selected are indicated in Fig. 1 by crosses and are listed in Table 4, which is explained fully in § 4. In Table 1 observed and calculated structure factors for this zone are compared. The percentage discrepancy *R*, given by $R = 100.\Sigma||F_o|-|F_c|| \div \Sigma|F_o|$, is 11·2% for this zone.

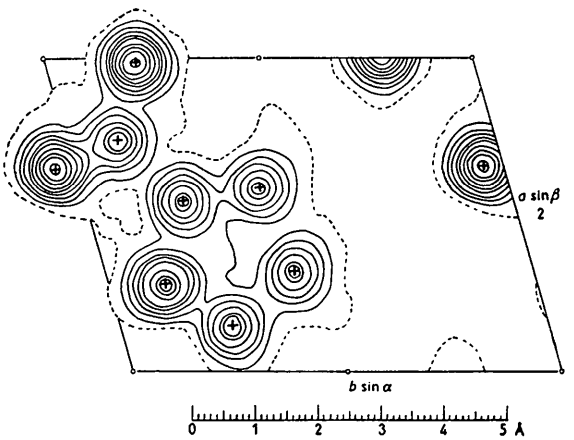


Fig. 1. Projection of furoic acid along [001]. Contours at intervals of approximately 1 e.Å$^{-2}$. One-electron line broken.

*(b) Projection along b axis*

Even though a centrosymmetrical space-group formula is clearly effectively correct for the projection along the *c* axis, the space group need not be $P\bar{1}$. However, applying Wilson's statistical criterion, the ratio $\langle F\rangle^2 : \langle I\rangle$ for (*h*0*l*) planes was found to be 0·62, indicating the presence of a centre of symmetry (Wilson, 1949).

It was obvious from Fig. 1 that projections in directions roughly at right angles to the *c* axis could not give complete resolution of many atoms. Further, since the *c* axis is so short, the *z* co-ordinates would be more difficult to determine than the others, as the maximum theoretically possible value of *l* in {*h*0*l*} and {0*kl*} for Cu $K\alpha$ radiation is 5; in practice the maximum observed value was 4. Again, the only planes in the {*h*0*l*} zone with fairly high intensities are (001), (101) and (10$\bar{1}$), all with low $\xi$ values, the rest being weak or very weak.

By comparing the postulated bond lengths with those in the {*hk*0} projection, the inclinations of the bonds could be calculated, subject to the errors in the dimensions assumed. The *z* co-ordinates of the

Table 1. *Observed and calculated structure factors for {hk0} zone*

| Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 100 | 8·9 | − 8·2 | 050 | 1·7 | 2·5 | 10,$\bar{3}$,0 | 1·7 | 1·2 |
| 200 | 12·7 | −13·0 | 150 | 1·3 | − 3·1 | 11,$\bar{3}$,0 | 1·1 | 1·0 |
| 300 | < 0·6 | − 1·7 | 250 | 3·2 | − 2·6 | 12,$\bar{3}$,0 | 1·1 | 0·7 |
| 400 | 4·8 | − 5·3 | 350 | < 1·1 | − 1·1 | 13,$\bar{3}$,0 | < 0·4 | − 0·9 |
| 500 | 22·8 | −23·5 | 450 | 6·1 | 5·3 | 1$\bar{4}$0 | 13·7 | 14·4 |
| 600 | 12·5 | 10·9 | 550 | 6·0 | 5·5 | 2$\bar{4}$0 | 6·9 | 6·4 |
| 700 | 1·6 | 1·5 | 650 | < 1·0 | 1·2 | 3$\bar{4}$0 | 6·2 | 5·1 |
| 800 | 3·2 | 3·0 | 750 | < 0·8 | 0·8 | 4$\bar{4}$0 | 7·3 | 7·8 |
| 900 | 4·0 | − 4·5 | 850 | < 0·4 | − 0·8 | 5$\bar{4}$0 | < 1·0 | − 0·8 |
| 10,0,0 | < 1·1 | − 0·8 | 060 | 5·1 | − 5·9 | 6$\bar{4}$0 | 4·1 | 4·5 |
| 11,0,0 | 1·4 | − 1·5 | 160 | 2·9 | 3·6 | 7$\bar{4}$0 | 8·2 | − 8·9 |
| 12,0,0 | < 0·7 | 0·6 | 260 | 2·3 | 2·8 | 8$\bar{4}$0 | 5·7 | − 4·8 |
| 010 | 16·9 | 19·2 | 360 | < 1·0 | 0·3 | 9$\bar{4}$0 | 2·3 | − 2·0 |
| 110 | 42·6 | −41·9 | 460 | < 1·0 | 0·4 | 10,$\bar{4}$,0 | < 1·1 | − 1·5 |
| 210 | 8·8 | 9·1 | 560 | 1·4 | − 1·5 | 11,$\bar{4}$,0 | < 0·9 | 0·3 |
| 310 | 1·7 | 0·4 | 660 | < 0·7 | 0·1 | 12,$\bar{4}$,0 | 3·2 | 3·6 |
| 410 | 10·7 | −10·8 | 070 | < 1·0 | 0·3 | 1$\bar{5}$0 | 4·7 | − 4·4 |
| 510 | 6·0 | − 6·0 | 170 | 4·7 | 5·3 | 2$\bar{5}$0 | 3·6 | 4·1 |
| 610 | 10·2 | 9·1 | 270 | 0·9 | − 1·4 | 3$\bar{5}$0 | 3·7 | − 4·1 |
| 710 | < 1·0 | − 1·5 | 370 | < 0·8 | − 0·3 | 4$\bar{5}$0 | 8·7 | 8·7 |
| 810 | < 1·1 | − 0·4 | 470 | < 0·6 | − 0·3 | 5$\bar{5}$0 | 2·8 | 1·6 |
| 910 | < 1·1 | − 0·3 | 080 | < 0·7 | 0·1 | 6$\bar{5}$0 | 1·9 | 1·8 |
| 10,1,0 | 2·7 | 2·5 | 180 | < 0·4 | 1·5 | 7$\bar{5}$0 | < 1·1 | − 0·4 |
| 11,1,0 | 1·1 | − 1·0 | 1$\bar{1}$0 | 21·1 | 20·1 | 8$\bar{5}$0 | 2·3 | 2·3 |
| 020 | 4·6 | − 7·3 | 2$\bar{1}$0 | 14·3 | 14·6 | 9$\bar{5}$0 | 3·2 | − 3·4 |
| 120 | 1·0 | 1·5 | 3$\bar{1}$0 | 17·0 | 17·9 | 10,$\bar{5}$,0 | 1·6 | 1·6 |
| 220 | 21·2 | 20·8 | 4$\bar{1}$0 | 3·0 | − 5·1 | 11,$\bar{5}$,0 | 0·9 | − 0·9 |
| 320 | 1·7 | − 0·4 | 5$\bar{1}$0 | 3·2 | − 1·7 | 12,$\bar{5}$,0 | < 0·7 | 1·4 |
| 420 | 5·2 | 4·0 | 6$\bar{1}$0 | < 0·9 | 0·2 | 1$\bar{6}$0 | 4·7 | − 4·6 |
| 520 | 7·5 | 6·9 | 7$\bar{1}$0 | 7·0 | − 7·5 | 2$\bar{6}$0 | 1·9 | 1·4 |
| 620 | 2·8 | 3·4 | 8$\bar{1}$0 | 5·3 | − 4·9 | 3$\bar{6}$0 | 5·7 | − 6·3 |
| 720 | 8·5 | 8·0 | 9$\bar{1}$0 | 6·9 | 6·7 | 4$\bar{6}$0 | 1·5 | − 1·7 |
| 820 | 1·3 | − 1·9 | 10,$\bar{1}$,0 | 4·6 | − 4·3 | 5$\bar{6}$0 | 8·9 | 9·7 |
| 920 | < 1·0 | − 1·1 | 11,$\bar{1}$,0 | 1·4 | − 1·8 | 6$\bar{6}$0 | < 1·1 | 0·8 |
| 10,2,0 | < 0·9 | 0 | 12,$\bar{1}$,0 | < 0·8 | − 0·4 | 7$\bar{6}$0 | 2·3 | − 1·4 |
| 11,2,0 | < 0·7 | − 0·9 | 1$\bar{2}$0 | < 0·6 | − 0·5 | 8$\bar{6}$0 | 0·7 | 0·5 |
| 030 | 13·8 | −14·7 | 2$\bar{2}$0 | 12·5 | −12·6 | 9$\bar{6}$0 | 1·6 | 1·1 |
| 130 | < 0·8 | − 1·5 | 3$\bar{2}$0 | 25·9 | 26·1 | 10,$\bar{6}$,0 | 1·2 | − 1·4 |
| 230 | 9·4 | − 8·1 | 4$\bar{2}$0 | 23·1 | −23·8 | 11,$\bar{6}$,0 | < 0·7 | 0·5 |
| 330 | 6·9 | 8·5 | 5$\bar{2}$0 | < 0·9 | 1·8 | 1$\bar{7}$0 | < 1·0 | − 0·1 |
| 430 | 7·9 | 7·6 | 6$\bar{2}$0 | 7·7 | 10·8 | 2$\bar{7}$0 | < 1·0 | 0·1 |
| 530 | 8·4 | 8·5 | 7$\bar{2}$0 | < 1·0 | 0·1 | 3$\bar{7}$0 | < 1·1 | − 1·5 |
| 630 | < 1·1 | − 1·2 | 8$\bar{2}$0 | 6·2 | − 6·0 | 4$\bar{7}$0 | 6·5 | − 6·8 |
| 730 | 1·3 | 0·6 | 9$\bar{2}$0 | 11·4 | 10·0 | 5$\bar{7}$0 | 2·5 | 1·6 |
| 830 | 5·1 | − 6·0 | 10,$\bar{2}$,0 | < 1·1 | 1·2 | 6$\bar{7}$0 | < 1·0 | − 0·2 |
| 930 | < 0·9 | 0 | 11,$\bar{2}$,0 | < 1·0 | − 0·1 | 7$\bar{7}$0 | 1·6 | 2·5 |
| 10,3,0 | < 0·7 | 0·4 | 12,$\bar{2}$,0 | < 0·8 | − 0·4 | 8$\bar{7}$0 | < 0·9 | 0 |
| 040 | < 0·9 | 0·1 | 13,$\bar{2}$,0 | < 0·4 | 0·1 | 9$\bar{7}$0 | < 0·8 | − 0·1 |
| 140 | 9·4 | 10·3 | 1$\bar{3}$0 | 4·4 | 4·5 | 10,$\bar{7}$,0 | < 0·6 | − 0·2 |
| 240 | < 1·0 | 1·6 | 2$\bar{3}$0 | 2·5 | 1·4 | 1$\bar{8}$0 | < 0·8 | 0·8 |
| 340 | 3·3 | − 2·5 | 3$\bar{3}$0 | 14·1 | 18·2 | 2$\bar{8}$0 | 1·3 | 1·3 |
| 440 | 8·7 | 8·2 | 4$\bar{3}$0 | 7·0 | − 8·6 | 3$\bar{8}$0 | < 0·8 | 0·2 |
| 540 | 2·8 | − 3·8 | 5$\bar{3}$0 | 9·4 | −10·8 | 4$\bar{8}$0 | 1·3 | − 0·9 |
| 640 | 6·0 | − 5·3 | 6$\bar{3}$0 | 4·7 | − 6·2 | 5$\bar{8}$0 | < 0·8 | 0·6 |
| 740 | < 1·0 | 0·2 | 7$\bar{3}$0 | 3·6 | − 3·2 | 6$\bar{8}$0 | 1·2 | − 2·1 |
| 840 | < 0·9 | − 0·3 | 8$\bar{3}$0 | 3·2 | 1·4 | 7$\bar{8}$0 | < 0·7 | − 0·4 |
| 940 | < 0·7 | − 0·6 | 9$\bar{3}$0 | 6·9 | 6·5 | 8$\bar{8}$0 | < 0·4 | 1·8 |

atoms were thus determined, and, from these, (*h*0*l*) structure factors were calculated. A Fourier synthesis gave the projection along [010] shown in Fig. 2.

The only atom clearly resolved in this projection is $O_2$, and there is therefore some uncertainty about the exact co-ordinates of the other atoms. By placing them at the points marked by crosses, $R$ was found to be 18·7%. Observed and calculated structure factors are compared in Table 2.

*(c) {0kl} structure factors*

For the reasons indicated in the previous section, it is useless to expect resolution of atoms in a projection down the $a$ axis, and so in this {0*kl*} zone only a comparison of observed and calculated structure factors has been made. These are shown in Table 3, the calculated $F$'s being obtained with the values of the $y$ and $z$ co-ordinates derived from Figs. 1 and 2 directly. The resulting discrepancy was $R_{0kl} = 14{\cdot}5\%$.

Table 2. *Observed and calculated structure factors for {h0l} zone*

| Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 001 | 25·8 | 24·0 | 604 | < 0·7 | − 1·8 | 40$\bar{1}$ | 2·7 | 3·2 |
| 002 | 10·6 | − 9·3 | 701 | 1·4 | − 2·8 | 40$\bar{2}$ | 5·4 | − 5·5 |
| 003 | 1·7 | − 3·1 | 702 | 2·0 | 2·7 | 40$\bar{3}$ | 2·1 | − 2·7 |
| 004 | < 0·8 | − 1·5 | 703 | 1·7 | 0·6 | 40$\bar{4}$ | 2·0 | 2·1 |
| 101 | 49·5 | 48·4 | 801 | 1·8 | − 0·8 | 50$\bar{1}$ | 9·3 | − 8·3 |
| 102 | 4·8 | − 7·2 | 802 | 1·1 | − 0·5 | 50$\bar{2}$ | 2·6 | 1·1 |
| 103 | 1·6 | − 0·3 | 803 | 2·6 | − 3·9 | 50$\bar{3}$ | 3·7 | − 4·5 |
| 104 | < 0·8 | − 1·3 | 901 | 2·3 | − 0·9 | 50$\bar{4}$ | 1·4 | − 0·4 |
| 201 | 7·5 | − 7·2 | 902 | 1·0 | 0·1 | 60$\bar{1}$ | 2·3 | − 0·7 |
| 202 | 3·1 | − 3·5 | 903 | < 0·5 | 1·3 | 60$\bar{2}$ | 4·3 | 4·9 |
| 203 | 3·1 | − 4·2 | 10,0,1 | 3·1 | 2·4 | 60$\bar{3}$ | 1·8 | − 0·6 |
| 204 | < 0·8 | 0·8 | 10,0,2 | < 0·8 | 0 | 60$\bar{4}$ | < 0·7 | − 0·7 |
| 301 | 1·8 | 0·7 | 11,0,1 | 1·3 | − 2·2 | 70$\bar{1}$ | 4·7 | − 4·1 |
| 302 | 1·8 | 1·0 | 11,0,2 | < 0·5 | − 1·5 | 70$\bar{2}$ | 3·4 | − 2·2 |
| 303 | 1·8 | 5·4 | 12,0,1 | < 0·5 | 1·1 | 70$\bar{3}$ | 1·7 | 2·3 |
| 304 | 0·8 | 2·8 | 10$\bar{1}$ | 25·1 | 23·4 | 70$\bar{4}$ | < 0·5 | − 0·8 |
| 401 | 9·0 | − 9·7 | 10$\bar{2}$ | 1·3 | 0·4 | 80$\bar{1}$ | 5·7 | 4·8 |
| 402 | 4·5 | − 3·5 | 10$\bar{3}$ | 1·6 | 3·0 | 80$\bar{2}$ | 5·5 | − 4·3 |
| 403 | 1·8 | 1·7 | 10$\bar{4}$ | < 0·8 | − 0·7 | 80$\bar{3}$ | 4·9 | − 3·7 |
| 404 | 1·5 | 0·3 | 20$\bar{1}$ | 8·7 | 9·0 | 90$\bar{1}$ | 5·3 | 4·6 |
| 501 | 4·0 | − 5·3 | 20$\bar{2}$ | 4·7 | − 7·3 | 90$\bar{2}$ | 5·5 | 6·7 |
| 502 | 4·8 | 4·6 | 20$\bar{3}$ | 4·6 | − 5·2 | 90$\bar{3}$ | 1·2 | 2·1 |
| 503 | 2·5 | 3·9 | 20$\bar{4}$ | < 0·8 | 0·8 | 10,0,$\bar{1}$ | 3·2 | − 2·7 |
| 504 | < 0·7 | − 0·6 | 30$\bar{1}$ | 12·8 | 13·8 | 10,0,$\bar{2}$ | < 0·8 | 0·2 |
| 601 | 11·3 | 11·4 | 30$\bar{2}$ | 12·4 | 12·2 | 11,0,$\bar{1}$ | 1·5 | − 1·5 |
| 602 | 1·8 | 3·7 | 30$\bar{3}$ | 4·6 | 6·4 | 11,0,$\bar{2}$ | < 0·7 | − 0·4 |
| 603 | < 0·9 | 0·7 | 30$\bar{4}$ | < 0·8 | 2·1 | 12,0,$\bar{1}$ | < 0·5 | − 0·5 |

Table 3. *Observed and calculated structure factors for {0kl} zone*

| Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ | Plane | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 011 | 16·8 | −10·3 | 043 | < 1·9 | 1·8 | 03$\bar{2}$ | 2·2 | 0·8 |
| 021 | 14·3 | −13·8 | 053 | 2·7 | 1·0 | 04$\bar{2}$ | < 2·1 | − 1·6 |
| 031 | 3·4 | − 2·6 | 063 | < 1·1 | 0·3 | 05$\bar{2}$ | 4·4 | − 5·2 |
| 041 | 9·5 | 7·5 | 014 | < 1·9 | 3·4 | 06$\bar{2}$ | < 2·1 | 1·6 |
| 051 | 6·2 | − 5·0 | 024 | < 1·7 | 0·8 | 07$\bar{2}$ | < 1·7 | − 1·5 |
| 061 | < 2·1 | 0·9 | 034 | < 1·7 | 1·3 | 01$\bar{3}$ | 7·4 | − 5·5 |
| 071 | < 1·7 | 0·4 | 044 | 1·7 | 1·5 | 02$\bar{3}$ | 6·1 | 7·6 |
| 081 | < 0·8 | 1·0 | 01$\bar{1}$ | 77·5 | 77·0 | 03$\bar{3}$ | 6·3 | 10·8 |
| 012 | 5·7 | − 7·2 | 02$\bar{1}$ | 9·0 | 7·0 | 04$\bar{3}$ | < 2·1 | − 0·3 |
| 022 | 3·6 | − 3·7 | 03$\bar{1}$ | < 1·5 | − 2·3 | 05$\bar{3}$ | < 1·9 | − 1·5 |
| 032 | 12·0 | 9·1 | 04$\bar{1}$ | 11·3 | −10·0 | 06$\bar{3}$ | < 1·7 | − 2·2 |
| 042 | < 2·1 | − 2·3 | 05$\bar{1}$ | < 2·1 | 2·2 | 07$\bar{3}$ | < 0·6 | 0·7 |
| 052 | < 2·1 | 2·2 | 06$\bar{1}$ | < 2·1 | − 0·6 | 01$\bar{4}$ | < 1·9 | − 1·6 |
| 062 | 1·9 | 0·9 | 07$\bar{1}$ | < 1·9 | − 3·9 | 02$\bar{4}$ | 2·3 | − 2·7 |
| 072 | < 1·2 | 0·8 | 08$\bar{1}$ | < 1·3 | − 0·1 | 03$\bar{4}$ | 2·5 | 3·6 |
| 013 | < 2·1 | − 2·7 | 01$\bar{2}$ | 16·5 | 14·7 | 04$\bar{4}$ | < 1·7 | 3·1 |
| 023 | 6·7 | 6·4 | 02$\bar{2}$ | 31·4 | 33·0 | 05$\bar{4}$ | < 1·1 | 0 |
| 033 | < 2·1 | 0·4 | | | | | | |

Table 4. *Co-ordinates of atoms*

| Atom | $X$ | $Y$ | $Z$ | $x$ | $y$ | $z$ | $X'$ | $Y'$ | $Z'$ |
|---|---|---|---|---|---|---|---|---|---|
| $C_1$ | 3·755 | 0·770 | 0·508 | 0·367 | 0·113 | 0·133 | 3·527 | 0·738 | 0·189 |
| $C_2$ | 2·740 | 1·552 | 0·775 | 0·267 | 0·228 | 0·203 | 2·293 | 1·486 | 0·491 |
| $C_3$ | 2·979 | 2·816 | 1·321 | 0·291 | 0·414 | 0·347 | 2·174 | 2·697 | 0·954 |
| $C_4$ | 1·596 | 2·991 | 1·473 | 0·156 | 0·440 | 0·387 | 0·745 | 2·865 | 1·201 |
| $C_5$ | 0·726 | 1·756 | 0·965 | 0·071 | 0·258 | 0·253 | 0·227 | 1·682 | 0·821 |
| $O_r$ | 1·400 | 0·895 | 0·572 | 0·137 | 0·132 | 0·150 | 1·143 | 0·857 | 0·421 |
| $O_1$ | 3·303 | −0·365 | 0·025 | 0·323 | −0·054 | 0·006 | 3·397 | −0·349 | −0·202 |
| $O_2$ | 5·036 | 1·416 | 0·648 | 0·492 | 0·208 | 0·170 | 4·621 | 1·356 | 0·200 |

$X, Y, Z$: triclinic co-ordinates in Å.
$x, y, z$: triclinic co-ordinates expressed as fractions of corresponding unit-cell axes.
$X', Y', Z'$: orthogonal co-ordinates in Å.

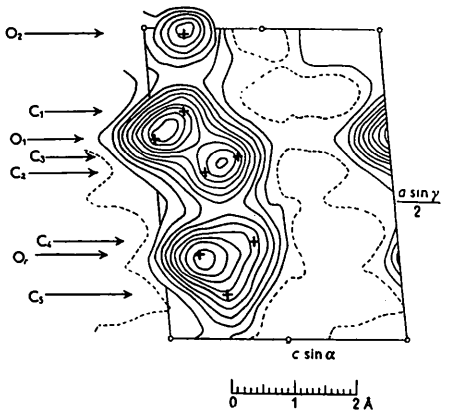


Fig. 2. Projection of furoic acid along [010]. Contours at intervals of approximately 1 e.Å$^{-2}$. One-electron line broken.

## 4. Co-ordinates, orientation, intramolecular and intermolecular distances

Table 4 gives the co-ordinates of the atoms in the asymmetric unit (one molecule). Triclinic co-ordinates are referred to the triclinic unit cell axes, $a$, $b$, $c$; orthogonal co-ordinates are referred to orthogonal axes $a'$, $b'$, $c'$, chosen as follows: $c'$ coincident with $c$; $a'$ the intersection of the (010) plane with the plane perpendicular to $c$; and $b'$ at right angles to $a'$ and to $c$. The inclinations of the triclinic axes to the orthogonal axes are given in Table 5.

Table 5. *Orientation of triclinic axes to orthogonal axes*

| | | | | | |
|---|---|---|---|---|---|
| $\chi_a = \beta - 90°$ | $= 4°\ 16'$ | $\chi_b$ | $= 106°\ 25'$ | $\chi_c$ | $= 90°$ |
| $\psi_a$ | $= 90°$ | $\psi_b$ | $= 16°\ 43'$ | $\psi_c$ | $= 90°$ |
| $\omega_a = \beta$ | $= 94°\ 16'$ | $\omega_b = \alpha =$ | $92°\ 57'$ | $\omega_c$ | $= 0°$ |

The distances of the atoms of the molecule from the plane

$$0{\cdot}1592X' - 0{\cdot}5553Y' + 1{\cdot}5111Z' - 0{\cdot}3427 = 0$$

lie within experimental error, so that the molecule is planar.

Fig. 3 shows the bond lengths and valency angles observed in furoic acid while Fig. 4 shows the relationship of a reference molecule to its neighbours, and the shortest intermolecular distances. A rigorous estimation of the accuracy of the bond lengths was not carried out in this investigation. In view of the poor resolution in the $\{h0l\}$ projection, and errors due to finite termination of the Fourier series, we consider the error in bond lengths to be of the order of $\pm 0{\cdot}05$ Å.

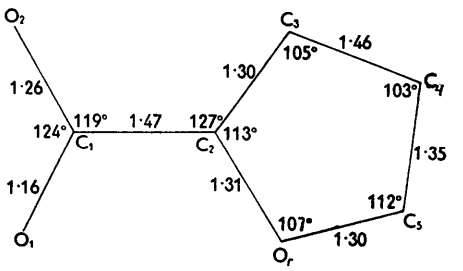


Fig. 3. Bond lengths and valency angles in furoic acid.

## 5. Discussion

I. *Molecular structure*

(*a*) *The furane ring.*—Table 6 gives a comparison of bond lengths and valency angles observed in the furane rings of furoic acid and of furane. The measurements on furane were made by electron diffraction (Schomaker & Pauling, 1939; Beach, 1941).

The agreement is satisfactory for bonds $C_2$–$C_3$, $C_3$–$C_4$ and $C_4$–$C_5$, but the bonds $C_2$–$O_r$ and $O_r$–$C_5$ are 0·1 Å shorter in furoic acid than in furane. In the latter compound, these bonds have values only slightly less than the formal C–O single bond (1·43 Å) though still shorter bonds might have been expected because of the electronegativity of the ring oxygen atom. In furoic acid, there is the further possibility of conjugation between the ring and the carboxyl group. The effect of this on bond lengths is discussed in § 5(*c*).

(*b*) *The carboxyl group.*—The dimensions of the carboxyl group show a significant difference between the bonds $C_1$–$O_2$ (1·26 Å) and $C_1$–$O_1$ (1·16 Å), as has been found, for example, in $\alpha$-oxalic acid (Cox, Dougill & Jeffrey, 1952) and in several aliphatic dicarboxylic acids (Morrison & Robertson, 1949*a*, *b*, *c*, *d*). In terms of valence bond structures this means

Table 6. *Comparison of bond lengths and valency angles*

| Furane | S & P | B | Furoic acid |
|---|---|---|---|
| $C_2$–$C_3$ | 1·35 Å* | 1·35 Å* | 1·30±0·05 Å |
| $C_3$–$C_4$ | 1·46 Å* | 1·46 Å* | 1·46±0·05 Å |
| $C_4$–$C_5$ | 1·35 Å* | 1·35 Å* | 1·35±0·05 Å |
| $C_5$–$O_r$ | 1·41±0·03 Å | 1·40±0·03 Å | 1·30±0·05 Å |
| $O_r$–$C_2$ | 1·41±0·03 Å | 1·40±0·03 Å | 1·31±0·05 Å |
| $C_2$–$C_3$–$C_4$ | 107 ±2° | — | 105 ±4° |
| $C_3$–$C_4$–$C_5$ | 109 ±2° | — | 103 ±4° |
| $C_4$–$C_5$–$O_r$ | 107 ±4° | 107 ±3° | 112 ±4° |
| $C_5$–$O_r$–$C_2$ | 109 ±3° | — | 107 ±4° |
| $O_r$–$C_2$–$C_3$ | — | — | 113 ±4° |

* Assumed values.

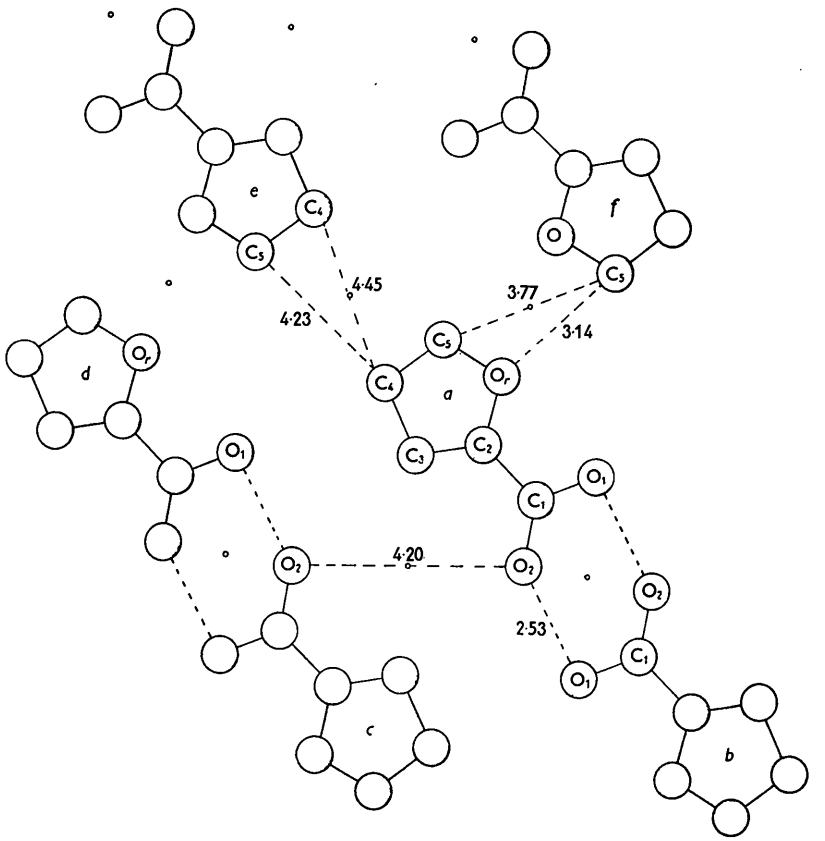


Fig. 4. Relative positions of the molecules (diagrammatic). The small circles are centres of symmetry.

that structure I is more favoured than structure II.

I II

The $C_1-O_2$ bond length agrees with the values found in these other carboxylic acids but that of $C_1-O_1$, while agreeing satisfactorily with the value found in $\alpha$-oxalic acid, is considerably shorter than that recorded for the corresponding bond in the aliphatic dicarboxylic acids, as can be seen from the following table:

| | $C_1-O_2$ | $C_1-O_1$ |
|---|---|---|
| Furoic acid | 1·26 Å | 1·16 Å |
| $\alpha$-Oxalic acid | 1·29 | 1·19 |
| $\beta$-Succinic | 1·30 | 1·25 |
| Adipic | 1·29 | 1·23 |
| Sebacic | 1·27 | 1·24 |
| $\beta$-Glutaric | 1·30 | 1·23 |

(*c*) *The molecule as a whole.*—Both the furane ring and the carboxyl group have electrons with orbitals of $\pi$-symmetry, and it would thus be expected that conjugation would take place provided the groups were co-planar. A planar molecule is therefore favoured, and this has been observed in furoic acid. The length of the bond $C_1-C_2$ (1·47 Å) linking the carboxyl group to the furane ring indicates that conjugation does take place between the two parts of the molecule. One result of this would be to shorten still further one or both of the bonds $C_5-O_r$ and $C_2-O_r$ in the furane ring of furoic acid from the lengths observed in furane itself. This shortening has been observed experimentally in the present investigation of furoic acid. It is interesting to note that a high electron concentration in these bonds in furoic acid is suggested by the relatively high dissociation constant of the compound, $7\times10^{-4}$ at 25° (*Handbook*, 1945), as compared with that of benzoic acid, $6{\cdot}3\times10^{-5}$ (*Handbook*, 1945).

II. *Crystal structure*

The distances $O_{1a}-O_{2b}$, $O_{2a}-O_{1b}$ (Fig. 4) are observed to be 2·53 Å, indicating that strong hydrogen bonds link the carboxyl groups of adjacent molecules, as shown in Fig. 4. The two molecules thus linked are not co-planar. This seems to support the theory that hydrogen linkages are electrostatic in character, and not resonance phenomena.

The only other intermolecular distance less than van der Waals distance is $O_{ra}-C_{5f}$, which is 3·14 Å, suggesting some attraction between these atoms. This could be explained by differences in charge distribution round the ring due to both the presence of the lone

Table 7. *Experimental atomic scattering factors for carbon*

| $\xi$ | $f$ | $\xi$ | $f$ | $\xi$ | $f$ | $\xi$ | $f$ |
|---|---|---|---|---|---|---|---|
| 0·0 | 6·11 | 0·5 | 3·92 | 1·0 | 1·63 | 1·5 | 0·60 |
| 0·1 | 5·70 | 0·6 | 3·46 | 1·1 | 1·32 | 1·6 | 0·49 |
| 0·2 | 5·32 | 0·7 | 2·92 | 1·2 | 1·10 | 1·7 | 0·40 |
| 0·3 | 4·85 | 0·8 | 2·48 | 1·3 | 0·90 | 1·8 | 0·33 |
| 0·4 | 4·40 | 0·9 | 2·02 | 1·4 | 0·72 | 1·9 | 0·30 |

pair $\pi$-electrons on the ring oxygen atom and the conjugation between the ring and the carboxyl group.

The structure in the crystal is thus a fairly open one consisting of layers of zigzag chains of molecules; each chain is divided up into pairs of molecules firmly linked together by hydrogen bonds, but with comparatively large spaces between the pairs.

## 6. Experimental

### (*a*) *Preparation of crystals*

The sample of furoic acid was supplied by Imperial Chemical Industries Ltd, as a brown amorphous powder. Purification was carried out by treatment with animal charcoal and slow crystallization from hot water. Colourless plate-like crystals, m.p. 133° C., were obtained in this way, repeated attempts to prepare crystals more equally developed in all directions being unsuccessful.

### (*b*) *Refractive indices*

These were measured by the Becke method of immersion in liquids of known refractive index.

### (*c*) *Pyroelectricity*

Pyroelectric tests were carried out by immersion in liquid air of crystals suspended side by side on silk fibres.

### (*d*) *X-ray work*

All measurements were carried out using a Metropolitan-Vickers X-ray set fitted with a copper target, the radiation from which was filtered through nickel foil. Rotation, oscillation and moving-film (Weissenberg) photographs were taken. Since the crystals were both thin and triclinic, some difficulty was experienced in locating the most suitable axis in a direction roughly perpendicular to the plate. Several axes of similar lengths, e.g. 10·24, 10·72, 19·3, 19·5 Å etc. were observed, the most convenient one eventually being located by means of a stereographic net.

Intensities were estimated by Robertson's (1943) multiple-moving-film technique, using crystals cut to approximately equal dimensions in the $a$ and $b$ directions when estimating the $\{hk0\}$ intensities, but applying corrections for absorption within the specimen when measuring the other zones because of the anisotropic crystal development. The range of intensities covered in each of the three principal zones was 2,000:1 and in the $\{hk0\}$ zone 70% of the 171 planes theoretically observable were recorded, in the $\{h0l\}$ zone 75% of the 93, and in the $\{0kl\}$ zone 64% of the 64.

### (*e*) *Atomic scattering factors*

Throughout this work the hydrogen atoms have been neglected, at the outset in accordance with custom, later because the zonal discrepancies were quite low without them and the contour lines in the various projections gave no indication that they were likely to be significant. Initially, the atomic scattering factor curves of Cox & Goodwin (1936) were used in calculating structure factors. Later, when the approximate positions of the atoms had been established, the oxygens were supposed to have $f$ values 9/6 times those of carbon, this ratio appearing, from work carried out on several compounds in these laboratories, to be more satisfactory than 8/6.

By comparison of $F(hk0)_o$ with $F(hk0)_c$ the observed $F$'s were placed on the absolute scale. The atomic scattering factors appropriate to this compound were calculated from

$$f(hk0) = F(hk0)/G(hk0) ,$$

where $G$ is the effective geometrical structure factor. By plotting these against the corresponding $\xi$, and drawing in the best curve, the figures in Table 7 were derived.

In conclusion, we wish to express our thanks to Imperial Chemical Industries Ltd for the loan of apparatus and the gift of furoic acid and to the Department of Scientific and Industrial Research for a Maintenance Allowance which allowed one of us (C.M.T.) to take part in this work. We are also very grateful to Prof. J. Monteath Robertson, F.R.S., for his continued interest in the investigation.

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# The Crystal Structure of Hydrogen Fluoride

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Hydrogen fluoride forms orthorhombic crystals in the space group $D_{2h}^{17}$–*Bmmb*, with four molecules in a unit cell of dimensions $a = 3{\cdot}42$, $b = 4{\cdot}32$ and $c = 5{\cdot}41$ Å. Infinite zigzag chains of hydrogen bonds exist parallel to (100). The FH · · · F hydrogen-bonded distance is $2{\cdot}49 \pm 0{\cdot}01$ Å, and the hydrogen-bond angle about fluorine is 120·1°. The anisotropic thermal motion of fluorine shows larger amplitudes of vibration perpendicular to the $y$ axis, the direction of the hydrogen bonds.

## Introduction

Solid hydrogen fluoride has been studied previously by the X-ray diffraction method by Gunther, Holm & Strunz (1939), who indexed powder photographs on a tetragonal unit cell with $a = 5{\cdot}45$ and $c = 9{\cdot}95$ Å. These results, as well as their hydrogen-bond distance of 2·7 Å and bond angle of 134°, are incorrect. The presence of a hydrogen-bonded structure, however, is demanded by a variety of physical data. In an electron-diffraction study (Bauer, Beach & Simons, 1939) an FH · · · F distance of 2·55 Å and a bond angle of 144° about fluorine are reported. Our distance of 2·49 Å and bond angle of 120·1°, obtained as described below, are considerably more precise and suggest that a re-investigation by the electron-diffraction method should be made to decide if the differences between the solid and the gas are real.

In addition our Fourier maps provide some support to the unsymmetrical nature of the hydrogen bond in hydrogen fluoride.

## Methods and results

Anhydrous hydrogen fluoride, 99·0% pure, was obtained from the Matheson Company, East Rutherford, New Jersey. The material was distilled through copper and Teflon tubing into thin-walled Fluorothene capillaries about 0·5 mm. in diameter, which were then sealed with the use of heated pliers. The observed melting point of our sample was within ±0·5° of the expected value of −83·4° C. (Hu, White & Johnston, 1953).

Precession photographs were taken of a single crystal at −125° C. with the use of Mo $K\alpha$ radiation and a precession angle of 28°. Successive, timed exposures were made of each zone, and intensities were estimated visually with the aid of standard, timed scales prepared from single-crystal reflections. Lorentz and polarization factors (Waser, 1951) were applied, and the structure factors were then obtained.

The symmetry of the reciprocal lattice is $D_{2h}$–*mmm*, and the dimensions of the orthorhombic unit cell are

$$a = 3{\cdot}42,\ b = 4{\cdot}32 \quad \text{and} \quad c = 5{\cdot}41 \text{ Å},$$

all within ±0·01 Å. If four molecules are assumed in this unit cell the calculated density is 1·663 g.cm.$^{-3}$ at −125° C., in very good agreement with the measured value of 1·658 g.cm.$^{-3}$ at −97·2° C. (Biltz, Boucher & Fischer, 1932). Systematic extinctions of $hkl$ when $h+l$ is odd, $hk0$ when either $h$ or $k$ is odd lead to the possible space groups $D_{2h}^{17}$–*Bmmb*, $C_{2v}^{16}$–*B*2*mb* or $C_{2v}^{12}$–$Bm2_1b$.

The structure was obtained by trial. The normal decline of $hk0$ reflections indicated special $x$ and $y$ coordinates, while the $0kl$ reflections indicate a general $z$ coordinate to be determined from the relative intensities. Thus the fourfold positions for fluorine

$$0, \tfrac{1}{4}, z;\ 0, -\tfrac{1}{4}, -z;\ \tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{2}+z;\ \tfrac{1}{2}, -\tfrac{1}{4}, \tfrac{1}{2}-z$$