Acta Cryst. (1962). **15**, 919

The crystal and molecular structure of α-furoic acid.

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(*Received* 3 *May* 1962)

As part of a study of heterocyclic 5-membered ring carboxylic acids, the structure of furane-2-carboxylic acid, or α-furoic acid, reported by Goodwin & Thomson (1954) has been refined by least-squares methods. The cell dimensions were reported as

$$a = 10{\cdot}24 \pm 0{\cdot}02,\ b = 6{\cdot}80 \pm 0{\cdot}02,\ c = 3{\cdot}81 \pm 0{\cdot}02\ \text{Å};$$
$$\alpha = 92°\ 57',\ \beta = 94°\ 16',\ \gamma = 106°\ 10'$$

and the space group $P\bar{1}$. They collected $0kl$, $h0l$ and $hk0$ data, solving the structure by trial-and-error methods, the final R values for the three zones were 11·2%, 18·7%, and 14·5% respectively. As the refinement consisted of only two cycles of Fourier syntheses for the $hk0$ zone, it was considered worthwhile to carry out further refinement—particularly for improving the z parameters.

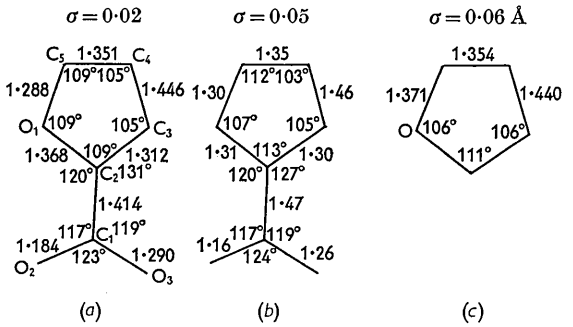

Fig. 1. Comparison of bond lengths and angles. Values reported for α-furoic acid by (*a*) the author, (*b*) Goodwin & Thomson; values for furane (*c*) given by Bak, Hansen & Rastrup-Andersen.

The three zones were treated together and subjected initially to two cycles of refinement with isotropic temperature factors and subsequently to eight cycles with anisotropic temperature factors. Corrections were applied for molecular vibration, the largest being 0·008 Å. The final R factor was 8·2%. Final coordinates, temperature parameters and standard deviations are given in Table 1. Molecular dimensions are displayed in Fig. 1 alongside those given by Goodwin & Thomson, and the values for furane obtained by microwave methods (Bak, Hansen & Rastrup-Andersen, 1955). Standard deviations of bond lengths are a substantial improvement on the original calculations where the error in bond lengths was estimated as of the order of ±0·05 Å. A difference map computed for the $hk0$ zone showed three well-resolved hydrogen peaks, but unfortunately the carboxyl group hydrogen could not be satisfactorily sited. Attempts to refine the hydrogen parameters were unsuccessful. The atomic scattering factor ratio of 9/6 for oxygen to carbon used by Goodwin & Thomson was discarded, the atomic scattering factors for oxygen and carbon given by Berghuis *et al.* (1955) being used instead.

The structure-factor calculations show eleven changes in sign when compared with the values published by Goodwin & Thomson. Many of the structure factors concerned are large, and Dr Goodwin has confirmed that these 'changes' correspond to misprints in the original paper. The reflections concerned are given in Table 2.

Table 2. *Structure factor sign changes*

Reflection	F_o	F_c (Goodwin & Thomson)	F_c (Hudson)
101	49·5	+48·4	−45·4
$1\bar{4}0$	13·7	+14·4	−13·6
210	8·8	+ 9·1	− 8·5
220	21·2	+20·8	−19·5
420	5·2	+ 4·0	− 4·6
550	6·0	+ 5·5	− 5·5
$8\bar{1}0$	5·3	− 4·9	+ 4·9
$8\bar{3}0$	3·2	+ 1·4	− 3·1
$10,\bar{5}0$	1·6	+ 1·6	− 1·4
$10\bar{3}$	1·6	− 0·3	+ 1·4
$60\bar{3}$	1·8	− 0·6	+ 1·9

The C_5 atom is not satisfactorily located, as its outstanding thermal parameters and the standard deviations indicate; this is because this atom suffers overlap in both ($0k0$) and ($l00$) projections. A great deal of significance is not therefore attached to the unusually short C_5–O_1 bond. The other bond lengths within the ring are in agreement with those observed in furane, with the exception of C_2–C_3 which is much shorter in the acid, and is presumably to some extent conjugated with the

Table 1. *Final atomic coordinates (in* Å*), anisotropic thermal parameters (in* Å^2*) and standard deviations*

	O_1	O_2	O_3	C_1	C_2	C_3	C_4	C_5
x	1·365	3·292	5·062	3·743	2·765	2·959	1·571	0·675
σ	0·008	0·008	0·007	0·010	0·011	0·012	0·012	0·015
y	0·865	−0·352	1·427	0·791	1·535	2·825	2·975	1·727
σ	0·008	0·008	0·010	0·013	0·011	0·014	0·016	0·015
z	0·589	0·000	0·709	0·522	0·784	1·272	1·367	0·913
σ	0·012	0·010	0·011	0·014	0·012	0·013	0·016	0·020
U_{11}	0·055	0·053	0·055	0·050	0·047	0·062	0·059	0·063
U_{22}	0·052	0·056	0·080	0·047	0·054	0·053	0·068	0·070
U_{33}	0·081	0·077	0·077	0·041	0·044	0·045	0·067	0·110
U_{12}	0·029	0·023	0·047	0·013	0·023	0·016	0·033	0·042
U_{23}	−0·022	0·037	−0·047	−0·057	−0·024	−0·038	0·006	0·049
U_{13}	0·012	−0·003	0·006	−0·004	0·016	0·025	0·035	0·002

carboxyl group. A plane can be drawn through the five ring atoms, from which the displacements are

$$O_1\ -0{\cdot}0076,\ C_2\ +0{\cdot}0077,\ C_3\ -0{\cdot}0026\ \text{Å},$$
$$C_4\ -0{\cdot}0035,\ C_5\ +0{\cdot}0086\ \text{Å},$$

all of which are less than the standard deviations. On the other hand a plane taken through the four carbon atoms of the ring, is very accurately planar; the deviations are

$$C_2\ -0{\cdot}0003,\ C_3\ +0{\cdot}0005,\ C_4\ -0{\cdot}0005,\ C_5\ +0{\cdot}003\ \text{Å},$$

and the ring oxygen lies 0·0224 Å below this plane, a displacement which is substantially greater than the standard deviation. In relation to this plane the carboxyl group is twisted by nearly 2° in a direction away from the ring oxygen, the displacements being

$$C_1\ -0{\cdot}0458,\ O_2+0{\cdot}0442,\ O_3\ -0{\cdot}0261\ \text{Å}.$$

The geometry of the carboxyl group is somewhat unusual; the longer bond of 1·29 Å is normal, the shorter, 1·18 Å, rather below average, but the relative size of the angles C–C–OH and C–C=O is reversed. Typical values are C–C–OH 116°, C–C=O 122° with O=C–OH 122°. In α-furoic acid the values are 119°, 117° and 123° respectively. It is also to be noted that the configuration of the carboxyl group is reversed compared with α-thiophenic acid and α-selenophenic acid (Nardelli, Fava & Giraldi, 1962), in both of which the hydroxyl group faces the ring hetero-atom. Both sulphur and selenium compounds display normal geometry in their angles, although there is a certain amount of distortion of the angles bringing the carboxyl group nearer to the hetero-atom. It seems therefore that although the configuration is reversed in α-furoic acid there is still an attraction between carboxyl group and the ring oxygen atom. The exocyclic bond C_1–C_2 is remarkably short, 1·41 Å, although it is comparable with the values observed for 1- and 2-naphthoic acids by Trotter (1960, 1961). This bond is usually shortened if the cyclic system is a conjugated one, but one would not expect shortening of quite such magnitude in α-furoic acid which is not strongly aromatic. The acid forms hydrogen-bonded centrosymmetric dimers, the molecules being nearly co-planar, the distance O–H · · · O being 2·54 Å.

Because the *c* axis is so very short, the *z* parameters are not very reliable—as the standard deviations indicate. A three-dimensional analysis is needed to make the results really reliable; this would clarify the position of the C_5 atom and make conclusions about the ring more dependable.

The author would like to record his thanks to Dr J. H. Robertson for his continual advice and encouragement, and to Dr T. H. Goodwin for his valuable comments on the results of the refinement.

References

Bak, B., Hansen, L. & Rastrup-Andersen, J. (1955). *Discuss. Faraday Soc.* **19**, 30.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Goodwin, T. H. & Thomson, C. M. (1954). *Acta Cryst.* **7**, 166.

Nardelli, M., Fava, G. & Giraldi, G. (1962). *Acta Cryst.* (In the press.)

Trotter, J. (1960). *Acta Cryst.* **13**, 732.

Trotter, J. (1961). *Acta Cryst.* **14**, 101.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (D. W. Smits, Mathematisch Instituut, University of Groningen, Reitdiepskade 4, Groningen, The Netherlands).

International Union of Crystallography

The Executive Committee of the Union much regrets to have to announce that the Technical Editor of *Acta Crystallographica*, Professor R. W. Asmussen, has expressed a wish to be relieved of his task with the completion of the current volume of the journal. Professor Asmussen has served as Technical Editor since May 1958, when he succeeded Dr R. C. Evans. The Union, and the community of crystallographers, is much indebted to him for his work on the journal, which during his tenure of office considerably expanded in size, and for the painstaking way in which he has carried out his duties.

No successor to Professor Asmussen has been found. Considering the increasing amount of work involved, the Executive Committee feels that the time has come to appoint a full-time technical editor for *all* Union publications. Attention is drawn to the relevant advertisement in this issue.

Book Reviews

Works intended for notice in this column should be sent direct to the Editor (A. J. C. Wilson, Department of Physics, University College, Cathays Park, Cardiff, Great Britain). As far as practicable books will be reviewed in a country different from that of publication.

Towards Information Retrieval. By R. A. Fairthorne. Pp. xxiv+211, 15 figs. London: Butterworths. 1961. Price 40*s*.

Crystallographers have always been interested in information retrieval, an early example being the list of all structures known in 1923 in Ewald's book 'Kristalle und Röntgenstrahlen'. Out of this interest has grown the continuing series of *Strukturbericht* and *Structure Reports*; indexes of a conventional but very thorough type have sufficed for retrieval of the information stored in these. Since its inception the International Union of Crystallo-