

ERASMUS, C. S. & BOEYENS, J. C. A. (1970a). *Acta Cryst.* B26, 1843.  
 ERASMUS, C. S. & BOEYENS, J. C. A. (1970b). *J. Cryst. Mol. Struct.* To be published.  
 EVANS, R. C. (1964). *Crystal Chemistry*, 2nd ed., p. 112. Cambridge: University Press.

*International Tables for X-ray Crystallography* (1965). 2nd ed. Vol. I, p. 99. Birmingham: Kynoch Press.  
 MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Quart. Rev.* 21, 109.  
 SPRINGER, C. S., MEEK, D. W. & SIEVERS, R. E. (1967). *Inorg. Chem.* 6, 1105.

*Acta Cryst.* (1971). B27, 702

## Crystal and Molecular Structure of Fluoromalonic Acid

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The structure of fluoromalonic acid (HOOC-CFH-COOH) has been determined from three-dimensional X-ray data. The accepted space group is *Pnam*. The unit cell, of dimensions  $a=4.606$ ,  $b=8.315$ ,  $c=11.220$  Å, contains four molecules, implying a plane of symmetry in the molecule. The structure has been refined to an *R* index of 0.047 by least-squares methods. The bond lengths (1.251 and 1.245 Å) in the carboxyl group and the C-C-O bond angles (116.7 and 116.9°) have values which differ from those usually observed.

### Introduction

Infrared and X-ray investigations of crystalline tartaric acid indicate that the aliphatic hydroxyl group is not involved in hydrogen bonding (van Eijck, Kanters & Kroon, 1965; Kanters, Kroon, Peerdeman & Vliegthart, 1969). In this structure the molecules form chains by carboxyl group coupling as is frequently observed in dicarboxylic acids. From the lack of hydrogen-bond interaction between these chains it was expected that substitution of the hydroxyl group by a fluorine atom would not essentially change this simple hydrogen bond scheme.

In order to verify this the structure of fluoromalonic acid was determined.

### Experimental

Small prismatic crystals of fluoromalonic acid were obtained by sublimation *in vacuo*. Because of its very hygroscopic character a single crystal of dimensions  $0.2 \times 0.2 \times 0.1$  mm<sup>3</sup> was sealed in a glass tube. The following crystal data were obtained: C<sub>3</sub>O<sub>4</sub>H<sub>3</sub>F;  $a=4.606 \pm 0.001$ ,  $b=8.315 \pm 0.001$ ,  $c=11.220 \pm 0.001$  Å;  $V=430$  Å<sup>3</sup>;  $D_c(Z=4)=1.88$  g.cm<sup>-3</sup>.

The unit-cell dimensions and their standard deviations, calculated by least-squares methods, were determined from the Cu  $K\alpha_1$  component ( $\lambda=1.54051$  Å) of 33 reflexions with  $2\theta > 130^\circ$ , measured on a General Electric diffractometer with a single-crystal orienter and equipped with a scintillation counter.

Intensity data were collected from one single crystal using the apparatus mentioned above. Ninety-five per cent of the independent reflexions within the Cu  $K\alpha$  sphere could be measured. Non-linearity was corrected

for experimentally

$$\left( I_{\text{corrected}} = I_{\text{obs}} \left[ \frac{5.46}{5.46 - 1.1033 \cdot 10^{-5} \cdot I_{\text{obs}}} \right] \right),$$

but absorption was neglected.

From Weissenberg photographs the following extinctions were deduced:  $0kl$ :  $k+l=2n+1$ ;  $h0l$ :  $h=2n+1$ ;  $(h00)$ :  $h=2n+1$ ;  $0k0$ :  $k=2n+1$ ;  $00l$ :  $l=2n+1$ . These extinctions are compatible with both space groups *Pnam* and *Pna2<sub>1</sub>*. As *Pnam* has an eightfold general position and the unit cell contains four molecules, the molecule must have a mirror plane in this space group.

### Structure determination

A strong resemblance between the cell dimensions and  $0kl$  reflexion intensities of tartaric acid ( $a=4.485$ ,  $b=8.813$ ,  $c=10.895$  Å; space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*) and those of fluoromalonic acid led us to accept the tartaric acid coordinates as starting parameters in the least-squares refinement of fluoromalonic acid (Table 1).

Table 1. *Starting parameters*

(*B* overall = 3 Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>
F	-0.1779	+0.0999	+0.2387
O(1)	+0.3797	-0.1403	+0.1101
O(2)	+0.2228	+0.0926	+0.0568
O(3)	+0.2662	+0.1161	+0.4128
O(4)	+0.3809	-0.1283	+0.3775
C(1)	+0.2267	-0.0154	+0.1253
C(2)	+0.0367	-0.0145	+0.2422
C(3)	+0.2433	-0.0011	+0.3545

Refinement in space group *Pna2<sub>1</sub>* of carbon, oxygen and fluorine atoms with isotropic thermal parameters

Table 2. Final parameters

The expression for the anisotropic thermal parameters ( $\text{\AA}^2$ ) is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2a^*b^*hkU_{12} + 2b^*c^*klU_{23} + 2c^*a^*lhU_{31})].$$

Estimated standard deviations are given in parentheses.

	x	y	z	1000 $U_{11}$	1000 $U_{22}$	1000 $U_{33}$	2000 $U_{12}$	2000 $U_{23}$	2000 $U_{31}$
F	-0.1222 (5)	+0.1066 (3)	+0.2500 (0)	49 (1)	59 (1)	48 (1)	+22 (2)	0	0
O(1)	+0.4345 (4)	-0.1204 (2)	+0.1197 (2)	62 (1)	50 (1)	37 (1)	+22 (2)	+3 (2)	+10 (2)
O(2)	+0.2265 (5)	+0.1125 (2)	+0.0711 (2)	64 (1)	52 (1)	39 (1)	+12 (2)	+22 (2)	+13 (2)
C(1)	+0.2645 (6)	-0.0065 (3)	+0.1376 (2)	51 (1)	42 (1)	32 (1)	-9 (2)	-4 (2)	-11 (2)
C(2)	+0.0763 (8)	-0.0151 (4)	+0.2500 (0)	48 (2)	43 (2)	40 (2)	+2 (4)	0	0
H(1)	-0.024 (9)	-0.118 (6)	+0.250 (0)						
H(2)	+0.365 (8)	+0.096 (4)	+0.008 (4)						

by a block-diagonal least-squares program (Peterse, 1969) including all non-zero observed reflexions, with the exception of the 020 reflexion which apparently suffered from extinction, yielded  $R=0.10$  ( $R = \sum|F_o - F_c| / \sum|F_o|$ ).

At this stage of the refinement a difference Fourier synthesis of low order terms ( $\sin \theta < 30^\circ$ ) was computed. It clearly revealed the position of the aliphatic hydrogen atom and indicated the positions of other hydrogen atoms. Further refinement with anisotropic thermal parameters, keeping the isotropic thermal parameters of the hydrogen atoms fixed, reduced the  $R$  index to a value of 0.049.

The structure was then refined in space group  $Pnam$  and this gave an  $R$  index of 0.047; thus the reduction of the number of parameters (from 81 in  $Pna2_1$  to 45 in  $Pnam$ ) has a lowering effect on the  $R$  value, which is contrary to expectation.

Refinements in both space groups were continued with a full-matrix least-squares program (Derissen, 1968). The correlation matrix showed large off-diagonal terms (up to |0.95|) between corresponding parameters of atoms that are independent in  $Pna2_1$ , but symmetry-related in  $Pnam$ .

After refining the structure in both space groups with the full-matrix least-squares program the  $R$  index was reduced to a final value of 0.042 for space group  $Pna2_1$  and 0.047 for space group  $Pnam$  (431 reflexions; 020 omitted). Also the two final difference Fourier syntheses, which showed no peaks above the level of  $0.30 \text{ e.}\text{\AA}^{-3}$ , justified termination of the refinement.

In our opinion the structure of fluoromalonic acid is not satisfactorily refinable in space group  $Pna2_1$  because of interactions between parameters of interdependent atoms. This leads to high estimated standard deviations, poor convergence and, in this particular case, to rather different bond lengths in the carbon chain (1.51 and 1.56  $\text{\AA}$ ). An analogous case was reported by Geller (1961). However, in space group  $Pnam$  the refinement proceeds smoothly and accordingly we accepted this space group for the description of fluoromalonic acid. Our experience with these refinements is in agreement with the observations of Ermer & Dunitz (1970) and Parthasarathy, Sime & Speakman (1969).

Table 2 shows the final positional and thermal parameters. Table 3 contains the structure factors, observed and calculated. Analytic constants for atomic scattering factors for F, O, C and H were taken from Moore (1963).

### Discussion of the structure

As has already been stated, there is a strong resemblance between the structures of fluoro- and hydroxymalonic acid. In tartronic acid the aliphatic hydroxyl group apparently does not participate in hydrogen bonding, which indicates that the stacking of the molecules is governed chiefly by polymer formation through coupling of the carboxyl groups only. The



Table 4. Bond lengths, bond angles and standard deviations (in parentheses)

C(2)-F	1.364 (4) Å	C(1)-C(2)-C(1 <sup>iv</sup> )	111.0 (3)°
C(1)-C(2)	1.532 (4)	F-C(2)-C(1)	110.2 (3)
C(1)-O(1)	1.251 (4)	O(1)-C(1)-O(2)	126.4 (3)
C(1)-O(2)	1.245 (4)	O(1)-C(1)-C(2)	116.9 (3)
C(2)-H(1)	0.97 (7)	O(2)-C(1)-C(2)	116.7 (3)
O(2)-H(2)	0.96 (7)	F-C(2)-H(1)	109 (5)
		C(1)-C(2)-H(1)	108 (5)
		C(1)-O(2)-H(2)	103 (5)
		Hydrogen bond distance O(2)-H(2)---O(1 <sup>iv</sup> )	2.651 (4) Å

The following superscripts are used in this Table and in Fig. 1:

( <sup>i</sup> ):	$\frac{1}{2} + x$	$\frac{1}{2} - y$	$z$
( <sup>ii</sup> ):	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$-z$
( <sup>iii</sup> ):	$-x$	$-y$	$-z$
( <sup>iv</sup> ):	$x$	$y$	$\frac{1}{2} - z$

of the C-O bond distances and C-C-O bond angles all values found are compatible with values reported in the literature. The bond lengths in the carboxyl group are equal within the limit of error, though obeying the Speakman rule (Manojlović & Speakman, 1967). The C-C-O bond angles are equal too. Average

values of C-O bond lengths and C-C-O bond angles of crystalline carboxylic acids from the literature are: 1.31 and 1.22 Å, and 113 and 123° respectively; however, exceptions have recently been reported (Sintes, Housty & Hospital, 1966; Manojlović & Speakman, 1967; Housty, 1968).

The atoms C(1), C(2) and O(1), O(2) are coplanar within experimental error. The carboxyl group is rotated 6.5° about the C-C bond out of the plane through C(1), C(2) and F. Corresponding values in tartronic acid are 16 and 18° respectively (Fig. 2). The distance O(1)-O(1<sup>iv</sup>) in fluoromalonic acid is equal to the corresponding distance O(1)-O(4) in tartronic acid.

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### References

- DERISSEN, J. L. (1968). *DERJ-D4. A Crystallographic Full Matrix Least-Squares Program Written in Algol*.
- EIJCK, B. P. VAN, KANTERS, J. A. & KROON, J. (1965). *Acta Cryst.* **19**, 435.
- ERMER, O. & DUNITZ, J. D. (1970). *Acta Cryst.* **A26**, 163.
- GELLER, S. (1961). *Acta Cryst.* **14**, 1026.
- HOUSTY, J. (1968). *Acta Cryst.* **B24**, 486.
- HUGHES, D. O. & SMALL, R. W. H. (1962). *Acta Cryst.* **15**, 933.
- KANTERS, J. A. (1971). To be published.
- KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & VliegENTHART, J. A. (1969). *Nature, Lond.* **222**, 370.
- KRAUSE, J. & DUNKEN, H. (1966). *Acta Cryst.* **20**, 67.
- KVICK, A., JONSSON, P. G. & OLOVSSON, I. (1969). *Inorg. Chem.* **8**, 2775.
- MANOJLOVIĆ, L. & SPEAKMAN, J. C. (1967). *J. Chem. Soc.* p. 971.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
- PARTHASARATHY, R., SIME, J. G. & SPEAKMAN, J. C. (1969). *Acta Cryst.* **B25**, 1201.
- PETERSE, W. J. A. M. (1969). *A Crystallographic Block-Diagonal Least-Squares Program H562*.
- SINTES, A., HOUSTY, J. & HOSPITAL, M. (1966). *Acta Cryst.* **21**, 965.

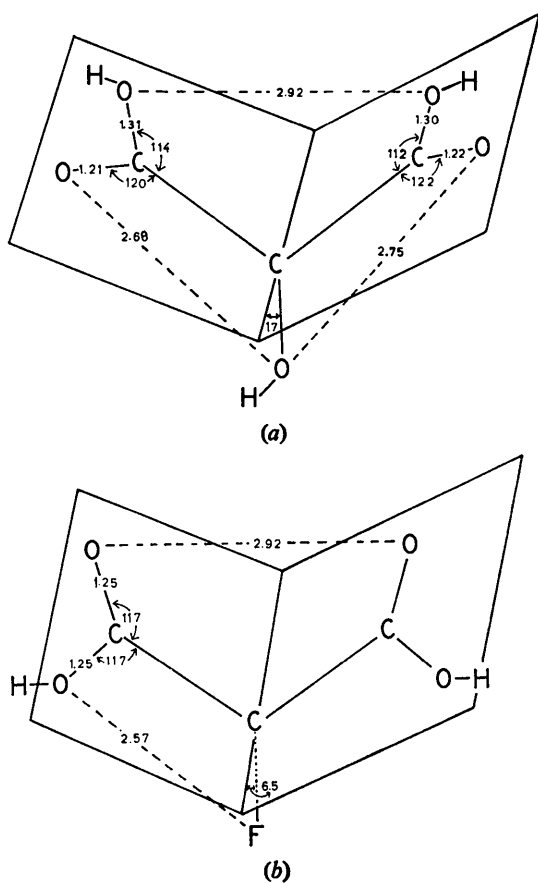


Fig. 2. Comparison between the carboxyl groups of (a) tartronic acid and (b) fluoromalonic acid.