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The crystal and molecular structure of *o*-fluorobenzoic acid. A correction.

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While preparing a paper on the correlation of X-ray crystal structure and infrared absorption for *o*-halogenoaroyl compounds (Eglinton, Ferguson, Islam & Glasby, 1966) we were surprised by the apparently anomalous angle of tilt (21°) of the carboxyl group plane to the benzene plane in *o*-fluorobenzoic acid (Krausse & Dunken, 1966). The corresponding values in *o*-chlorobenzoic acid (Ferguson & Sim, 1961), *o*-bromobenzoic acid (Ferguson & Sim, 1962*a*), and 2-chloro-5-nitrobenzoic acid (Ferguson & Sim, 1962*b*) are 13·7, 18·3 and 23·0° respectively. In *o*-chlorobenzoylacetylene (Ferguson & Islam, 1966*a*) and *o*-bromobenzoylacetylene (Ferguson & Tyrrell, 1965) the angles between the benzene and ethynylcarbonyl planes are 7·1 and 13·1° respectively.

Krausse & Dunken's (henceforth K-D) coordinates for *o*-fluorobenzoic acid do not refer to one molecule. When appropriate transformations are made (*e.g.* adding 1 to the fluorine and O(1) x coordinates) and a printing error corrected (the C(1) y coordinate should be 0·255, not 0·225), mean molecular plane calculations using the method of Schomaker, Waser, Marsh & Bergman (1959) yield equations for the carboxyl and benzene planes from which an interplanar angle of 6·7° is found, close to a value (8°) obtained by Krausse (1962) from graphical work.

The atoms of the benzene ring are best fitted by the plane with equation

$$-0{\cdot}4015X' - 0{\cdot}9134Y + 0{\cdot}0674Z' + 2{\cdot}5946 = 0 .$$

The atoms of the carboxyl group C(7), O(1), O(2), and C(1) of the benzene plane lie on the plane

$$-0{\cdot}4323X' - 0{\cdot}8960Y - 0{\cdot}0409Z' + 3{\cdot}0472 = 0 .$$

Table 1. *Deviations* (Å) *from the mean planes*

(*a*) Plane through benzene ring C(1)···C(6).
(*b*) Plane through carboxyl group C(7)O(1)O(2), and C(1) of the benzene ring.

	(*a*)	(*b*)
F	−0·034	—
O(1)	+0·003	0·005
O(2)	−0·227	0·005
C(1)	−0·001	0·004
C(2)	+0·002	—
C(3)	−0·002	—
C(4)	−0·001	—
C(5)	+0·002	—
C(6)	−0·002	—
C(7)	−0·096	−0·014

Coordinates X', Y, Z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, and expressed in Å. The displacements of the atoms from the planes are given in Table 1.

Thus the extent of rotation of the carboxyl plane out of the benzene plane in *o*-halogenobenzoic acids is seen to increase in the series: fluorine, chlorine, bromine. We therefore conclude that the size of the halogen atom plays a more important role in determining the extent of rotation of the adjacent carboxyl plane than do dipole–dipole interactions between halogen and carbonyl oxygen atoms.

In view of the fact that K-D had only 365 data available for their analysis, and of their lack of adequate refinement facilities, their estimated standard deviations must be regarded as optimistic. In this light it is debatable how much significance should be given to the molecular plane displacements listed in Table 1.

A complete data collection for *o*-fluorobenzoic acid is now in progress (Ferguson & Islam, 1966*b*). Full details of the refinement of the structure will be reported in due course.

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