Absolute Configuration and Different Conformations in the Crystal of (—)-$Fe(CO)_4$–Fumaric Acid

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IN a previous Communication,[1] we reported data concerning the crystal structure of racemic $Fe(CO)_4$–fumaric acid. Here we give some features of the optically active (—)-form.

Crystal data: Orthorhombic; $a = 6{\cdot}10 \pm 2$, $b = 13{\cdot}37 \pm 4$, $c = 19{\cdot}20 \pm 6$ Å, $Z = 6$; space group uniquely identified as $P2_12_12$.

The structure has been solved using some 600 reflections estimated from Weissenberg photographs taken with Fe–K_α radiation. The structure contains three crystallographically distinct pairs of formula units, each of which, therefore, has C_2 symmetry and lies on one of the diad axes parallel to *c*. For convenience, they are distinguished by calling them A, B, and C. Refinement was carried out by differential synthesis calculations, and finally by least squares. At present the discrepancy factor, *R*, is 0·092. A complete report of the structure will be given elsewhere, but certain features are noteworthy.

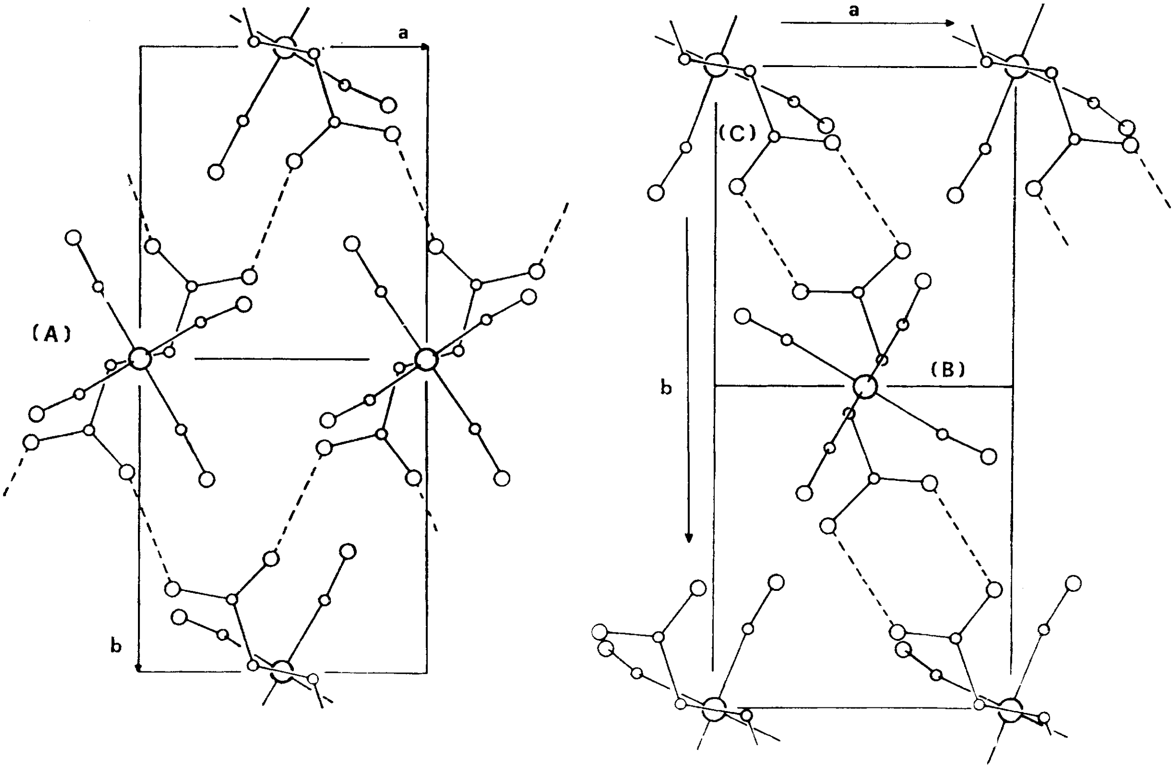

FIGURE. *Projections of layers of the structure of* (—)-Fe(CO)$_4$-fumaric acid (a) *layer centred on* Z = 0; (b) *layer centred on* Z = ½.

First, the four carbon atoms of each fumaric acid molecule are non-coplanar, as was found in the racemate. If the carbon atoms are designated as

$$\overset{1}{HO_2C}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CO_2H}$$

the angle of torsion around the CH=CH bond, *i.e.* between the planes C(1) C(2) C(3) and C(2) C(3) C(4), is 151°, 148°, and 146° in each of the three distinct molecules, A, B, and C.

Secondly, whereas Luxmoore and Truter[2] have found that the carbon atoms of the $CH_2=CH$ group of Fe(CO)$_4$-acrylonitrile lie in the equatorial plane of a triangular bipyramid, we found in the racemic form of Fe(CO)$_4$-fumaric acid that the CH=CH group is significantly inclined to the equatorial plane. In the (—)-form both co-ordinations occur. Thus, Figures 1 and 2 show that in the (—)-form, the axis of the double bond in molecules A and C is also significantly tilted, whereas that for molecule B is not.

The difference in energy of the two conformations must be small enough to be compensated by the formation of stronger hydrogen bonds. These form two distinct patterns: parallel 1-dimensional chains in the layer at $Z = 0$ (Figure 1a), and a two-dimensional network in the layer at $Z = \frac{1}{2}$ (Figure 1b). These different arrangements of hydrogen bonds presumably stabilise the different co-ordinations.

Thirdly, the absolute configuration of the structure has been determined using anomalous diffraction by the iron atoms of Cu-K_α radiation. It is shown in Figures 1a and 1b. All three cyrstallographically distinct molecules have the same (R,R) dissymmetry induced by the metal co-ordination at atoms C(2) and C(3).

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[1] P. Corradini, C. Pedone, and A. Sirigu, *Chem. Comm.*, 1966, 341.
[2] A. R. Luxmoore and M. R. Truter, *Acta Cryst.*, 1962, **15**, 1117.