

## 74. The Crystal Structure of *trans-trans-Methyl Fumarate* and *trans-trans-Methyl Muconate*.

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The two esters have been examined by X-ray (including "diffuse-spot") photographic methods and found to crystallise in the triclinic system, with one molecule per unit cell in each case. The structures are very similar, the centrosymmetrical molecules being nearly, if not quite, plane, and arranged parallel, or nearly parallel, to (100), in chains whose length is near the long diagonal of that crystal plane. The general structure has been confirmed by optical observations on the muconate (which is positively birefringent) and by detailed measurements of the magnetic anisotropies of both compounds. The latter are typical of relatively long-chain conjugated molecules.

The esters named in the title are those of the first two members of a series of polyenedicarboxylic acids of general formula  $\text{CO}_2\text{H}\cdot[\text{CH}:\text{CH}]_n\cdot\text{CO}_2\text{H}$  of which the known acids are those in which  $n = 1, 2, 3, 4, 5$ , or 7 (Kuhn, *Angew. Chem.*, 1937, 50, 703). Both esters crystallise in the triclinic system, and for their description the simplest unit cells which show their crystallographic similarity have been chosen.

### EXPERIMENTAL.

*trans-trans-Methyl Fumarate*,  $\text{C}_8\text{H}_8\text{O}_4$ .—The crystal class is triclinic pinacoidal, the space-group  $P\bar{1}(C_2^1)$ , and there is one centrosymmetrical molecule in a unit cell of dimensions:

$$\begin{array}{lll} a = 3.92 \text{ \AA.} & \alpha = 101^\circ 47' & d_{100} = 3.22 \text{ \AA.} \\ b = 9.24 \text{ \AA.} & \beta = 112^\circ 49' & d_{010} = 8.06 \text{ \AA.} \\ c = 5.93 \text{ \AA.} & \gamma = 109^\circ 20' & d_{001} = 5.05 \text{ \AA.} \end{array}$$

The observed density  $d_4^{20}$  is 1.37 g./c.c.

Most of the crystals (grown from solution in ethyl alcohol and chloroform) are flat tabular on {010} with smaller {100} and {001} planes. One batch of crystals showed in addition {205}. The crystals are colourless, very soft, and bend easily parallel to {100}.

X-Ray examination by ordinary rotation and moving-film (Weissenberg) photographs, using Cu-K $\alpha$  radiation, showed the (100) planes to be the strongest reflectors, and the falling off of intensity with angle for the higher orders to be approximately normal. These two observations lead to the conclusion that the molecules lie in or nearly in the (100) planes. Moreover, the spacing  $d_{100}$  is 3.22 Å., which is reasonable for a layer lattice parallel to (100). The next strongest reflecting planes are (101), (020), and (001).

The measurement of the magnetic properties, which is sometimes difficult for triclinic crystals, was simplified by the parallelism of the molecules to one crystal face. A quick examination showed at once that there was a principal direction of (numerically maximum) diamagnetic susceptibility normal to the (100) plane, and the orientation of the remaining principal susceptibilities was readily found by suspending the crystals with (100) horizontal in the magnetic field (Krishnan's second method). The absolute value of the numerically minimum susceptibility was determined by the Rabi-Krishnan method, an appropriate mixture of strontium bromide and nickel chloride solutions being used. The following results ( $\times 10^{-6}$ ) were obtained:

$$\text{(Measured)} \quad \chi_3 - \chi_2 = -17.45, \quad \chi_3 - \chi_1 = -31.0, \quad \chi_2 - \chi_1 = -13.5, \quad \chi_1 = -57.4.$$

Whence,  $\chi_2 = -70.9$ ,  $\chi_3 = -88.4$ ,  $\bar{\chi} = -72.2$  (cf.  $-69.9$  calculated from Pascal's additive constants).

$\chi_3$  is normal to (100). The measured angle  $\chi_1 : c$  in the obtuse angle  $\alpha$  is  $30^\circ$ . The direction of  $\chi_2$  is therefore approximately along the trace of the (012) plane in (100), and this, according to the usual interpretation of such results, must be near to the direction of maximum length of the molecule.

FIG. 1.

*trans-trans-Methyl fumarate*: projection on (100).

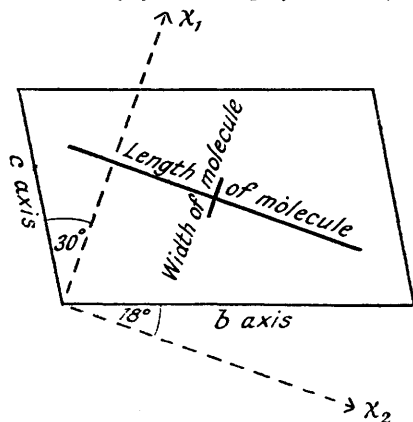
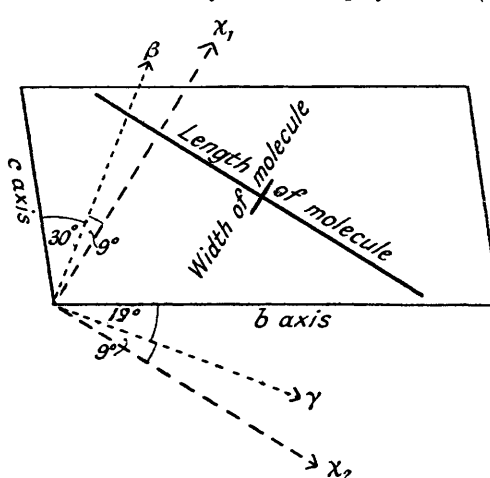


FIG. 2.

*trans-trans-Methyl muconate*: projection on (100).



*trans-trans-Methyl Muconate*,  $\text{C}_8\text{H}_{10}\text{O}_4$ .—Again the crystal class is triclinic pinacoidal, the space group  $P\bar{1}(C_2^1)$ , and there is one centrosymmetrical molecule in the unit cell of dimensions

$$\begin{array}{lll} a = 5.83 \text{ \AA.} & \alpha = 100^\circ 39' & d_{100} = 3.18 \text{ \AA.} \\ b = 11.71 \text{ \AA.} & \beta = 87^\circ 50' & d_{010} = 6.29 \text{ \AA.} \\ c = 5.82 \text{ \AA.} & \gamma = 146^\circ 2' & d_{001} = 5.59 \text{ \AA.} \end{array}$$

The observed density  $d_4^{20}$  is 1.33 g./c.c.

The crystals are soft, colourless, and are mostly prismatic parallel to the  $c$ -axis, the {010} and  $\{\bar{1}10\}$  planes being most developed, with smaller {100} planes. The prisms are terminated by {001} and smaller {012} planes.

As with the fumarate, the  $X$ -ray reflections from the (100) planes were the strongest, the intensities for higher orders again falling off approximately normally with increase in reflecting angle, with the exception of the fifth order, which was considerably greater. This fact was observed accidentally: the fifth order for copper radiation could not appear on the film, since  $2\theta_{500}$  for  $\text{Cu-K}\alpha > 180^\circ$ ; however, a photograph taken on Muller and Clay's 50 K.W.  $X$ -ray tube (*J. Inst. Elect. Eng.*, 1939, **84**, 261) with a copper target, which had become contaminated by tungsten sputtering, showed a 500 reflection due to tungsten  $L\beta$  radiation. From these observations it is evident that there is an approximation to a layer lattice in which most of the atoms are in or nearly in the (100) planes and that some atom or atoms are lying close to the (500) planes. The next strongest reflections are from the planes (01 $\bar{1}$ ), (011), and ( $\bar{1}11$ ). In all, more than 200 different reflections were observed from five crystal zones.

Again, the directions of the principal magnetic susceptibilities were easily determined, since  $\chi_3$  is normal to (100), the layer plane. The following results were obtained for  $10^{-6} \chi$ , etc.:

(Measured)  $\chi_3 - \chi_2 = -26.6$ ,  $\chi_3 - \chi_1 = -42.2$ ,  $\chi_2 - \chi_1 = -15.7$ ,  $\chi_1 = -67.0$ .

Whence  $\chi_2 = -82.6$ ,  $\chi_3 = -109.2$ ,  $\bar{\chi} = -86.6$  (cf.  $-82.7$ , as calculated from Pascal's additive constants).

The measured angle  $\chi_1 : c$  in the obtuse angle  $\alpha$  is  $39^\circ$ . Some crystals were sufficiently well formed for observation of the optical properties to be carried out. The birefringence is positive,  $\alpha < \beta < \gamma$ , the obtuse bisectrix  $\alpha$  being normal to (100); the angle  $\beta : c$  is  $30^\circ$  in the obtuse angle  $\alpha$ , and the directions of  $\gamma$  and  $\chi_2$  differ by only  $9^\circ$ .

*Discussion of Structure.*—Although not isomorphous in the generally accepted crystallographic sense of the word, methyl fumarate and muconate are clearly very similar in structure. They both have centrosymmetrical, nearly plane molecules arranged parallel or nearly parallel to the (100) crystal planes. On the other hand, the positive birefringence shows that the muconate is essentially a chain structure, and this has been confirmed by Laue photographs, which show the elongated type of diffuse spot characteristic of such structures (cf. Lonsdale, Robertson, and Woodward, *Proc. Roy. Soc.*, 1941, *A*, **178**, 43), as well as the one very intense elliptical diffuse spot, for the (100) plane, which is always associated with the layer plane of a layer-type structure (Lonsdale, *ibid.*, 1941, *A*, **177**, 272; Lonsdale and Smith, *ibid.*, 1941, *A*, **179**, 8). It is evident, therefore, that the muconate can be regarded as a chain structure, in that the length of the molecule, which must be very near to the direction of  $\gamma$  and  $\chi_2$ , is approximately along the long diagonal of the (100) plane, one molecule linking up with the next by relatively strong hydroxyl bonds. The length of the shorter fumarate molecule is nearer to the trace of the (012) plane in (100) and the chain of molecules is more of a zigzag, but the parallelism of the magnetic data is convincing evidence of the fundamental similarity of the two structures.

That the maximum diamagnetic susceptibility  $\chi_3$  and the minimum optical polarisability  $\alpha$  are normal to the molecular plane in each case is a further example of the fact that such conjugated compounds behave magnetically and optically like aromatic molecules even when the chain is open and comparatively straight (Lonsdale, *ibid.*, 1939, *A*, **171**, 541; *J.*, 1938, 364).

It is clear that for molecules containing an open conjugated chain Pascal's constants do not give an accurate value of the mean susceptibility unless an additional allowance is made for the large diamagnetism normal to such a chain.

The forces between atoms in successive (100) planes are of the weaker, van der Waals type, thus permitting the larger amplitudes of atomic vibration normal to those planes, which account for the very intense diffuse spot found, even on a Weissenberg photograph, as a background to the normal 100 Bragg reflection.

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