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The Crystal Structure of Malonic Acid*

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At room temperature malonic acid, COOH.CH_2.COOH, is triclinic; $a = 5{\cdot}33$ Å, $b = 5{\cdot}14$ Å, $c = 11{\cdot}25$ Å, $\alpha = 102^\circ\,42'$, $\beta = 135^\circ\,10'$ $\gamma = 85^\circ\,10'$, $Z = 2$. On the basis of space group $P\bar{1}$ good agreement between photographically observed and calculated intensities was obtained. Molecules are arranged in zigzag chains along the c axis, with the carboxyl groups linked through two hydrogen bonds as in the higher dicarboxylic acids. Unlike those, however, only one of the carboxyl groups is approximately coplanar with the carbon atoms. The significance of this is discussed.

Introduction

The crystal structures of the dicarboxylic acids COOH$(CH_2)_n$COOH, with $n = 2, 3, 4, 5, 8$, have been determined by Verweel & MacGillavry (1939), MacGillavry (1941), MacGillavry, Hoogschagen & Sixma (1948), and Morrison & Robertson (1949). Although the (monoclinic) space group is different for the even and odd members, they are built on the same principle: the molecules are arranged in chains along the c axis, with the carboxyl groups of successive molecules in the chain joined by two hydrogen bonds and related to each other by a centre of symmetry.

Malonic acid, the member with $n = 1$, is triclinic at room temperature, and it therefore seemed of interest to see in what respects the arrangement of the molecules differs from that found in the higher homologues.

The unit-cell dimensions previously measured by Gerstäcker, Möller & Reis (1928) were confirmed by the present investigation. However, in order to facilitate comparison with the other dicarboxylic acids a different choice of axes was made as follows:

$$a = 5{\cdot}33\ \text{Å},\quad b = 5{\cdot}14\ \text{Å},\quad c = 11{\cdot}25\ \text{Å};$$
$$\alpha = 102^\circ\,42',\quad \beta = 135^\circ\,10',\quad \gamma = 85^\circ\,10'.$$

This cell contains two molecules, and thus there were 21 position co-ordinates of C and O atoms to be determined if there is a centre of symmetry, and double that number otherwise.

Experimental

Suitable crystals were grown from an aqueous solution. They were shaped into small cylinders on a lathe. Weissenberg photographs were made around the a and c axes, using Cu $K\alpha$ radiation. Multiple films and visual estimation were used to obtain the intensities.

Determination of the structure

In the initial stages the simple model shown in Fig. 1 was used, with reasonable values assigned to the various bond lengths and bond angles. The only two parameters this leaves within one molecule are the azimuths of the two carboxyl groups around the direction of the C–C bond. Now if one constructs a chain of such molecules in the same way as found in the higher carboxylic acids, i.e. with successive molecules related by a centre of symmetry and connected through two hydrogens bonds between facing carboxyl groups, and assigns again a reasonable length to these hydrogen bonds, the period along the chain (containing two molecules) is found to be about equal to the

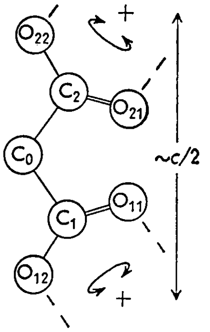

Fig. 1. Molecule of malonic acid with numbering used in this paper. The principal unknowns are the orientations of the two carboxyl groups around the C–C bond (curved arrows). Crosses denote assumed centres of symmetry which generate chain of molecules connected by hydrogen bonds (broken lines). Assuming normal values for bond lengths and bond angles, the distance between symmetry centres equals about half the c axis.

Table 1. *Atomic co-ordinates for one molecule*

Atom	x/a	y/b	z/c
C_0	0·620	0·129	0·250
C_1	0·565	0·297	0·361
O_{11}	0·565	0·542	0·371
O_{12}	0·570	0·170	0·449
C_2	0·557	0·290	0·134
O_{21}	0·815	0·415	0·185
O_{22}	0·220	0·274	−0·013

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* A preliminary account of this investigation was given at the 1950 Pennsylvania State College meeting of the American Crystallographic Association. Some better intensity data have been collected since then, but this final publication has mainly been delayed so long owing to pressure of other work.

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Table 2. *Observed and calculated structure factors*

(Values in parentheses are upper bounds of $|F_o|$ for non-observed reflexions)

hkl	$\|F_o\|$	F_c
001	1·7	−1·7
002	1·5	1·1
003	1·3	1·3
004	2·1	−1·5
005	6·9	6·9
006	3·0	2·9
007	0·5	0·5
008	2·5	2·1
009	0·7	0·7
0,0,10	(0·5)	−1·1
$0,1,\overline{10}$	1·0	−1·1
$01\bar{9}$	2·1	1·9
$01\bar{8}$	1·8	−1·8
$01\bar{7}$	1·3	1·9
$01\bar{6}$	6·3	−6·5
$01\bar{5}$	6·0	−5·0
$01\bar{4}$	0·7	0·5
$01\bar{3}$	1·0	0·2
$01\bar{2}$	1·3	2·6
$01\bar{1}$	10·9	12·0
010	8·7	−9·8
011	13·2	−14·4
012	1·6	2·8
013	3·7	−3·1
014	10·6	11·0
015	2·1	−3·0
016	0·5	−0·8
017	2·0	1·8
018	(0·5)	0·6
019	(0·3)	0·2
$0,2,\overline{10}$	0·9	0·9
$02\bar{9}$	0·6	−0·5
$02\bar{8}$	2·3	−1·7
$02\bar{7}$	4·6	−4·3
$02\bar{6}$	3·1	−2·6
$02\bar{5}$	6·8	6·3
$02\bar{4}$	3·5	−2·8
$02\bar{3}$	0·8	0·0
$02\bar{2}$	14·6	−15·0
$02\bar{1}$	3·3	−4·5
020	6·0	−6·4
021	4·9	−4·0
022	1·0	0·0
023	1·8	−2·7
024	1·9	−2·6
025	3·2	−3·8
026	0·6	0·2
027	1·0	−1·1
028	0·7	−0·6
$03\bar{9}$	1·3	−1·2
$03\bar{8}$	1·6	1·8
$03\bar{7}$	2·4	2·4
$03\bar{6}$	4·0	3·5
$03\bar{5}$	3·7	3·3
$03\bar{4}$	3·3	−3·3
$03\bar{3}$	3·4	−3·0
$03\bar{2}$	4·4	5·0
$03\bar{1}$	5·8	6·9
030	2·6	−2·6
031	5·6	4·8
032	2·9	−3·9
033	4·0	4·2
034	1·1	0·2
035	2·8	−2·3
036	1·1	1·2
037	0·5	−1·0
$04\bar{9}$	1·5	1·6
$04\bar{8}$	1·3	1·3
$04\bar{7}$	2·3	−2·4
$04\bar{6}$	3·6	3·1
$04\bar{5}$	4·3	−3·3
$04\bar{4}$	0·8	1·1
$04\bar{3}$	4·2	4·9
$04\bar{2}$	(0·5)	0·6
$04\bar{1}$	2·9	2·2
040	0·9	0·6
041	(0·5)	0·7
042	2·8	3·9
043	(0·5)	1·4
044	2·6	−3·2
045	2·7	2·8
046	(0·3)	0·5
$05\bar{8}$	2·1	−2·3
$05\bar{7}$	0·8	0·3
$05\bar{6}$	1·1	−0·7
$05\bar{5}$	1·5	−1·4
$05\bar{4}$	1·7	0·7
$05\bar{3}$	3·0	−3·7
$05\bar{2}$	3·2	2·2
$05\bar{1}$	2·5	−2·1
050	1·8	−1·6
051	0·7	0·3
052	1·1	−1·9
053	(0·4)	−1·1
054	0·7	0·5
$06\bar{6}$	(0·2)	−0·2
$06\bar{5}$	(0·3)	−0·8
$06\bar{4}$	(0·4)	0·1
$06\bar{3}$	0·4	0·6
$06\bar{2}$	0·4	−0·2
$06\bar{1}$	2·5	−2·5
060	(0·4)	0·3
061	(0·3)	−0·7
$1\bar{6}0$	(1·0)	−1·3
$1\bar{5}0$	3·7	3·4
$1\bar{4}0$	(1·5)	1·5
$1\bar{3}0$	1·5	−0·9
$1\bar{2}0$	2·2	2·2
$1\bar{1}0$	3·0	−3·0
100	16·5	−19·3
110	4·5	3·6
120	5·2	3·8
130	7·1	7·1
140	1·5	−2·0
$2\bar{6}0$	1·2	1·5
$2\bar{5}0$	3·0	−2·6
$2\bar{4}0$	1·9	2·4
$2\bar{3}0$	6·4	−6·0
$2\bar{2}0$	4·1	5·2
$2\bar{1}0$	7·1	7·0
200	2·6	2·4
210	5·2	−5·2
220	3·4	−4·3
230	(1·5)	1·7
$3\bar{4}0$	1·9	−2·6
$3\bar{3}0$	2·3	2·3
$3\bar{2}0$	1·9	−1·5
$3\bar{1}0$	2·6	−2·4
300	4·5	−4·3
310	7·5	7·7
320	(1·3)	2·2
330	3·4	−3·2
410	2·3	−2·4

length of the *c* axis. As, moreover, there is easy cleavage of the crystal along both (100) and (010) it is reasonable to proceed on the assumption that such a chain arrangement does in fact exist and that *c* is the chain direction. This implies the assumption of space group $P\bar{1}$. The three carbon atoms are then roughly in one plane through the *c* axis and the orientation of this plane remains to be determined in addition to the two molecular parameters already mentioned.

These three parameters were roughly determined by inspection of the [001] Patterson projection. The carbon atoms were found to be approximately in a plane (210), and of the two carboxyl groups one was found to be roughly in this plane, the other turned about 90° out of it. Other possibilities would not fit the Patterson map.

Starting from this configuration, the atomic co-ordinates were refined by means of standard Fourier and difference synthesis techniques in the [100] and [001] projections.* The final [100] electron-density map is shown in Fig. 2 (because of severe overlapping the [001] map is not very instructive). Final atomic co-ordinates are presented in Table 1, and observed and calculated structure factors in Table 2. A temperature factor $\exp[-B(\sin\theta/\lambda)^2]$ has been applied to the calculated structure factors with $B = 2{\cdot}62$ Å^{-2}. Reliabilities $R = \Sigma||F_o|-|F_c||\div\Sigma|F_c|$ are 16·1% for 0*kl* and 13·2% for *hk*0.

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* In the initial stages of refinement some use was made of X-RAC. The authors wish to thank Prof. Ray Pepinsky for making the machine available to them.

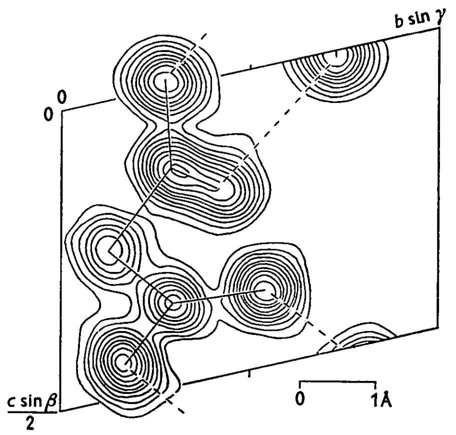

Fig. 2. Electron density projected along [100]. Half a unit cell is shown. Contours are at intervals of 1 e.Å^{-2}, starting at 2 e.Å^{-2}.

Discussion of the structure

Table 3 shows bond lengths and bond angles of primary interest. The dimensions of the two carboxyl groups and the lengths of the hydrogen bonds agree reasonably well with the values reported for similar molecules in recent years.

Table 3. *Bond lengths and bond angles*

C_1–C_0–C_2 110°

Carboxyl group 1		Carboxyl group 2	
C_0–C_1	1·54 Å	C_0–C_2	1·52 Å
C_1–O_{11}	1·24 Å	C_2–O_{21}	1·22 Å
C_1–O_{12}	1·29 Å	C_2–O_{22}	1·31 Å
C_0–C_1–O_{11}	117°	C_0–C_2–O_{21}	119°
C_0–C_1–O_{12}	115°	C_0–C_2–O_{22}	113°
O_{11}–C_1–O_{12}	128°	O_{21}–C_2–O_{22}	128°
Hydrogen bond	2·71 Å	Hydrogen bond	2·68 Å

One of the carboxyl groups is turned 13° out of the plane through the carbon atoms, the other one about 90°. In this respect malonic acid is different from the higher carboxylic acids, where the two carboxyl groups in the molecule are related by symmetry. In fact, in the even members of the series there is a centre of symmetry on the central C–C bond, and the molecule is virtually planar. The odd members, on the other hand, have a twofold symmetry axis through the central carbon atom, and here the chain is slightly twisted, with the two carboxyl groups rotated in opposite directions. MacGillavry *et al.* (1948) ascribe the relatively high energy content of the odd members of the series in the solid state (resulting in the well known alternation of heats of combustion, solubility, and melting point) to the fact that the stable configuration of the free dicarboxylic acids is the planar one, but that the requirements of packing the carboxyl groups in the crystal force the odd molecules to twist. On this theory one would expect malonic acid to show an even greater extra energy content. This is indeed found to be the case (Fig. 3), but it is difficult to say to what extent this energy is due to internal strain of the malonic acid molecule, and to what extent to other effects, such as different packing of the molecules in the crystal.

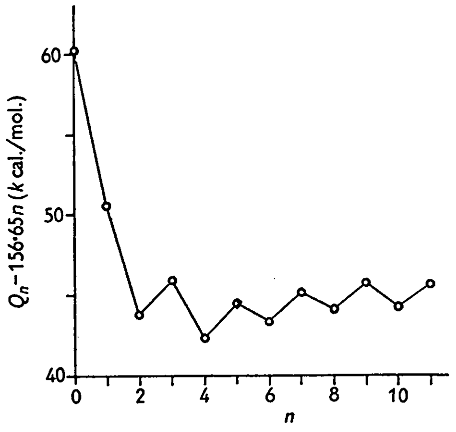

Fig. 3. Heat of combustion Q_n of solid $COOH(CH_2)_nCOOH$. In order to show the alternation effect more clearly, the general rise of Q_n with n has been eliminated by plotting $Q_n - 156{\cdot}65n$ versus n.

It should be pointed out that, unlike the other dicarboxylic acids, malonic acid could hardly be planar as a free molecule, because the distance between the oxygen atoms of the two carboxyl groups would then be about 2·2 Å, whereas the van der Waals radius of oxygen is at least 1·4 Å. Thus at least one of the carboxyl groups should be turned out of the plane. The configuration of the molecule as found here in the crystal seems to suggest that as a compromise one of the carboxyl groups stays roughly in the plane, and the other finds the most favourable position by turning perpendicular to it.

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