Acta Cryst. (1975). B**31**, 2874

The Crystal Structure of Benzylmalonic Acid

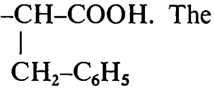
By U. Lepore, G. Castronuovo Lepore and Paolo Ganis

Laboratorio di Chimica Generale ed Inorganica, Università di Napoli, Via Mezzocannone 4, 80134 *Napoli, Italy*

(*Received* 14 *April* 1975; *accepted* 6 *May* 1975)

Benzylmalonic acid ($C_{10}H_{10}O_4$) crystallizes in the space group *Pbca* with $a=20{\cdot}780\pm0{\cdot}029$, $b=12{\cdot}184\pm0{\cdot}014$, $c=7{\cdot}332\pm0{\cdot}009$ Å, $Z=8$. Data for 1001 non-zero independent reflexions were collected on a Picker automated diffractometer. The crystal structure was solved by direct methods; refinement was carried out by full-matrix least-squares procedures including anisotropic thermal parameters. The conformation of the carboxylic groups is very similar to that of malonic acid. The molecules are held together in rows parallel to 2_1 axes by hydrogen bonds ($O\cdots O=2{\cdot}73$ Å); these rows are linked by different hydrogen bonds ($O\cdots O=2{\cdot}67$ Å) near symmetry centres. A two-dimensional network of hydrogen bonds is formed parallel to the plane (100).

Introduction

The dicarboxylic acids $COOH[CH_2]_nCOOH$ with *n* even or odd conform in general to the principle that the molecules in the crystal state are arranged in chains with the carboxylic groups of successive units joined by two hydrogen bonds related to each other by a centre of symmetry. This regularity has not always been observed in alkyl (Avitabile, Ganis & Lepore, 1971) or aryl (Avitabile, Ganis & Martuscelli, 1970) derivatives of dicarboxylic acids or in unsaturated dicarboxylic acids (Shahat, 1952). The mode of packing and the linking of these molecules through different systems of hydrogen bridges depend on the nature of the derivative. In order to gain more insight in this problem we have undertaken a structural study of a number of derivatives of malonic acid. In this paper we report the X-ray single crystal analysis of benzylmalonic acid  $COOH{-}\underset{\underset{\displaystyle CH_2{-}C_6H_5}{|}}{CH}{-}COOH$. The crystal structure analysis of some n-alkyl derivatives of the same acid and a comparative study in relationship with some of their physical properties is in progress and will be published elsewhere.

Experimental

A single crystal of benzylmalonic acid of dimensions $0{\cdot}20\times0{\cdot}20\times0{\cdot}15$ mm was chosen. Weissenberg photographs showed the crystal to belong to the orthorhombic space group *Pbca*. The crystal was mounted on a Picker automated diffractometer with the *c* axis parallel to the spindle axis. The cell constants were determined from a least-squares fit of the angular positions of 12 independent reflexions. Data were taken to a 2θ value of 45° with Zr-filtered Mo $K\alpha$ radiation. No attenuators were used. A take-off angle of 3°, a 2θ scan mode and a scan rate of $2°\ \mathrm{min}^{-1}$ were used for the data collection. Data were collected for 1233 reflexions of which 1001 were observed. The data were corrected for Lorentz and polarization effects but not for absorption.

Crystal data

Space group *Pbca*, $a=20{\cdot}780\pm0{\cdot}029$, $b=12{\cdot}184\pm0{\cdot}014$, $c=7{\cdot}332\pm0{\cdot}009$ Å; M.W. 194·19. $V=1856$ Å^3. $D_m=1{\cdot}37$, $D_x=1{\cdot}39$ g cm^{-3}. $Z=8$. $\mu(\mathrm{Mo}\ K\alpha)=2{\cdot}97$ cm^{-1}.

Determination of the structure and refinement

An overall temperature factor ($B=4{\cdot}00$) and a scale factor were calculated (Wilson, 1942) and used to compute normalized structure factors (E) (Karle & Hauptman, 1956). The structure was solved by weighted multisolution tangent refinement (Germain, Main & Woolfson, 1971). The 140 largest E's were used. The starting set of phases selected by iterative procedure (*CONVERGE*) was:

h	*k*	*l*	Phase	
3	6	1	0	origin fixing
2	4	3	0	
12	5	1	0	
0	12	2	$0,\pi$	
14	7	1	$0,\pi$	
3	2	2	$0,\pi$	
3	0	2	$0,\pi$	
2	8	1	$0,\pi$	

Of the 25 possible solutions, on the basis of probability characteristics, only one set of phases seemed to be correct. The corresponding E map revealed the whole structure except the hydrogen atoms. The structure was refined by a total of 13 full-matrix least-squares cycles; anisotropic thermal factors were assigned to all the non-hydrogen atoms after the seventh cycle when the conventional R value $(=\sum||F_o|-|F_c||/\sum|F_o|)$ was 0·15. When the value of R reached 0·085 the hydrogen atoms were included in the calculations with their geometrically determined positions and with isotropic thermal factors equal to the isotropic thermal factor of the carrier atom. They were not refined. The

R index dropped to the final value of 0·066. The function minimized was $\sum(w|F_c-KF_o|)^2$. The form of Cruickshank's (1949) weighting function was:

$$w=(0{\cdot}11111+1{\cdot}92\times10^{-3}F_{o\min}+3{\cdot}12\times10^{-6}F^2_{o\max})\,.$$

The atomic scattering factors were calculated from the analytical constants given by Moore (1963). The final positional and thermal parameters together with the corresponding standard deviations (for the non-hydrogen atoms) are listed in Table 1.*

Description of the structure

The most important conformational parameters of the molecule of benzylmalonic acid are listed in Table 2 and reported in Fig. 1. Most of them are quite normal and agree reasonably well with the values reported in the literature for similar compounds. For the short bond distance C(3)–C(4) 1·349 Å no specific explanation can be suggested, apart from casual errors in intensity data. Bond distances and bond angles of

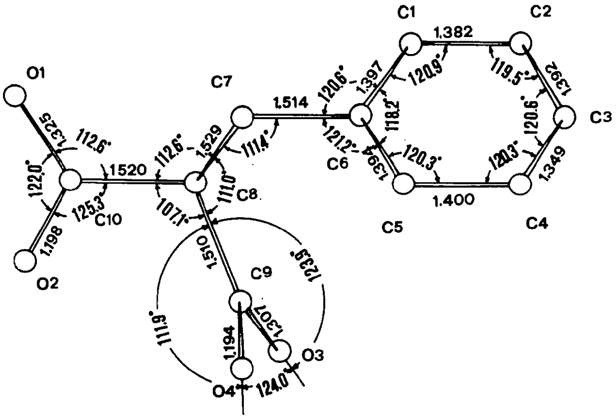


Fig. 1. Some molecular conformational parameters of benzylmalonic acid.

Table 1. *Final atomic parameters with their standard deviations*

(*a*) Positional parameters

	x	y	z
C(1)	0·7241 (2)	1·0168 (3)	0·4023 (6)
C(2)	0·7727 (2)	1·0942 (4)	0·4080 (6)
C(3)	0·7610 (2)	1·1960 (4)	0·4875 (6)
C(4)	0·7020 (2)	1·2215 (4)	0·5516 (7)
C(5)	0·6521 (2)	1·1444 (3)	0·5441 (6)
C(6)	0·6630 (2)	1·0403 (3)	0·4715 (5)
C(7)	0·6098 (2)	0·9554 (3)	0·4681 (6)
C(8)	0·5917 (2)	0·9242 (3)	0·2728 (5)
C(9)	0·5631 (2)	1·0209 (3)	0·1727 (5)
C(10)	0·5425 (2)	0·8320 (3)	0·2652 (5)
O(1)	0·5639 (1)	0·7400 (2)	0·3400 (4)
O(2)	0·4900 (1)	0·8385 (2)	0·1985 (4)
O(3)	0·5814 (1)	1·0241 (3)	0·0023 (4)
O(4)	0·5256 (1)	1·0835 (2)	0·2389 (4)
H(O1)	0·5293	0·6798	0·2986
H(O3)	0·5553	1·0697	−0·0733
H(C1)	0·7338	0·9363	0·3460
H(C2)	0·8198	1·0748	0·3523
H(C3)	0·7996	1·2567	0·4952
H(C4)	0·6932	1·3015	0·6112
H(C5)	0·6040	1·1663	0·5945
H(C7)	0·6254	0·8829	0·5413
H′(C7)	0·5676	0·9889	0·5364
H(C8)	0·6350	0·8984	0·1996

(*b*) Thermal parameters in the form:

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+B_{23}klb^*c^*)\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2·5 (1)	3·0 (2)	4·1 (2)	0·0 (1)	−0·3 (1)	0·3 (1)
C(2)	2·6 (2)	4·5 (2)	4·5 (2)	−0·5 (2)	−0·4 (2)	0·7 (2)
C(3)	4·2 (2)	3·6 (2)	5·1 (2)	−1·2 (2)	−1·1 (2)	0·6 (2)
C(4)	4·6 (2)	3·3 (2)	5·1 (2)	−0·6 (2)	−0·7 (2)	−1·0 (2)
C(5)	3·4 (2)	3·3 (2)	4·4 (2)	0·1 (2)	−0·2 (2)	−0·7 (2)
C(6)	2·3 (1)	2·2 (1)	3·4 (2)	−0·2 (1)	−0·3 (1)	0·2 (1)
C(7)	2·7 (1)	2·8 (2)	3·7 (2)	−0·3 (1)	−0·2 (1)	0·1 (1)
C(8)	2·2 (1)	1·7 (1)	3·3 (2)	0·0 (1)	0·0 (1)	0·2 (1)
C(9)	2·2 (1)	1·8 (2)	4·0 (2)	−0·2 (1)	−0·1 (1)	0·1 (1)
C(10)	2·8 (1)	1·9 (1)	3·6 (2)	0·2 (1)	0·0 (1)	0·3 (1)
O(1)	3·4 (1)	1·8 (1)	5·8 (2)	−0·2 (1)	−1·3 (1)	0·9 (1)
O(2)	2·4 (1)	2·9 (1)	5·8 (2)	−0·4 (1)	−1·0 (1)	1·1 (1)
O(3)	3·4 (1)	4·3 (1)	4·7 (1)	1·1 (1)	0·1 (1)	1·8 (1)
O(4)	4·3 (1)	2·4 (1)	5·4 (2)	1·3 (1)	−0·3 (1)	−0·2 (1)

Table 2. *Molecular geometry*

Bond distances (Å)

C(1)—C(2)	1·382 (6)
C(2)—C(3)	1·392 (7)
C(3)—C(4)	1·349 (7)
C(4)—C(5)	1·400 (6)
C(5)—C(6)	1·394 (6)
C(6)—C(1)	1·397 (5)
C(6)—C(7)	1·514 (5)
C(7)—C(8)	1·529 (5)
C(8)—C(9)	1·510 (5)
C(8)—C(10)	1·520 (5)
C(10)-O(1)	1·325 (5)
C(10)-O(2)	1·198 (4)
C(9)—O(3)	1·307 (5)
C(9)—O(4)	1·194 (4)

Bond angles (°)

C(1)—C(2)—C(3)	119·5 (2)
C(2)—C(3)—C(4)	120·6 (2)
C(3)—C(4)—C(5)	120·3 (2)
C(4)—C(5)—C(6)	120·3 (2)
C(5)—C(6)—C(1)	118·2 (2)
C(6)—C(1)—C(2)	120·9 (2)
C(5)—C(6)—C(7)	120·6 (2)
C(1)—C(6)—C(7)	121·2 (2)
C(6)—C(7)—C(8)	111·4 (1)
C(7)—C(8)—C(9)	111·0 (2)
C(7)—C(8)—C(10)	112·6 (2)
C(10)-C(8)—C(9)	107·1 (2)
C(8)—C(10)-O(1)	112·6 (2)
C(8)—C(10)-O(2)	125·3 (2)
O(1)—C(10)-O(2)	122·0 (2)
C(8)—C(9)—O(3)	111·9 (2)
C(8)—C(9)—O(4)	123·9 (2)
O(3)—C(9)—O(4)	124·0 (2)

Internal rotation angles (°)

C(5)—C(6)—C(7)—C(8)	117
C(6)—C(7)—C(8)—C(9)	65
C(6)—C(7)—C(8)—C(10)	175
C(7)—C(8)—C(10)-O(1)	61
C(7)—C(8)—C(10)-O(2)	119
C(7)—C(8)—C(9)—O(3)	142
C(7)—C(8)—C(9)—O(4)	41
O(1)—C(10)-C(8)—C(9)	176
O(2)—C(10)-C(8)—C(9)	3
C(10)-C(8)—C(9)—O(4)	82
C(10)-C(8)—C(9)—O(3)	95

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31108 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

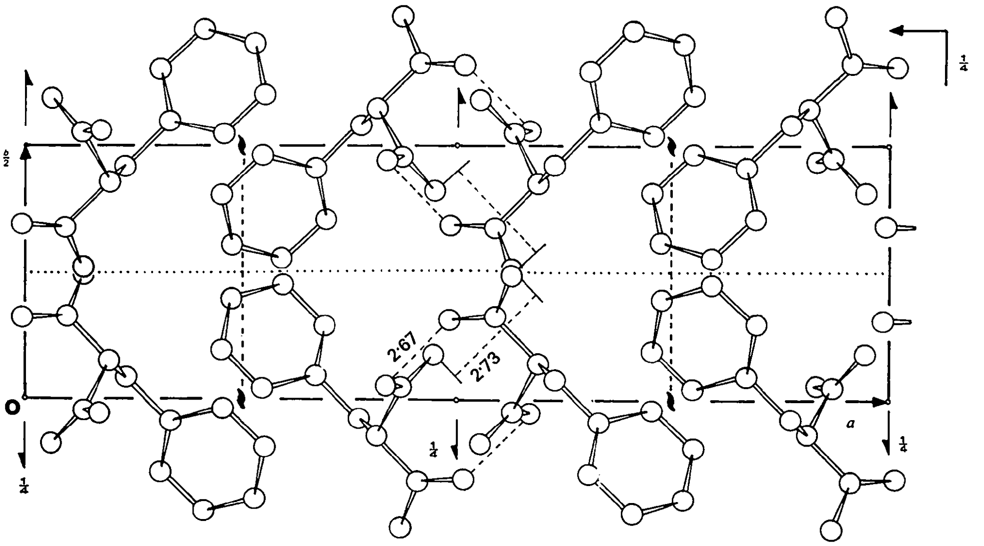


Fig. 2. Mode of packing of benzylmalonic acid along the [001] direction. Dotted lines indicate the hydrogen-bond distances.

the carboxylic groups clearly indicate the location of the carbonylic and carboxylic oxygens. One of the carboxylic groups is turned about 3° out of the plane C(9)–C(8)–C(10) while the other forms an angle with the same plane of about 84°; in this way O(2) realizes almost equal intramolecular contact distances with O(3) and O(4) [O(2)···O(3) = 3·1, O(2)···O(4) = 3·0 Å]. This conformation is almost identical with that found for malonic acid (Goedkoop & MacGillavry, 1956). The bond C(7)–C(6) is *trans* to the bond C(10)–C(8) [C(10)–C(8)–C(7)–C(6) = 175°] and the plane of the phenyl group nearly bisects the angle C(8)–C(7)–HC(7)1 [C(8)–C(7)–C(6)–C(5) = 117°].

Fig. 2 shows the mode of packing of the molecules along the [001] direction. The dotted lines indicate the hydrogen-bond distances. No significantly short intermolecular contact distances are found. The molecules are linked through hydrogen bonds (2·73 Å) along 2_1 axes parallel to **b**. These molecular rows are linked together through a different system of hydrogen bonds (2·67 Å) about symmetry centres. Thus a two-dimensional network parallel to the plane (100) is formed. The arrangement of one layer (at $x=0$) of molecules of benzylmalonic acid is shown in Fig. 3. Such a system of hydrogen bridges is quite unusual for dicarboxylic acids; two-dimensional networks of hydrogen bonds were found in other cases (Shahat, 1952), but they are realized in a completely different way. The layers are bound together by weak dispersion forces which arise between phenyl groups piled along 2_1 axes parallel to **c** and interlocked through the glide planes *c* giving intermolecular contact distances greater than 3·4–3·5 Å.

The weakness of these forces accounts for larger thermal parameters normal to the layers (B_{33}).

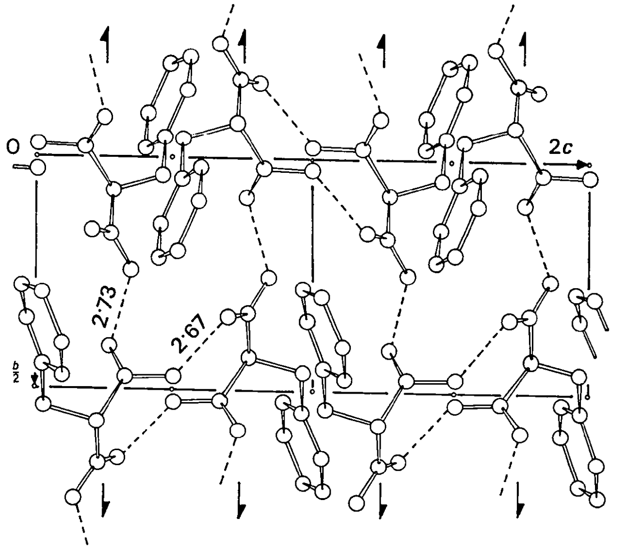


Fig. 3. Arrangement of one layer (at $x=0$) of benzylmalonic acid (one unit cell).

We are most grateful to Dr G. Germain, who made possible for us the use of programs and computer facilities in the first stages of the calculations, and to Professor M. Goodman for giving us the opportunity of using the Picker automated diffractometer.

References

Avitabile, G., Ganis, P. & Lepore, U. (1971). *Macromolecules*, **4**, 239–241.

Avitabile, G., Ganis, P. & Martuscelli, E. (1970). *Chem. Commun.* pp. 1362–1363.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65–82.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Goedkoop, J. A. & MacGillavry, C. H. (1956). *Acta Cryst.* **10**, 125–127.

Karle, J. & Hauptman, H. (1956). *Acta Cryst.* **9**, 635–651.

Moore, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.

Shahat, M. (1952). *Acta Cryst.* **5**, 763–768.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.