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Crystal Structure and Conformation of Methylmalonic Acid

BY J. L. DERISSEN

Laboratorium voor Kristalchemie, Rijksuniversiteit, Utrecht, The Netherlands

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The conformation and molecular structure of methylmalonic acid in the crystalline state have been investigated by three-dimensional X-ray analysis of twinned crystals. One of the carboxyl groups is nearly coplanar with the methyl carbon atom, the other carboxyl group is rotated out of the plane of the carbon atom chain and decreases intramolecular oxygen–oxygen interaction.

Introduction

In monocarboxylic acids the β-carbon atom is fairly coplanar with the atoms of the CCOOH group (Kanters, Kroon, Peerdeman & Schoone, 1967). In dicarboxylic acids the same situation is found for the even members of the series, whereas for the odd members the carboxyl groups are rotated several degrees out of the chain plane (Kanters *et al.*, 1967).

In malonic acid (Goedkoop & MacGillavry, 1957) the two carboxyl groups are nearly perpendicular to each other. This is easily explained by steric hindrance of the oxygen atoms involved. Substitution of one of the α-hydrogen atoms by a hydroxyl, fluoro, amino or methyl group gives rise to several possibilities: the α-substituent may be coplanar with one of the two carboxyl groups while the other carboxyl group takes a favourable position with respect to the carbon atom chain, or with respect to the α-hydrogen atom, or the α-substituent may be as coplanar as possible with both carboxyl groups. In all cases the oxygen–oxygen interactions of the two carboxyl groups have to be taken into account.

In tartronic (=hydroxymalonic) acid (van Eijck, Kanters & Kroon, 1965) it appears that both carboxyl groups are nearly coplanar with the hydroxyl group. The same conformation has been found in aminomalonic acid (Kanters, Kroon, Beurskens & Vliegenthart, 1966). However, in this case, electrostatic forces due to the zwitterion may play an important part. In fluoromalonic acid (Roelofsen, 1969) the same conformation has again been found.

In methylmalonic acid one might expect to find this conformation also. However, when the α-substituent is a methyl group, the energy barriers for rotation of a carboxyl group around a C–C bond are expected to be much less than in a hydroxyl- or fluoro-substituted molecule (van Eijck, 1966). Therefore it might be possible that in this case the effect of oxygen–oxygen interaction is more important than the formation of two nearly coplanar systems of a carboxyl group and a methyl group. The most favourable situation would then be the occurrence of one coplanar system of a carboxyl group and a methyl group and rotation of the other carboxyl group to a position where there is no steric hindrance of the oxygen atoms. The latter position could be one where the carboxyl group and the α-hydrogen atom, or the carboxyl group and the carbon atom chain, are coplanar.

Experimental

Slow evaporation of a 1:1 benzene–acetone solution of methylmalonic acid yielded twinned triclinic crystals. The measured density was 1·47 g.cm^{-3}. The cell constants were determined as:

$a=5{\cdot}63, b=5{\cdot}24, c=11{\cdot}39$ Å; $\alpha=117, \beta=76, \gamma=114°$.

(A reduced cell can be determined with:

$a=5{\cdot}63, b=10{\cdot}14, c=5{\cdot}24$ Å; $\alpha=94, \beta=114, \gamma=93°$.

The transformation matrix between the set used here and the reduced set is 100/011/010). The calculated density, with 2 molecules in the unit cell is 1·455 g.cm^{-3}.

The space group was assumed to be $P\bar{1}$ and this was later corroborated by the structure analysis. The twinned lattices had a common a^* axis (*i.e.*(100) was the twin-plane).

With Cu $K\alpha$ radiation the integrated intensities of 376 reflexions were measured on $h0l$, $h1l$, $hk0$ and $0kl$ Weissenberg diagrams and on $h1l$, $h2l$, $h3l$, $h4l$ and $h5l$ retigrammes. The average ratio of the intensities of the two lattices was 1·25 (varying from 1·10 to 1·40). The scaling factors for the $h2l$, $h3l$, $h4l$ and $h5l$ reflexions were rather uncertain because of the small number of reflexions available for scaling.

Structure determination and refinement

From a sharpened (Jacobsen, Wunderlich & Lipscomb, 1961) Patterson synthesis and comparison with the structure of malonic acid (Goedkoop & MacGillavry, 1957) the structure of methylmalonic acid could be found directly by verification of O–O vectors. The structure was refined by the least-squares [block-diagonal approximation (Rutten-Keulemans, 1961)] method. All weights were taken as 1·0 (an approximation in accordance with the large intensity errors). After a few cycles of refinement and the inclusion of hydrogen atoms the R value ($R=\sum ||F_{\text{obs}}|-|F_{\text{calc}}||/\sum |F_{\text{obs}}|$) was

0·080. Calculated and observed structure factors are given in Table 1, temperature factors and coordinates in Table 2.

The average standard deviations from the least-squares program are: for oxygen and carbon coordinates 0·01 Å, for hydrogen coordinates 0·12 Å and for any anisotropic U_{ij} term 0·005 units.

Description of the structure

The molecular parameters are given in Fig. 1. Because of the large uncertainties in the intensity measurements, the accuracy of the molecular parameters is not very high; the accuracy of the bond lengths is approximately 0·03 Å.

Table 1. *Observed and calculated structure factors*

Scaling factor = 5·0.

h	k	l	F_c	F_o
0	0	1	-16	-16
		2	-29	-29
		3	-38	-39
		4	-145	-141
		6	-91	-91
		7	31	31
		8	37	39
		10	10	13
1	0	-10	-26	-26
		-7	-31	-32
		-6	-26	-29
		-5	-27	-26
		-4	110	111
		-3	149	146
		-2	-88	-86
		0	-63	-59
		2	-105	-98
		3	-145	-142
		4	120	123
		5	16	14
		6	48	50
		7	36	37
		8	-37	-38
2	0	-10	9	9
		-9	-6	-9
		-8	21	23
		-6	-36	-34
		-5	21	27
		-4	34	35
		-3	12	11
		-2	-61	-65
		-1	-24	-28
		0	-54	-53
		2	55	56
		3	31	33
		4	18	14
		5	-23	-26
		6	10	8
		7	-20	-22
		8	-19	-15
		9	10	10
		10	26	24
3	0	-10	-25	-20
		-9	-15	-17
		-6	30	29
		-5	16	15
		-4	37	37
		-3	-35	-39
		0	-58	-62
		1	58	62
		2	-12	-12
		3	26	28
		4	-37	-37
		5	-18	-18
		6	59	60
		7	-19	-17
4	0	-9	18	16
		-8	18	17
		-6	8	9
		-5	-15	-17
		-4	-58	-57
		-3	-17	-16
		-2	22	25
4	0	0	32	34
		1	-8	-11
		2	32	34
		4	-52	-54
		5	35	37
		6	-8	-10
		9	-19	-21
		10	15	18
5	0	-7	-12	-8
		-3	21	17
		-2	28	30
		-1	10	11
		0	-27	-28
		1	-13	-11
		2	10	11
		3	-13	-14
		4	10	12
-6	1	-1	-25	-30
		1	15	21
-5	1	-8	13	17
		-4	-26	-22
		-3	34	29
		0	27	27
		3	-31	-31
-4	1	-5	-31	-26
		-4	27	21
		-3	22	21
		-2	-22	-22
		0	-54	-57
		3	11	15
		4	46	47
		5	16	17
		8	-15	-16
-3	1	-5	-50	-42
		-3	-35	-34
		-2	-20	-22
		-1	26	30
		0	19	18
		1	65	72
		2	38	45
		3	31	34
		4	-17	-19
		5	-67	-68
		6	-34	-36
-2	1	-8	-46	-34
		-5	43	42
		-4	60	57
		-3	-90	-88
		-2	138	130
		0	20	23
		1	-27	-36
		2	-97	-109
		3	55	61
		4	-75	-84
		5	-14	-15
		6	47	51
		7	30	32
		8	27	24
		9	-13	-13
-1	1	-8	33	29
		-4	-132	-122
		-3	18	19
		-2	-9	-13
-1	1	-1	127	112
		0	100	106
		1	-242	-238
		2	112	121
		3	-32	-38
		4	-10	-12
		5	42	48
		6	-28	-30
		7	33	34
		8	-28	-27
		9	-17	-18
0	1	-12	17	20
		-11	-41	-43
		-10	8	8
		-9	22	21
		-3	-32	-35
		-2	7	10
		-1	61	70
		0	-218	-209
		1	-76	-86
		2	-25	-28
		3	8	13
		4	96	101
		5	-6	-10
		6	25	30
		7	-18	-18
		8	-20	-19
		9	21	19
1	1	-8	48	40
		-5	36	35
		-4	-65	-80
		-3	-81	-77
		-2	-147	-139
		0	25	30
		1	161	167
		2	75	82
		4	20	21
		5	-40	-49
		6	-17	-21
		7	-33	-37
		9	29	28
2	1	-5	-48	-44
		-4	23	19
		-2	93	92
		0	59	59
		1	70	80
		2	-116	-121
		3	-26	-29
		4	-60	-64
		5	31	36
		6	24	27
		7	-24	-25
		8	39	39
3	1	-3	49	42
		-1	-39	-34
		1	-30	-29
		2	17	20
		3	-26	-26
		4	20	19
		5	51	49
		6	-33	-34
		8	-15	-15
4	1	-4	25	16
4	1	-1	-26	-24
		1	18	15
		5	-16	-16
-4	2	1	32	33
-3	2	-8	-33	-32
		-7	25	31
		-5	48	49
		-3	24	23
		-2	80	78
		-1	-60	-66
		1	-45	-50
		2	-21	-22
		4	-44	-38
		5	52	48
-2	2	-9	38	35
		-8	18	21
		-7	50	52
		-6	74	75
		-5	-41	-44
		-4	-105	-107
		-2	-65	-81
		-1	-23	-23
		0	-51	-52
		1	15	13
		2	122	117
		4	45	40
		6	-30	-23
-1	2	-10	92	90
		-9	-25	-28
		-8	-40	-43
		-7	-13	-14
		-6	-71	-71
		-5	-18	-23
		-4	-52	-56
		-3	48	52
		-1	22	25
		1	54	57
		3	-24	-25
		4	-15	-16
		5	-41	-38
0	2	-13	26	32
		-12	-30	-34
		-11	40	34
		-10	-11	-13
		-9	-44	-45
		-8	6	8
		-7	-35	-34
		-6	103	107
		-5	-21	-30
		-4	16	15
		-3	15	13
		-2	-73	-75
		-1	54	57
		0	-34	-32
		1	28	28
		2	-41	-43
		4	18	16
		5	-22	-19
		6	16	17
		8	21	17
		9	-9	-9
1	2	-8	-21	-20
		-6	-25	-29
1	2	-5	-17	-18
		-4	38	46
		-3	-29	-28
		-2	52	52
		0	67	70
		1	-57	-54
		2	-70	-65
		3	35	36
		4	-21	-19
		5	35	25
2	2	-5	22	22
		-4	52	56
		-3	-22	-24
		-2	-54	-58
		0	-12	-13
		1	-25	-23
		2	21	18
		4	44	37
3	2	-6	-46	-46
		-5	34	30
		-3	-20	-22
		0	39	39
-4	3	-6	-32	-32
		-5	-31	-33
		-4	-27	-26
-3	3	-6	-35	-33
		-5	-27	-28
		-3	27	25
		-2	-22	-27
		0	-19	-15
-2	3	-9	-84	-85
		-8	21	23
		-7	-32	-36
		-6	-37	-41
		-5	32	32
		-3	68	58
		0	32	37
-1	3	-10	-36	-84
		-8	24	28
		-7	23	31
		-6	103	118
		-5	-12	-17
		-4	51	61
		-2	-46	-49
		0	-59	-58
		3	30	27
0	3	-13	-30	-29
		-12	-6	-7
		-10	13	16
		-9	59	57
		-8	19	19
		-7	10	14
		-6	-36	-36
		-5	-36	-38
		-4	-49	-51
		-3	-40	-39
		-2	44	42
		-1	17	20
		0	24	19
		1	-22	-22
		2	36	37
		3	15	16
0	3	4	-22	-19
		5	7	11
		6	-18	-16
		7	7	9
1	3	-8	-58	-55
		-5	34	34
		-4	23	23
		-2	40	37
		0	-36	-27
2	3	-7	-15	0
		-5	43	38
		-4	-59	-53
		0	27	25
-5	4	-6	-27	-26
-4	4	-5	61	58
		-4	39	39
-3	4	-8	66	63
		-7	-19	-19
		-6	22	21
		-4	-46	-43
		-3	-23	-26
		-2	-36	-35
-2	4	-10	-18	-23
		-9	44	44
		-5	-40	-39
		-4	22	16
		-2	33	33
-1	4	-10	18	20
		-9	18	20
		-8	-24	-28
		-6	-16	-19
		-5	-18	-22
		-4	3	11
		-3	16	20
		-2	15	19
0	4	-12	23	23
		-11	-10	-6
		-9	-44	-48
		-8	-44	-44
		-7	34	37
		-6	-8	-9
		-5	39	39
		-4	4	6
		-3	10	10
1	4	-8	43	39
		-6	31	35
		-5	-13	-19
		-4	-46	-48
		-3	24	29
		-2	-32	-32
0	5	-11	6	7
		-10	-12	-14
		-9	8	9
		-8	26	26
		-7	-15	-22
		-6	6	17
		-5	-22	-23
		-4	5	11
		-3	14	17
		-2	-17	-15
		-1	21	18
		0	-11	-12

Table 2. *Final fractional atomic coordinates and thermal parameters*

The U_{ij} coefficients are given by the expression for the temperature factor:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2a^*b^*hkU_{12}+2b^*c^*klU_{23}+2c^*a^*lhU_{31})\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
O(1)	0·4560	0·3320	0·1028	0·064	0·076	0·054	0·104	0·073	0·049
O(2)	0·2447	0·6303	0·1068	0·086	0·088	0·053	0·112	0·099	0·043
O(3)	0·5030	0·6845	0·3978	0·068	0·049	0·041	0·007	0·052	−0·023
O(4)	0·2182	0·2742	0·4234	0·066	0·047	0·040	0·002	0·056	−0·018
C(5)	0·2897	0·4606	0·1529	0·035	0·044	0·018	0·006	0·036	0·005
C(6)	0·1246	0·4423	0·2738	0·047	0·049	0·020	0·044	0·032	0·015
C(7)	0·2801	0·4553	0·3705	0·051	0·043	0·013	0·023	0·016	−0·005
C(8)	−0·1139	0·1473	0·2295	0·035	0·064	0·052	0·012	0·060	0·001
H(9)	0·966	0·959	0·193	B isotropic = 3·5 Å^2					
H(10)	0·767	0·145	0·302						
H(11)	0·764	0·188	0·175						
H(12)	0·050	0·620	0·321						
H(13)	0·377	0·610	0·035						
H(14)	0·621	0·696	0·459						

As in malonic acid (Goedkoop & MacGillavry, 1957) the molecules are arranged in infinite chains, the double hydrogen-bonded carboxyl groups being grouped in the well-known ring configuration around centres of symmetry. The molecular orientation is shown in Fig. 2.

The carbon atoms C(5), C(6), C(7) are located in a plane nearly parallel to the *ac* crystallographic plane. Any carboxyl group and the central carbon atom form a planar group. It appears that one of these groups is nearly coplanar with the methyl group (the angle between the C(5), C(6), C(7) plane and the C(8), C(6), C(7) plane is 60°, the relevant angle between the C(5), C(6), C(7) and C(6), C(7), O(3), O(4) planes is 52°). The carbonyl oxygen atom is *cis* to the methyl group, which is usual for α-substituted carboxylic acids [one exception is known, the hydroxyl oxygen atom in the *cis* position in *meso*-tartaric acid (Bootsma & Schoone, 1967)]. The other CCOOH group is located in a position midway between the carbon atom chain and the α-hydrogen atom (the relevant angle between the C(5), C(6), O(2), O(1) and C(5), C(6), C(7) planes is 38°). Atoms O(1), C(8) and O(4) are on the same side of plane C(5), C(6), C(7), and the angle between the planes O(3), O(4), C(7) and O(1), O(2), C(5) is 71°.

In contrast with the situation in tartronic (van Eijck *et al.*, 1965) and fluoromalonic (Roelofsen, 1969) acid, only the second carboxyl group has rotated, increasing the O(1)–O(3) distance to 3·03 Å. Hence it might be inferred that the barrier to rotation for a carboxyl group in an α-methyl substituted carboxylic acid is rather low compared with that in –F or –OH substituted acids.

In contrast to what might be expected from the usual coplanarity of a carboxyl group and the carbon atom chain in monocarboxylic acids, the second carboxyl group takes a rather arbitrary position. To explain this it might be necessary to perform rather laborious calculations on the conformational energy.

Two more remarkable points are the long O(4)–O(3′) bridge distance and the large O(4)–C(7)–C(6) angle.

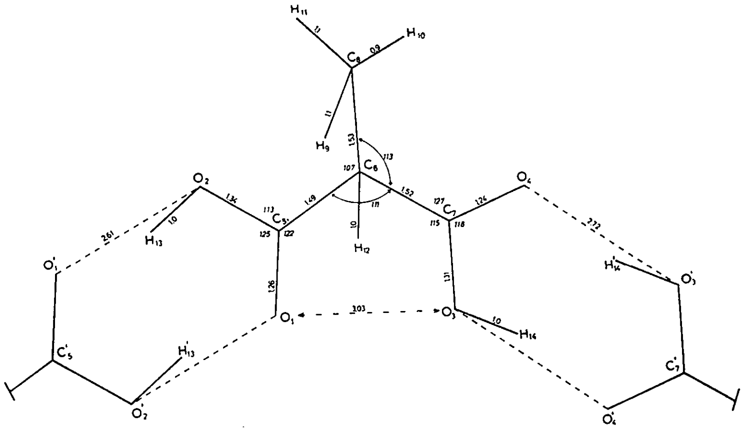

Fig. 1. Distances (Å) and angles (degrees) in methylmalonic acid.

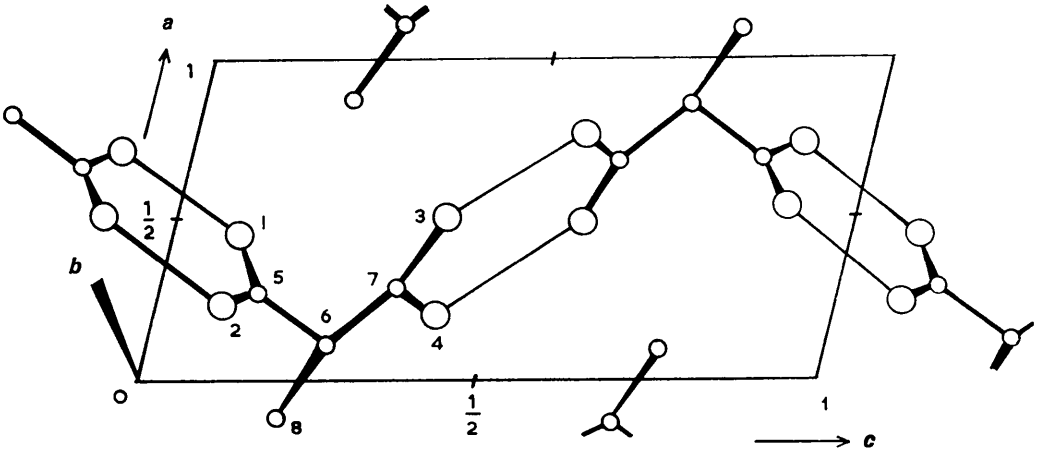

Fig. 2. Projection of methylmalonic acid structure on the *ac* plane.

The conformation of the hydrogen atoms around the C(6)–C(8) bond is staggered.

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References

Bootsma, G. A. & Schoone, J. C. (1967). *Acta Cryst.* **22**, 522.

Eijck, B. P. van (1966). *Rec. Trav. Chim. Pays-Bas*, **85**, 1129.

Eijck, B. P. van, Kanters, J. A. & Kroon, J. (1965). *Acta Cryst.* **19**, 435.

Goedkoop, J. A. & MacGillavry, C. H. (1957). *Acta Cryst.* **10**, 125.

Kanters, J. A., Kroon, J., Beurskens, P. T. & Vliegenthart, J. A. (1966). *Acta Cryst.* **21**, 990.

Kanters, J. A., Kroon, J., Peerdeman, A. F. & Schoone, J. C. (1967). *Tetrahedron*, **23**, 4027.

Jacobsen, R. A., Wunderlich, J. A. & Lipscomb, W. N. (1961). *Acta Cryst.* **14**, 598.

Roelofsen, G. (1969). Private communication.

Rutten-Keulemans, E. W. M. (1961). *Least Squares Program for Electrologica X1 Computer.*

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Refinement of the Structure of Ammonium Triiodide, NH_4I_3

By G. H. Cheesman and A. J. T. Finney

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

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A new study closely confirms the structure and dimensions ascribed by R.C.L. Mooney in 1935, but indicates the triiodide ion to be linear.

The initial investigation by Mooney (1935) into the structure of ammonium triiodide, NH_4I_3, confirmed the assignment of this polyiodide to the orthorhombic system made by Groth (1908) on the basis of morphology. Mooney found that the unit cell contained four molecules and that the systematic absences were consistent with the space group *Pmcn*, limiting the atomic positions of the triiodide group to planes with x coordinates $x=\frac{1}{4}$ and $x=\frac{3}{4}$. The structural analysis was carried out through trial-and-error methods based on 144 qualitatively visually estimated intensities collected photographically by the oscillation method. She found the triiodide unit to be both non-linear (177°) and asymmetric with interiodine distances of 2·82 and 3·10 Å.

In view of the recent theoretical interest in crystalline polyiodides, in particular the work of Brown & Nunn (1966) on the configuration of the triiodide ion, it was considered worth while to attempt the refinement of this structure. In this connexion it was hoped that an examination of the thermal parameters of the triiodide iodine atoms would support their hypothesis that the asymmetric electrostatic environment of the anion stabilizes the asymmetric anion geometry.

This refinement confirms to a remarkable degree Mooney's structure for this compound.

Experimental

Crystals of ammonium triiodide suitable for X-ray analysis were prepared from a concentrated aqueous solution of A.R. grade ammonium iodide and resublimed iodine. The composition of this solution was adjusted with reference to Briggs's (Briggs, Ballard, Alrich & Wikswo, 1940) phase diagram for the system iodine–ammonium iodide–water to ensure that the only solid phase formed on evaporation was the anhydrous triiodide. The crystals so prepared were freed from mother liquor by rapid suction filtration on a sintered glass disk and then rapidly transferred to a dry Lindemann glass tube which was then sealed. As ammonium triiodide readily decomposes with loss of iodine, a number of crystals were packed into the one tube and some of these intentionally destroyed during the sealing process in order to create a significant iodine partial pressure within the tube from the outset. It was found that specimens prepared in this way could be preserved intact out of the X-ray beam for periods in excess of one month. However, as Mooney observed, as soon as a small crystal was brought into the X-ray beam, decomposition began with free iodine being deposited on the tube walls adjacent to the crystal.

The cell dimensions as determined from single-crystal photographs agreed with those found by Mooney and the same systematic absences were observed. In Table 1 the cell dimensions measured in this study and those of Mooney are compared; for convenience in the subsequent refinement calculations the axial labelling has been changed to conform to *International Tables for X-ray Crystallography* (1952) standard orientation for space group *Pnma*.