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Application of the Symbolic Addition Method to Dimethylmalonic Acid

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Dimethylmalonic acid, $C(CH_3COOH)_2$, crystallizes in the tetragonal system with the space group $I4_1/acd$ and lattice constants: $a=12{\cdot}644$, $c=16{\cdot}233$ Å. The crystal structure was determined by the symbolic addition method and refined by least-squares methods. The structure consists of spirals of doubly hydrogen bonded molecules which form a 163° angle between the planes of the carboxyl groups. The molecule rests on, and is hydrogen bonded across, twofold axes; the hydrogen bonding distance is 2·64 Å.

Introduction

Studies several years ago (Box, Freund & Lilga, 1961) on radiation induced free radical formation in crystalline dimethylmalonic acid, $C(CH_3COOH)_2$, stimulated an attempt to solve the crystal structure by conventional methods. This attempt failed, but the crystal structure has now been determined without difficulty by the application of the symbolic addition method (Karle & Karle, 1963).

We describe in this paper the application of the symbolic addition method to dimethylmalonic acid, which belongs to the high symmetry space group $I4_1/acd$.

Experimental

Preliminary crystallographic investigation established the crystals to be tetragonal with the lattice constants: $a=12{\cdot}64_4$, $c=16{\cdot}23_3$ Å (both $\pm 0{\cdot}005$ Å) and systematic absences:

hkl	$h+k+l=2n+1$
$0kl$	$l=2n+1$
$hk0$	$h=2n+1$
hhl	$2h+l=4n+1$

The space group is uniquely determined by these conditions to be $I4_1/acd$ (no. 142; origin at $\bar{1}$). The measured density, 1·35 g.cm^{-3}, indicated that there are 16 molecules in the unit cell (calc. density, 1·352 g.cm^{-3}); this requires the central carbon atom to be on one of the three different sets of twofold axes, and the asymmetric unit to be one-half of the molecule.

Three-dimensional intensities with $2\theta \le 160°$ were collected by the stationary-crystal stationary-counter technique on a General Electric XRD5 spectrogoniometer with the Single Crystal Orienter using Cu $K\alpha$ radiation and Ni–Co balanced filters. A total of 652 independent reflections were measured of which 342 (52·5%) had intensities less than twice the background. This distribution of intensities was attributed to the high symmetry of the crystal.

The intensities were converted to $|F|^2_{\text{obs}}$ and corrected for $K\alpha$ splitting; no absorption correction was applied (the unobserved intensities were given a value equal to one-half of the minimum observable value). The $|F|^2_{\text{obs}}$ were put on an absolute scale as well as corrected for vibrational motions by least-squares fitting a $K(s)$ curve ($s=\sin\theta/\lambda$) of the form $K(s)=\exp(A+Bs^{2X})$ (Karle & Hauptman, 1953; Karle, Hauptman & Christ, 1958; Clark & Christ, 1960); the resulting parameters are: $A=1{\cdot}21$, $B=12{\cdot}73$, and $X=1{\cdot}5$.

Using the following values for ε as dictated by the space group, the normalized structure factors $|E_h|$ were calculated (Karle & Hauptman, 1956): $\varepsilon=4$ for $00l$, $\varepsilon=2$ for $hk0$, $0kl$, and hhl; otherwise, $\varepsilon=1$. The statistical averages of the normalized structure factors $|E|$ are shown in Table 1. The experimental values are compared with the theoretical values obtained for a random distribution of atoms in the unit cell. The experimental averages of the normalized structure factors indicated that the structure is hyper-centrosymmetric and gave an abnormal distribution of $|E|$ values.

Table 1. *Normalized structure factors*

Averages

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle\|E\|\rangle$	0·661	0·798	0·886
$\langle\|E^2-1\|\rangle$	1·097	0·968	0·736

Distribution

	Experimental	Theoretical
$\|E\|>3$	1·4%	0·3%
$\|E\|>2$	4·3	5·0
$\|E\|>1$	14·9	32·0

Structure determination and refinement

A listing of the vector combinations in the Σ_2 sum for all vectors in reciprocal space with $|E|\ge 1{\cdot}5$ was prepared. Only one phase need be assigned in order to fix the unit cell origin in this space group (Hauptman & Karle, 1953, p. 14); this assignment must be made to a vector of the form *guu* or *ugu*. As no suitable large $|E|$ with *hkl* of this form was available, the assignment was not made until near the end of the phase determination when the vector (1, 14, 1) was given the phase of zero. Six letters were assigned to large $|E|$ values as needed in order to give letter phases to 60 vectors (Table 2). By suitable letter combinations found during this process, the number of unknown letters was reduced to

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two, *c* and *e*. The letter *a* was found to be minus from various combinations. No combination of signs for these two letters could be eliminated, for all four combinations gave 30 plus and minus phases to the 60 vectors (Karle & Karle, 1964).

Table 2. *Letter assignments and combinations*

Letter assignments

hkl	*E*	Phase	
1,14, 1	2·49	+	Origin assignment
8, 8, 0	3·96	*a*	
1, 5,14	3·54	*b*	
3, 5,12	3·37	*c*	
0, 8,10	3·29	*e*	
2, 8,12	3·20	*f*	
5, 7,16	3·45	*h*	

Letter combinations

$a=-$ $f=-e$

$b=-c$ $h=-c$

The correct phase for both *c* and e is minus.

Four *E* maps (Karle, Hauptman, Karle & Wing, 1958) were computed using the 60 vectors. Two of the maps were readily rejected as no peak occurred along any of the three twofold axes. One of the other two maps had two peaks 1·6 Å apart on the twofold axis at $\frac{1}{4}$, *y*, 0 and was eliminated for this reason. The fourth map (Fig. 1), computed with both *c* and *e* as minus signs, had one peak on the twofold axis $\frac{1}{4}$, *y*, 0 and a suitable set of surrounding peaks, all greater than three times the background.

The five positions obtained from the fourth *E* map were subjected to a least-squares refinement (Busing, Martin & Levy, 1962; scattering factor curves from *International Tables for X-ray Crystallography*, 1962) on the IBM 7030 computer (STRETCH). After two cycles of refinement, these coordinates gave an *R* value of 0·25. With two more cycles of refinement with isotropic temperature factors and three cycles with anisotropic temperature factors [for all atoms except C(2)], the *R* value was reduced to 0·098 (unit weights were used for all structure factors, and the unobserved intensities were not included in these refinements).* The results of the least-squares refinement are presented in Table 3, and the final electron-density synthesis is shown in Fig. 2; significant interatomic distances and angles are listed in Table 4.

It is worth noting that 59 of the 60 phases used to compute the fourth *E* map had the correct phase; the incorrect one was the smallest *E* value (1·5) of the 60.

Table 4. *Significant interatomic distances* (±0·010 Å) *and angles* (±0·5°)

O(1)–C(1)	1·317 Å
O(2)–C(1)	1·214
C(1)–C(2)	1·533
C(2)–C(3)	1·551
O(1)---O(2′)	2·645 Hydrogen bond
O(1)–C(1)–O(2)	122·7°
O(1)–C(1)–C(2)	133·9
O(2)–C(1)–C(2)	123·3
C(1)–C(2)–C(3)	110·0
C(3)–C(2)–C(1′)	107·5
C(1)–C(2)–C(1′)	106·2
C(3)–C(2)–C(3′)	115·2
C(1)–O(1)---O(2′)	111·3

Angle between planes O(1)–C(2)–O(2) and C(1)–C(2)–C(1′) is 89·4°.

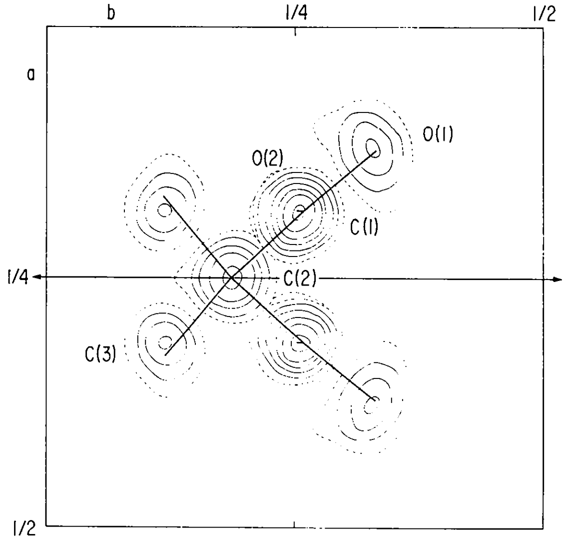

Fig. 1. View down the *c* axis of one dimethylmalonic acid molecule obtained from an *E* map computed with 60 phases. Background peaks were less than the first solid contour (contours at equal but arbitrary levels; zero contour dotted).

Table 3. *Coordinates and thermal parameters* of the atoms*

Atom	*x*	*y*	*z*	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23} (×10⁴)
O(1)	0·1281	0·3310	0·0170	88	80	34	31	08	05
σ	5	4	3	5	5	3	4	3	3
O(2)	0·1852	0·2525	0·1311	75	80	27	21	08	02
σ	4	5	3	5	5	2	4	3	3
C(1)	0·1858	0·2607	0·0566	55	54	34	−09	14	−02
σ	6	7	4	6	6	3	5	4	4
C(2)	0·2500	0·1879	0·0000	53	53	32			
σ	0	8	0	4	4	3			
C(3)	0·3296	0·1222	0·0515	105	71	49	39	33	25
σ	7	7	5	9	7	4	6	5	5

* $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$

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* A 35 mm microfilm containing the observed and calculated structure factors has been deposited as Document Number 8380 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington, D.C. Microfilm copies can be obtained by an advance payment of $1·25 to the Chief, Photoduplication Service, Library of Congress.

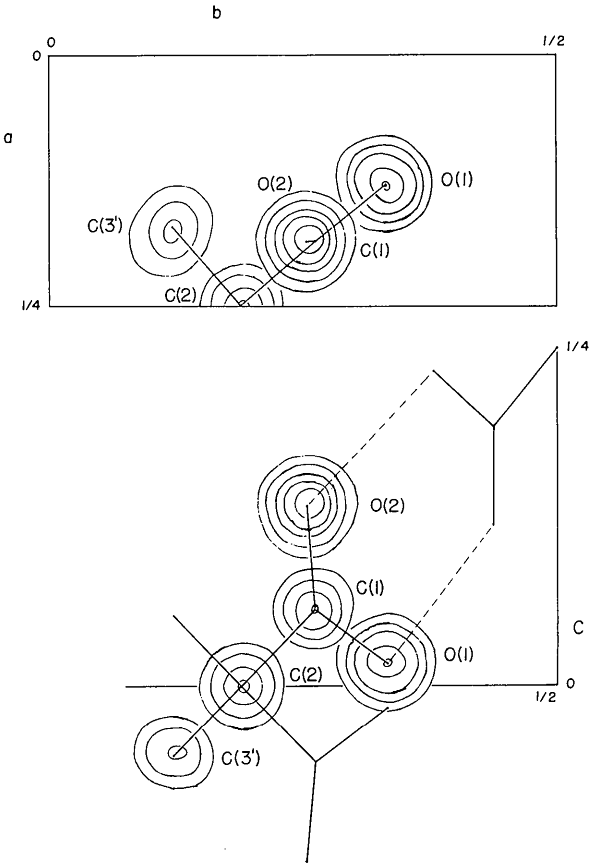


Fig. 2. The final electron-density synthesis showing the molecule as in Fig. 1 as well as a composite projection on a plane at $x=\frac{1}{4}$.

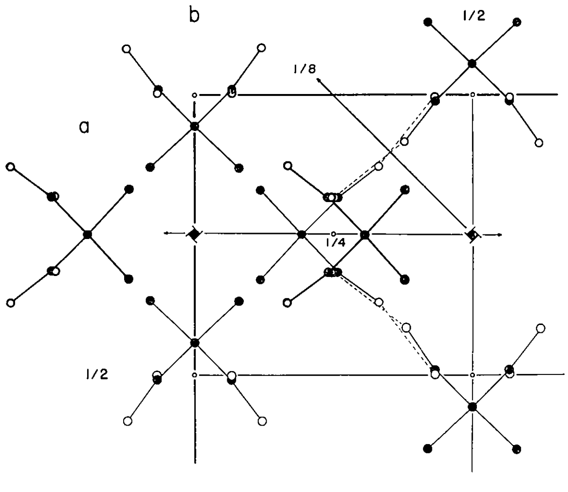
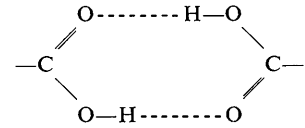


Fig. 3. Packing diagram showing the spirals of doubly hydrogen bonded molecules parallel to the *c* axis and the various twofold axes.

Discussion

The molecular dimensions obtained here are very similar to those obtained from the crystal structure of malonic acid (Goedkoop & MacGillavry, 1957). The carboxyl groups are doubly hydrogen bonded in the same manner, *i.e.*



but across a twofold axis instead of a center of inversion. The dimethylmalonic acid molecule rests on the twofold axis $\frac{1}{4}, y, 0$ and is hydrogen bonded to a symmetry related molecule across the twofold axis $x, \frac{1}{4}+x, \frac{1}{8}$. As the plane of the carboxyl group is not perpendicular to the latter twofold axis, the doubly hydrogen bonded carboxyl groups form a dihedral angle of 163°. The oxygen–oxygen distance is 2·645 Å.

The crystal structure consist of spirals of hydrogen bonded molecules with the methyl groups of other molecules filling the helical grooves (Fig. 3). The hydrogen bonds hold the molecules rigid and do not permit the methyl groups to make close contacts with each other; the nearest methyl–methyl contact is 4·33 Å.

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