Crystal and Molecular Structures of DL-Methylsuccinic Acid.
I. A Modification Obtained by Sublimation at 70°C *in vacuo*

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The structure of the modification of DL-methylsuccinic acid [HOOC–CH$_2$–CH(CH$_3$)–COOH], obtained by sublimation at 70°C, has been determined from three-dimensional X-ray data. The crystals are monoclinic with $a=22\cdot119$, $b=5\cdot230$, $c=11\cdot239$ Å, $\beta=103\cdot73°$, $Z=8$, space group $C2/c$. The structure was solved by direct methods and refined by block-diagonal least-squares methods to $R=0\cdot060$. The succinic acid skeleton of the molecule is bent. The molecules are linked into chains by centrosymmetric pairs of carboxyl groups.

Introduction

This investigation was undertaken because of our interest in the molecular conformation of DL-methylsuccinic acid and in the intermolecular hydrogen bonds of carboxylic acids in general. If the molecule had the same conformation as the acid methylsuccinate ion in potassium hydrogen DL-methylsuccinate (Schouwstra, 1972) (which implies that one carboxyl group is rotated out of the average molecular plane) then we might expect effects similar to those found by Housty (1968) in the crystal and molecular structures of several saturated dicarboxylic acids with an odd number of CH$_2$ groups. These effects may be due to disorder of the carboxyl group that is rotated out of the molecular plane. As a consequence it would be difficult, if not impossible, to find the hydrogen atom of the 'disordered' carboxyl group.

Experimental

The sample used was from Fluka A.G. (puriss.). Crystals were obtained by sublimation at 70°C *in vacuo*. The unit-cell dimensions were calculated from 25 reflexions ($100° < 2\theta < 120°$) measured on a Nonius automatic three-circle diffractometer AD3 with Cu $K\alpha_1$ radiation ($\lambda=1\cdot5405$ Å) and were refined by least-squares (van den Berg & Rutten-Keulemans, 1963). The values obtained were:

$$a=22\cdot119\ (6), \quad b=5\cdot230\ (2), \quad c=11\cdot239\ (3)\ \text{Å},$$
$$\beta=103\cdot73\ (5)°, \quad V=1263\ \text{Å}^3.$$

From Weissenberg and precession photographs, the extinctions hkl for $h+k=2n+1$, and $h0l$ for $l=2n+1$ were found; the space group is thus $C2/c$ or Cc.

With $Z=8$ the calculated density is $1\cdot38$ g cm^{-3}; the density measured by flotation is $1\cdot39$ g cm^{-3}.

Integrated intensities of 688 independent reflexions ($2\theta < 120°$) were measured on the diffractometer with Ni-filtered Cu radiation. The diffractometer is equipped with a scintillation counter, a discriminator and an automatic filter disk. The ω-scanning technique was applied and the scanning range was adjusted to the width of the peaks. The intensities were corrected for Lorentz and polarization factors.

Structure determination

An overall temperature factor ($B=3\cdot3$ Å^2) and the scaling factor were determined by Wilson's (1942) method and normalized structure factors were calculated.

The distribution function of Ramachandran & Srinivasan (1959) indicated the presence of a centre of inversion. Space group $C2/c$ was accepted, and was confirmed by the successful convergence of the least-squares refinement. Signs were determined for 256 reflexions with $E>0\cdot9$ by a symbolic method developed by Spek (1972), yielding 16 solutions. For each solution a reliability index, c, was evaluated, where

$$c=\sum_{h,k} s_\mathbf{h} \cdot s_\mathbf{k} \cdot s_{\mathbf{h}+\mathbf{k}} \quad |E_\mathbf{h} \cdot E_\mathbf{k} \cdot E_{\mathbf{h}+\mathbf{k}}| \,.$$

The E-Fourier map, corresponding to the solution with the highest c, showed all the non-hydrogen atoms.

Refinement of the structure

The structure was refined by block-diagonal least-squares methods. The atomic form factors for O were taken from Doyle & Turner (1968), those for C from Allmann (1967) and those for H from Moore (1963). All reflexions were included in the refinement and were given unit weight. The 'heavy atom' model was refined with isotropic thermal parameters to $R=0\cdot178$. The disagreement index decreased to $0\cdot099$ on introduction of anisotropic thermal parameters. A difference-Fourier map revealed seven hydrogen atoms. As expected the absent hydrogen atom belongs to the carboxyl group with which the methyl group is in the α-position. Several cycles of refinement with the isotropic thermal parameters of H fixed at $3\cdot5$ Å^2 and anisotropic thermal parameters for C and O lowered R to $0\cdot061$. The difference Fourier map showed no peaks higher than $0\cdot3$ e Å^{-3}.

The weighting scheme was then changed and the standard deviations of the observed structure factors were calculated from:

$$\sigma|F|_{obs} = (|F|_{obs}/2P)\sqrt{T} + B$$

where T, B and P are the number of counts for (peak + background), background and peak respectively. The weights were then $W = (\sigma|F|_{obs})^{-2}$, and the disagreement index decreased to 0·060. The difference-Fourier map showed no peaks higher than 0·2 e Å^{-3}. The highest peak was found at one of the expected positions of the absent hydrogen atom, but the difference in height from the other peaks was too small to attach much significance to it.

The final coordinates are listed in Table 1 and the observed and calculated structure factors in Table 2.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and thermal parameters with* ($\times 10^4$) *estimated standard deviations in parentheses*

(*a*) Fractional coordinates

Hydrogen coordinates are $\times 10^3$.

	x	y	z
O(1)	497 (1)	3832 (5)	1325 (3)
O(2)	479 (1)	7607 (6)	405 (3)
O(3)	1954 (1)	6252 (6)	631 (3)
O(4)	2363 (1)	10147 (6)	909 (3)
C(1)	703 (2)	6106 (8)	1256 (4)
C(2)	1217 (2)	6944 (8)	2334 (4)
C(3)	1613 (2)	9095 (8)	2004 (4)
C(4)	1991 (2)	8367 (8)	1117 (4)
C(5)	919 (2)	7782 (11)	3366 (4)
H(1)	149 (2)	539 (9)	263 (4)
H(2)	66 (2)	631 (9)	363 (4)
H(3)	65 (2)	940 (9)	314 (4)
H(4)	126 (2)	797 (9)	408 (4)
H(5)	193 (2)	968 (9)	281 (4)
H(6)	135 (2)	1064 (9)	163 (4)
H(7)	261 (2)	959 (9)	38 (4)

Discussion of the structure

1. The molecular structure

Correction of anisotropic thermal motion was not applied in the calculation of bond lengths and angles (Tables 3 and 4).

C(2), C(1), O(2) and O(1) are in one plane; the average deviation from planarity is 0·006 Å. C(3), C(4), O(3) and O(4) are also coplanar with an average deviation of 0·003 Å. The two carboxyl groups differ: The C–O bond lengths are 1·301 and 1·228 Å in the carboxyl group relative to which the methyl group is in the β-position, and 1·282 and 1·245 Å in the other carboxyl group of which the α-substituent, the methyl group, lies outside the plane of the carboxyl group; the angle between the C(2)–C(1)–O(2)–O(1) and C(5)–C(2)–C(1) planes is 84·4°. The unusually small difference between the two C–O bond lengths, when the α-substituent is rotated out of the plane of the car-

Table 2. *Observed and calculated structure factors*

Reflexions with zero intensities have been omitted.

[Table 2 structure factor data — illegible]

Table 1 (*cont.*)

(*b*) Thermal parameters

The β_{ij} coefficients are given by:

$$\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})\right].$$

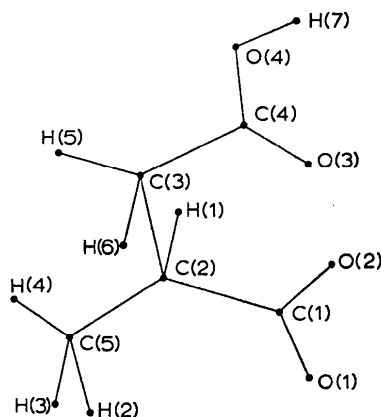|	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
O(1)	19 (1)	288 (13)	96 (3)	−15 (5)	26 (11)	3 (3)
O(2)	19 (1)	369 (13)	78 (3)	9 (5)	−72 (11)	−7 (2)
O(3)	23 (1)	333 (14)	139 (4)	38 (6)	116 (13)	54 (3)
O(4)	22 (1)	353 (14)	130 (4)	−53 (6)	−90 (13)	46 (3)
C(1)	12 (1)	292 (18)	67 (4)	−15 (7)	6 (15)	17 (3)
C(2)	14 (1)	335 (20)	62 (4)	3 (8)	15 (15)	−2 (3)
C(3)	14 (1)	313 (19)	80 (4)	8 (9)	61 (15)	8 (4)
C(4)	11 (1)	303 (19)	88 (5)	− 4 (8)	−10 (16)	−3 (3)
C(5)	26 (1)	644 (29)	70 (5)	56 (11)	79 (19)	22 (4)

Fig. 1. The structure of the methylsuccinic acid molecule; the hydrogen atom of the carboxyl group relative to which the methyl group is in α-position is not included. The figure also represents the structure of the methylsuccinate ion by virtue of the small difference between these two structures.

boxyl group, was also observed by Housty (1968). Ascribing the effect to disorder of the carboxyl group, which would indeed make locating the hydrogen atom difficult, seems contradictory to the evidence that the thermal motion of the oxygen atoms is the smallest in the anomalous carboxyl group. Rejecting disorder as a cause of the small difference mentioned, the unusual geometry of this carboxyl group could be caused by the fact that the methyl group is rotated nearly 90° out of the plane of the carboxyl group.

The two C–C bonds, which involve C atoms of a carboxyl group, are also different; the C atom of the carboxyl group with a normal free acid geometry participates in the longer C–C bond. This effect was also found in L-aspartic acid (Derissen, Endeman & Peerdeman, 1968) and in potassium hydrogen DL-methylsuccinate (Schouwstra, 1972). The charges of the methylsuccinic acid molecule and of the methylsuccinate ion in potassium hydrogen DL-methylsuccinate (Schouwstra, 1972) are different but the conformations are nearly the same (Fig. 1, Tables 3 and 4). In both these structures the succinic acid skeletons are bent. The methyl groups are roughly coplanar with the carboxyl group relative to which they are in the β-position (in this structure the average deviation from planarity is 0·045 Å) but lie out of the planes of the carboxyl group relative to which they are in the α-position; the angle between the C(2)–C(1)–O(2)–O(1) and C(5)–C(2)–C(1) planes is 86·1° in the acid methylsuccinate ion and 84·4° in the methylsuccinic acid molecule. These two structures have staggered conformations around the bond C(2)–C(3).

2. The crystal structure

Two chains of DL-methylsuccinic acid molecules can be distinguished (Fig. 2). These chains are related by a twofold axis and are linked only by van der Waals interactions.

The molecules in a chain are connected by planar, centrosymmetric pairs of carboxyl groups; the average deviation from planarity of the related carboxyl groups is 0·009 Å, when anomalous carboxyl groups are involved, and 0·003 Å, when carboxyl groups with a normal free-acid geometry participate. The lengths of the intermolecular hydrogen bonds are 2·651 for the first pair and 2·656 Å for the second.

The hydrogen atom involved in the intermolecular hydrogen bond is coplanar with the heavy atoms, the deviation being 0·03 Å. The deviation from linearity in this intermolecular hydrogen bond is 4°.

Table 3. *Bond lengths (Å) of (A)* DL-*methylsuccinic acid and (B) the acid methylsuccinate ion, with estimated standard deviations in parentheses*

	A	B		A
	A	**B**		**A**
C(1)–O(1)	1·282 (5)	1·270 (3)	C(2)–H(1)	1·02 (4)
C(1)–O(2)	1·245 (5)	1·242 (3)	C(5)–H(2)	1·04 (4)
C(4)–O(3)	1·228 (5)	1·213 (3)	C(5)–H(3)	1·03 (4)
C(4)–O(4)	1·301 (5)	1·313 (3)	C(5)–H(4)	0·97 (4)
C(1)–C(2)	1·517 (6)	1·524 (4)	C(3)–H(5)	1·05 (4)
C(2)–C(3)	1·525 (6)	1·516 (4)	C(3)–H(6)	1·02 (4)
C(3)–C(4)	1·493 (6)	1·504 (4)	O(4)–H(7)	0·95 (4)
C(2)–C(5)	1·529 (7)	1·533 (4)		

Table 4. *Bond angles (°) of (A)* DL-*methylsuccinic acid and (B) the acid methylsuccinate ion, with estimated standard deviations in parentheses*

	A	B		A
	A	**B**		**A**
O(1)–C(1)–O(2)	123·4 (4)	123·0 (2)	C(3)–C(2)–H(1)	110 (2)
O(3)–C(4)–O(4)	122·9 (4)	123·3 (2)	C(1)–C(2)–H(1)	107 (2)
C(2)–C(1)–O(1)	115·4 (4)	118·7 (2)	C(2)–C(5)–H(2)	112 (2)
C(2)–C(1)–O(2)	121·1 (4)	118·2 (2)	C(2)–C(5)–H(3)	112 (2)
C(3)–C(4)–O(3)	122·5 (4)	124·3 (2)	C(2)–C(5)–H(4)	105 (2)
C(3)–C(4)–O(4)	114·6 (4)	112·4 (2)	C(2)–C(3)–H(5)	108 (2)
C(1)–C(2)–C(3)	112·6 (4)	114·2 (2)	C(4)–C(3)–H(5)	106 (2)
C(1)–C(2)–C(5)	108·1 (4)	108·5 (2)	C(4)–C(3)–H(6)	106 (2)
C(5)–C(2)–C(3)	110·5 (4)	109·9 (2)	C(4)–O(4)–H(7)	112 (3)
C(2)–C(3)–C(4)	114·8 (3)	114·5 (2)	C(2)–C(3)–H(6)	112 (2)
			H(2)–C(5)–H(3)	111 (3)
			H(2)–C(5)–H(4)	102 (3)
			H(3)–C(5)–H(4)	114 (3)
			H(6)–C(3)–H(5)	109 (3)

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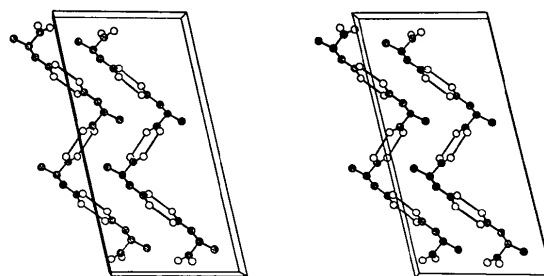RAMACHANDRAN, G. N. & SRINIVASAN, R. (1959). *Acta Cryst.* **12**, 410–411.

Fig. 2. A stereoscopic view of the crystal structure along [010]. Hydrogen atoms are not included. The carbon atoms are dotted.

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Variation of the Optical Properties of *Laevo-* and *Dextro-*Rotatory NaBrO₃ with Crystal-Growth Temperature

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Single crystals of (+) and (−)-NaBrO₃ were grown from slightly supersaturated water solution at various temperatures between 10 and 50°C. It was found that, for both (+) and (−)-NaBrO₃, the cube faces become more and more prominent with increase in the crystal-growth temperature (CGT). When crystallized at 10°C the colour of the crystals becomes faint yellow. The observed specific gravity (SG) and the optical properties, *i.e.* (1) the refractive index (RI), (2) the optical rotatory power (ORP) and (3) the Brewster angle (BA), vary with the CGT. The magnitudes of the optical properties mentioned above for (+) and (−)-NaBrO₃ crystals agree above 35°C, but differ considerably below 35°C. All the measurements were made at room temperature and with Na light, $\lambda = 5893$ Å.

Introduction

In general, sodium bromate (NaBrO₃) is a water-soluble, colourless, stable crystal, which crystallizes in the cubic tetrahedral class and has no water of crystallization. It is an ionic crystal, with four molecules in a unit cell of length $a = 6.705$ Å. Solid NaBrO₃ is optically active and crystallizes in two isomeric forms, *laevo-* and *dextro*-rotatory, though its aqueous solution is not optically active.

Kremers (1857) and Le Blanc & Rohland (1896) found that crystals of NaBrO₃ had a specific gravity 3·339 (with respect to water at 17·5°C), and 3·254. Craw (1896) found that NaBrO₃ crystals had a refractive index (RI) 1·5943, for $\lambda = 5893$ Å. The interpolated RI, for $\lambda = 5893$ Å, is 1·6165, obtained from the data given by Rose (1910). Poinsot & Mathieu (1955) gave the value of the RI as 1·6157, for $\lambda = 5893$ Å. Traube (1894) found that NaBrO₃ crystals had an ORP of 2·166° mm⁻¹, for $\lambda = 5893$ Å; Rose (1910) found 2·11 and 2·15 °.mm⁻¹, on plates 4·7 and 2·46 mm thick re-

spectively, the weighted mean of which is 2·12 °.mm⁻¹. The calculated ORP, from the formula for the optical rotatory dispersion given by Kizel, Krasilov & Shamraev (1964) is 2·055 °.mm⁻¹ for $\lambda = 5893$ Å. A value of 2·102°.mm⁻¹ for the ORP is obtained from the formula of Chandrasekhar & Madhava (1967).

It is seen that the values of the SG, RI and ORP given by different workers for NaBrO₃ crystals, do not agree well. The variation of the CGT may be one of the causes of the above disagreement. It appears that no attempt has been made to determine systematically the variation of the optical properties of (+) and (−)-NaBrO₃ crystals grown at different temperatures. Hence the object of the present investigation was to test whether the optical properties of (+) and (−)-NaBrO₃ crystals vary with the CGT or not.

Experimental

Single crystals of (+) and (−)-NaBrO₃ were grown from slightly supersaturated water solution (AR grade