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The Crystal and Molecular Structures of DL-Methylsuccinic Acid. II.* Two Modifications Obtained by Slow Evaporation of Aqueous Solutions

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The structures of the two modifications of DL-methylsuccinic acid obtained by slow evaporation of aqueous solutions at room temperature and at 1 °C have been determined from three-dimensional X-ray data. The crystals of the modification obtained at room temperature are monoclinic, with $a=7{\cdot}54$, $b=16{\cdot}46$, $c=5{\cdot}47$ Å, $\beta=113{\cdot}4°$, $Z=4$, space group $P2_1$. The structure was solved by Patterson and molecular-shift methods and refined without constraints to $R=0{\cdot}145$ and with geometrical constraints to $R=0{\cdot}156$. The crystals of the modification obtained at 1 °C are triclinic, with $a=7{\cdot}284$, $b=16{\cdot}551$, $c=5{\cdot}450$ Å, $\alpha=93{\cdot}3$, $\beta=108{\cdot}6$, $\gamma=95{\cdot}2°$, $Z=4$, space group $P\bar{1}$. This structure was solved by molecular-shift methods and refined by the block-diagonal least-squares method to $R=0{\cdot}110$. In both modifications the carbon atoms of the succinic acid skeletons are in one plane and the carboxyl groups are rotated in such a way that the methyl groups are outside the planes of the carboxyl group relative to which they are in the α-position. The molecules are linked into chains with the identical molecules in the next unit cell by planar acentric pairs of carboxyl groups.

Introduction

We started these investigations because of our interest in the molecular conformations of methylsuccinic acid and in intermolecular hydrogen bonds in carboxylic acids in general.

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE MONOCLINIC MODIFICATION

Experimental

Crystals of this modification of methylsuccinic acid were difficult to grow; the best results were obtained by slow evaporation of an aqueous solution at room temperature.

The unit-cell dimensions were obtained from equi-inclination Weissenberg photographs and from oscillation photographs (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å):

$a=7{\cdot}54$ (2), $b=16{\cdot}46$ (4), $c=5{\cdot}47$ (2) Å,
$\beta=113{\cdot}4$ (3)°, $V=623$ Å^3.

From Weissenberg photographs the extinctions $k=2n+1$ for $0k0$ were found, thus the space group is $P2_1$ or $P2_1/m$. With $Z=4$ the calculated density is 1·40 g cm^{-3}; that found by flotation is 1·42 g cm^{-3}.

Integrated equi-inclination Weissenberg photographs (multiple-film technique) were taken at room temperature of the $hk0$–4 and $0kl$ reflexions. Only 430 independent reflexions of poor quality could be observed. The intensities were corrected for Lorentz and polarization effects and put on the same scale.

Structure determination and refinement

An overall temperature factor ($B=3{\cdot}8$ Å^2) and the scaling factor were determined by Wilson's (1942) method.

Because of the poor quality of the data direct methods did not reveal the structure. After the structure had been found, it turned out that solution by direct methods did show the correct structure, but the peaks were at a low level.

The Patterson synthesis showed only one low peak on the [010] axis, so space group $P2_1$ was accepted. A very high peak was found at $x=0{\cdot}34$, $y=0{\cdot}29$, $z=0{\cdot}65$; from this we assumed that the succinic acid skeletons of the two independent molecules are nearly parallel. The space group of the Patterson synthesis is $P2/m$ so the Patterson map will show four symmetry-related orientations for a pair of carboxyl groups and four symmetry-related orientations for the mutual shift vector between the two independent molecules, of which one is at $x=0{\cdot}34$, $y=0{\cdot}29$, $z=0{\cdot}65$. In the Patterson map each mutual shift vector has its converse, so only two orientations, related by a twofold axis, will give different relative positions for the two independent molecules. A pair of carboxyl groups is nearly planar and centrosymmetric, so only two orientations need to be taken into account. Thus we get four relative positions; each position can be transformed into another position of this set by a twofold axis. Because of the symmetry of the Fourier space only two relative positions need be considered. The two independent molecules, fixed at one of the possible relative positions, are shifted through the cell in steps of 0·25 Å; we need shift only in the x and z directions. For each trial structure R is calculated for a given set of 40 randomly chosen reflexions. The solution with the lowest R was refined by the full-matrix least-squares method. The atomic form factors were taken from *International Tables for X-ray Crystallography* (1962). All reflexions were included in the refinement with unit weight, because of the poor quality of the data. After two cycles R was 0·20. The difference Fourier map showed the carbon atoms of the two methyl groups,

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Table 1. *Fractional atomic coordinates of the two independent molecules A and B of the unconstrained model of the monoclinic modification*

The estimated standard deviations are given in parentheses.

	x		*y*		*z*		B_{iso} (Å²)	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
O(1)	0·226 (3)	1·123 (3)	0·062 (2)	0·278 (2)	0·667 (4)	−0·157 (6)	3·7 (6)	4·4 (6)
O(2)	0·150 (3)	1·201 (4)	0·005 (2)	0·344 (2)	0·275 (5)	0·236 (5)	3·6 (6)	4·8 (6)
O(3)	0·865 (3)	0·496 (3)	0·043 (2)	0·304 (2)	0·590 (5)	−0·083 (5)	4·4 (6)	4·3 (6)
O(4)	0·779 (3)	0·558 (4)	−0·013 (2)	0·363 (2)	0·190 (5)	0·305 (6)	4·2 (6)	5·6 (7)
C(1)	0·275 (4)	1·087 (5)	0·037 (3)	0·310 (3)	0·468 (6)	0·014 (8)	2·2 (7)	4·3 (9)
C(2)	0·484 (5)	0·880 (4)	0·055 (3)	0·286 (3)	0·493 (8)	−0·008 (6)	4·0 (9)	2·7 (7)
C(3)	0·553 (5)	0·818 (6)	0·009 (3)	0·351 (3)	0·334 (6)	0·173 (9)	2·6 (7)	4·8 (1·0)
C(4)	0·761 (5)	0·612 (4)	0·014 (3)	0·334 (3)	0·372 (7)	0·117 (6)	2·7 (7)	2·4 (7)
C(5)	0·478 (6)	0·885 (6)	0·149 (4)	0·198 (4)	0·415 (8)	0·096 (8)	6·2 (1·2)	5·4 (1·0)

and proved the compound to be the racemate. After three cycles of refinement with all the heavy atoms, *R* remained 0·145. Anisotropic thermal parameters were not introduced, because of the small number of reflexions. The bond lengths were very unusual (C–C bond lengths ranging from 1·48 to 1·68 Å). However, the difference Fourier map only revealed peaks less than 0·7 e Å^{-3}.

Several other solutions were refined with even worse results. Attempts to solve the structure in $P2_1/m$ were unsuccessful. Therefore the refinement, starting from the solution with the lowest value of *R*, was carried out with the constraint that the bond lengths and angles, set at normal values, did not change. The final *R* was 0·156.

A test developed by Hamilton (1965) showed that the structure might be as well described by the unconstrained model as by the constrained model.

Final atomic parameters are shown in Tables 1 and 4. This structure is discussed below together with the triclinic modification.

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TRICLINIC MODIFICATION

Experimental

Crystals of the triclinic modification were obtained by slow evaporation of an aqueous solution at 1 °C. The unit-cell dimensions were calculated from 25 reflexions ($90 < 2\theta < 110°$) measured on a Nonius automatic three-circle AD3 diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}5405$ Å) and were refined by least-squares (van den Berg & Rutten-Keulemans, 1963). The values obtained were

$a = 7{\cdot}284\ (9)$, $b = 16{\cdot}551\ (16)$, $c = 5{\cdot}450\ (7)$ Å,
$\alpha = 93{\cdot}3\ (2)$, $\beta = 108{\cdot}6\ (2)$, $\gamma = 95{\cdot}2\ (2)°$,
$V = 617$ Å^3.

Table 2. *Bond lengths* (Å) *of the independent molecules A and B of the unconstrained model of the monoclinic modification*

When an atom of the next identical molecule is involved in the bonding this atom is primed.

	A	*B*
C(1)–O(1)	1·35	1·19
C(1)–O(2)	1·21	1·30
C(4)–O(3)	1·16	1·21
C(4)–O(4)	1·23	1·34
C(1)–C(2)	1·57	1·58
C(2)–C(3)	1·49	1·65
C(3)–C(4)	1·68	1·48
C(2)–C(5)	1·60	1·55
O(1)–O(3)′	2·60	2·71
O(2)–O(4)′	2·66	2·59

Table 3. *Bond angles* (°) *of the two independent molecules A and B of the unconstrained model of the monoclinic modification*

	A	*B*
O(1)–C(1)–O(2)	118	131
O(3)–C(4)–O(4)	137	121
O(1)–C(1)–C(2)	117	111
O(2)–C(1)–C(2)	124	116
O(3)–C(4)–C(3)	109	113
O(4)–C(4)–C(3)	113	126
C(1)–C(2)–C(3)	117	108
C(1)–C(2)–C(5)	104	109
C(5)–C(2)–C(3)	110	110
C(2)–C(3)–C(4)	120	106

Table 4. *Fractional atomic coordinates of the independent molecules A and B of the constrained model of the monoclinic modification*

	x		*y*		*z*		B_{iso}	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
O(1)	0·228	1·126	0·062	0·280	0·661	−0·169	3·9	4·7
O(2)	0·157	1·202	0·003	0·339	0·267	0·224	3·8	4·8
O(3)	0·863	0·492	0·040	0·302	0·580	−0·091	4·2	4·0
O(4)	0·791	0·564	−0·016	0·361	0·187	0·296	4·3	5·0
C(1)	0·270	1·087	0·037	0·304	0·469	0·025	2·9	3·0
C(2)	0·473	0·886	0·056	0·284	0·498	0·002	2·8	3·5
C(3)	0·534	0·820	0·001	0·345	0·322	0·159	2·8	3·8
C(4)	0·743	0·611	0·012	0·332	0·370	0·115	2·6	2·6
C(5)	0·480	0·888	0·145	0·198	0·431	0·099	5·8	4·6

With $Z=4$ the calculated density is 1·41 g cm^{-3}; that measured by flotation is 1·42 g cm^{-3}.

Integrated intensities of 1273 independent reflexions ($2\theta < 110°$) were measured with Ni-filtered Cu $K\alpha$ radiation on the diffractometer equipped with a discriminator, a scintillation counter and an automatic filter disk. The ω-scan technique was used and the scanning range was adapted to the width of the peaks. The peaks of the reflexions were broad, because of the indifferent quality of the crystals. The intensities were corrected for Lorentz and polarization effects.

Solution and refinement of the structure

As the volumes of the unit cells of the triclinic modification and of the monoclinic modification are nearly the same, the cell of the triclinic modification was transformed to a cell with dimensions:

$$a = 7{\cdot}58,\quad b = 16{\cdot}55,\quad c = 5{\cdot}45\ \text{Å},$$
$$\alpha = 93{\cdot}3,\quad \beta = 114{\cdot}4,\quad \gamma = 82{\cdot}6°,$$

showing a clear resemblance to the unit cell of the monoclinic modification. The transformation matrix is

$$\begin{pmatrix} 1 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}.$$

An overall temperature factor ($B = 3{\cdot}6$ Å^2) and the scaling factor were determined by Wilson's (1942) method. The distribution function of Ramachandran & Srinivasan (1959) indicates the presence of a centre of inversion. $P\bar{1}$ could not be accepted yet, because there might be pseudo-centres of inversion, as in the monoclinic conformation described above.

The $0kl$ reflexions of this and the monoclinic modification are nearly the same, so we may accept the same y and z coordinates for the succinic acid skeletons. One oxygen atom of each independent skeleton was given the coordinate $x=0$ and the x coordinates of the other heavy atoms were calculated. Only one set of x coordinates was found for each molecule because, as in the monoclinic modification, the molecules are connected by intermolecular hydrogen bonds to the identical molecule in the next unit cell. In space group $P1$ one molecule can be fixed at an arbitrary position. The other molecules were shifted independently in the direction of the [100] axis in steps of 0·25 Å. For each trial structure R was calculated for a given set of 40 randomly chosen reflexions. A difference Fourier map, calculated for the solution with the lowest disagreement index, clearly showed the carbon atoms of the methyl groups. This solution showed a centrosymmetric structure.

The structure was refined by the block-diagonal least-squares method in space group $P\bar{1}$. 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 non-zero reflexions were

Table 5. *Intermolecular distances* (Å) *of the two independent molecules A and B of the constrained model of the monoclinic modification*

An atom of the next identical molecule is primed.

	A	*B*
O(1)–O(3)′	2·63	2·63
O(2)–O(4)′	2·64	2·64

Table 6. *The observed and calculated structure factors of the triclinic modification*

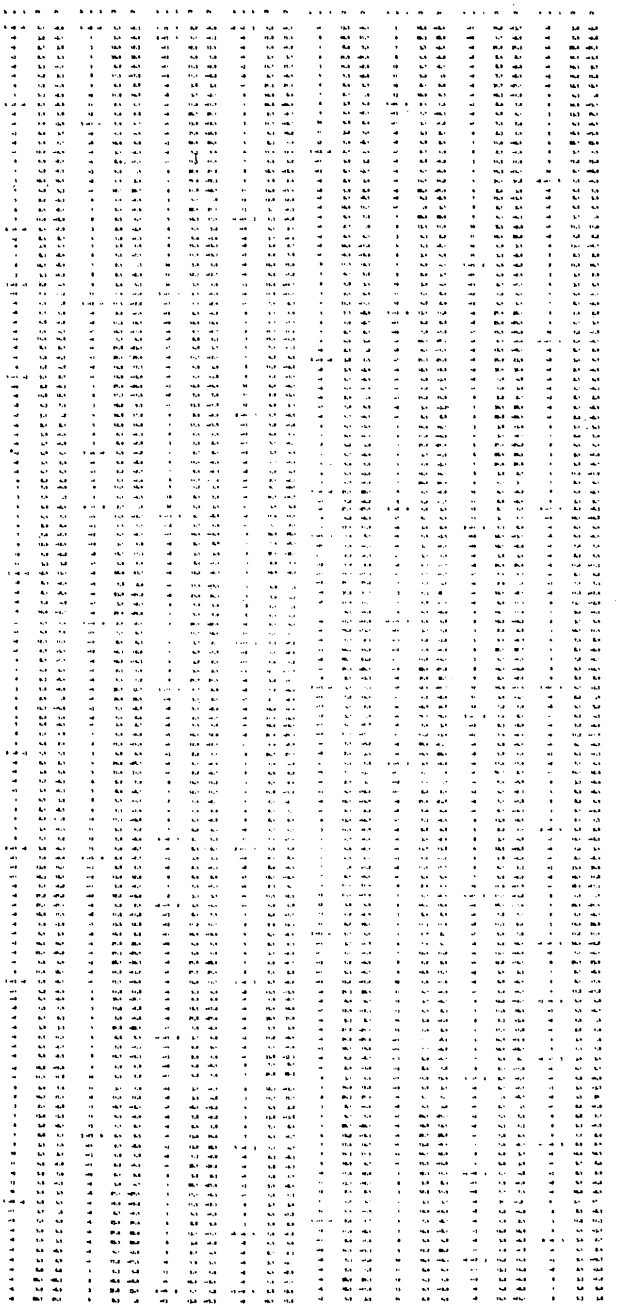

Table 7. *Final fractional atomic coordinates of the two independent molecules A and B of the triclinic modification*

The estimated standard deviations are given in parentheses.

	x		*y*		*z*	
	A	*B*	*A*	*B*	*A*	*B*
O(1)	0·474 (1)	0·092 (1)	0·1095 (4)	0·6062 (5)	1·387 (1)	−0·333 (1)
O(2)	0·568 (1)	0·030 (1)	0·1693 (4)	0·6684 (4)	1·088 (1)	−0·001 (1)
O(3)	−0·156 (1)	0·729 (1)	0·1306 (4)	0·6293 (4)	0·678 (1)	0·383 (1)
O(4)	−0·058 (1)	0·670 (1)	0·1883 (4)	0·6904 (5)	0·377 (1)	0·713 (1)
C(1)	0·440 (1)	0·136 (1)	0·1356 (6)	0·6316 (5)	1·155 (2)	−0·094 (2)
C(2)	0·233 (1)	0·331 (1)	0·1149 (6)	0·6122 (5)	0·981 (2)	0·077 (2)
C(3)	0·186 (1)	0·412 (1)	0·1692 (6)	0·6731 (6)	0·763 (2)	0·317 (2)
C(4)	−0·025 (1)	0·616 (1)	0·1611 (6)	0·6604 (6)	0·601 (2)	0·477 (2)
C(5)	0·210 (2)	0·304 (2)	0·0232 (6)	0·5255 (7)	0·874 (2)	0·147 (2)
H(1)	0·137	0·432	0·123	0·616	1·089	−0·028
H(2)	0·242	0·253	−0·014	0·485	1·027	−0·024
H(3)	0·309	0·202	0·016	0·521	0·768	0·247
H(4)	0·067	0·439	0·005	0·509	0·747	0·267
H(5)	0·233	0·408	0·230	0·733	0·839	0·261
H(6)	0·272	0·318	0·155	0·664	0·642	0·433

included in the refinement with unit weight because of the indifferent quality of the crystal. The 'heavy-atom' model was refined to $R=0{\cdot}188$. R decreased to 0·133 when anisotropic thermal parameters were introduced. The difference Fourier map showed 20 peaks above 0·4 e Å^{-3}. The 12 highest peaks corresponded to the aliphatic hydrogen positions; only small peaks were found near the expected positions of the hydrogen atoms of the carboxyl groups. Two cycles of refinement with fixed positions and fixed isotropic thermal parameters (4 Å^2) for the aliphatic H and anisotropic thermal parameters for O and C reduced R to 0·110. The final difference Fourier map showed three peaks of 0·5 e Å^{-3}; only small peaks were found near the expected positions of the missing hydrogen atoms. The final coordinates (in the original cell) are listed in Tables 7 and 8, and the observed and calculated structure factors in Table 6.

Table 8. *Final thermal parameters* ($\times 10^3$) *of the two independent molecules A and B of the triclinic modification*

The estimated standard deviations are given in parentheses. The β_{ij} coefficients are given by

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2lh\beta_{31})\right].$$

A	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
O(1)	12 (2)	4·8 (4)	27 (3)	3 (1)	5 (2)	3 (4)
O(2)	11 (2)	4·9 (4)	36 (3)	0 (1)	7 (2)	8 (4)
O(3)	11 (2)	4·1 (3)	37 (3)	0 (1)	6 (2)	7 (4)
O(4)	13 (2)	4·8 (4)	29 (3)	−1 (1)	9 (2)	−3 (4)
C(1)	14 (3)	3·5 (5)	24 (4)	2 (2)	3 (2)	7 (5)
C(2)	8 (2)	3·8 (5)	24 (4)	4 (2)	2 (2)	−6 (5)
C(3)	8 (2)	4·0 (5)	26 (4)	3 (2)	2 (2)	−8 (5)
C(4)	12 (2)	3·0 (5)	25 (4)	0 (2)	0 (2)	9 (5)
C(5)	23 (3)	2·7 (5)	40 (6)	−1 (3)	2 (3)	−9 (7)
B						
O(1)	12 (2)	6·2 (4)	27 (3)	3 (1)	0 (2)	−3 (4)
O(2)	12 (2)	4·9 (4)	29 (3)	4 (1)	−7 (2)	−6 (4)
O(3)	10 (2)	5·3 (4)	29 (3)	4 (1)	−2 (2)	4 (4)
O(4)	11 (2)	6·2 (4)	24 (3)	6 (1)	−4 (2)	−10 (4)
C(1)	12 (2)	2·0 (4)	27 (4)	0 (2)	−3 (2)	1 (5)
C(2)	8 (2)	2·1 (4)	33 (4)	2 (1)	2 (2)	9 (5)
C(3)	8 (2)	4·0 (5)	22 (4)	2 (2)	−2 (2)	−6 (5)
C(4)	14 (2)	2·9 (4)	21 (4)	−2 (2)	1 (2)	7 (5)
C(5)	18 (3)	3·2 (5)	48 (6)	3 (2)	2 (3)	−6 (7)

Table 9. *Bond lengths* (Å) *of the two independent molecules A and B of the triclinic modification*

The average estimated standard deviation is 0·015 Å. When an atom of the next identical molecule is involved in the bonding this atom is primed.

	A	*B*
C(1)–O(1)	1·31	1·27
C(1)–O(2)	1·20	1·24
C(4)–O(3)	1·24	1·23
C(4)–O(4)	1·28	1·28
O(1)–O(3)′	2·63	2·67
C(1)–C(2)	1·50	1·50
C(2)–C(3)	1·50	1·52
C(3)–C(4)	1·50	1·50
C(2)–C(5)	1·57	1·52
O(2)–O(4)′	2·66	2·66

Table 10. *Bond angles* (°) *of the two independent molecules A and B of the triclinic modification*

The average estimated standard deviation is 1°.

O(1)–C(1)–O(2)	122	124
O(3)–C(4)–O(4)	123	122
O(1)–C(1)–C(2)	114	115
O(2)–C(1)–C(2)	124	121
O(3)–C(4)–C(3)	123	123
O(4)–C(4)–C(3)	115	115
C(1)–C(2)–C(3)	111	111
C(1)–C(2)–C(5)	107	108
C(3)–C(2)–C(5)	111	112
C(2)–C(3)–C(4)	114	112

DISCUSSION OF THE STRUCTURE OF THE MONOCLINIC AND TRICLINIC MODIFICATIONS

If we compare the two modifications described in this paper (Tables 2, 3, 5, 9 and 10, Figs. 1, 2 and 3) we see a striking resemblance, though only the gross features can be compared because of the poor quality of the monoclinic crystals. Both structures are built up from the same chains of molecules. The carbon chain of the succinic acid skeleton is in one plane; the carboxyl groups are rotated out of this plane, the dihedral angle being about 20° (Table 11). The carboxyl groups are rotated in such a way that the methyl group lies outside the plane of the carboxyl group with respect to which it is

in the α-position; the angle between the planes C(2)C(1)-O(1)O(2) and C(5)C(2)C(1) is about 80° (Table 11). This effect was also found in potassium hydrogen *dl*-methylsuccinate (Schouwstra, 1972), in the modification of *dl*-methylsuccinic acid obtained by sublimation at 70°C *in vacuo* (Schouwstra, 1973) and in *l*-chlorosuccinic acid (Kryger, Rasmussen & Danielsen, 1972).

Table 11. *Dihedral angles* (°) *of the two independent molecules A and B of the triclinic modification*

Plane	Plane	*A*	*B*
C(2)C(1)O(1)O(2)	C(1)C(2)C(5)	80	82
C(1)C(2)C(3)C(4)	O(1)O(2)C(1)	23	26
C(1)C(2)C(3)C(4)	O(3)O(4)C(4)	21	24

Each molecule is linked with the identical molecule in the next unit cell by a planar, acentric pair of carboxyl groups; thus two chains of *d*- and two chains of *l*-methylsuccinic acid molecules exist. In the monoclinic modification the stacking of the chains results in a structure in which crystallographic $P2_1$ axes are combined with pseudocentres of inversion. In the triclinic modification crystallographic centres of inversion combined with pseudo-$P2_1$ axes parallel to [010] are found. In the monoclinic modification the chains are parallel to [100], in the triclinic modification to [101]. In the triclinic modification the bond length C(7)–C(9), in which the carbon atom of a methyl group is involved, is 1·57 Å; this may be due to the indifferent quality of the crystals. In this modification

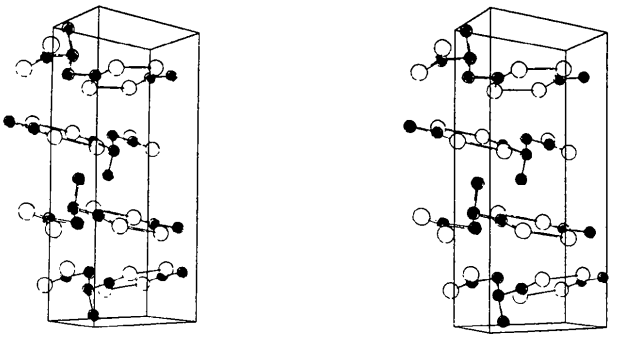

Fig. 2. A stereoscopic view of the crystal structure of the monoclinic modification along [001]. Hydrogen atoms are not included.

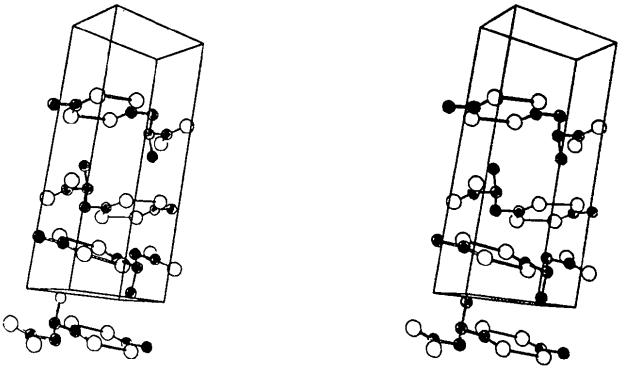

Fig. 3. A stereoscopic view of the crystal structure of the triclinic modification along [001] in the transformed cell. Hydrogen atoms are not included.

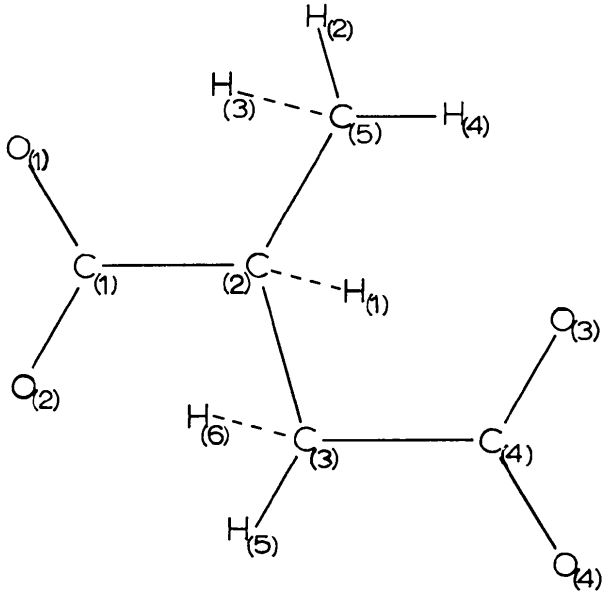

Fig. 1. The molecular structure of the methylsuccinic acid molecule in the triclinic modification. This figure also represents the structure of the methylsuccinic molecule of the monoclinic modification by virtue of the small differences between the two structures.

it is also found that in three of the carboxyl groups the C–O bond lengths are nearly the same (C–O 1·28 Å and C=O 1·24 Å). In the carboxyl group C(1)O(2)O(3), relative to which a methyl group is in the α-position, the bond length of C–O is 1·31 Å and the length of C=O is 1·20 Å. These values differ by about 2σ from the values found in the other carboxyl groups, so we cannot state that we have found an effect contrary to that found in the modification of *dl*-methylsuccinic acid obtained by sublimation at 70°C *in vacuo* (Schouwstra, 1973), where the difference in C–O bond lengths was the smallest in the carboxyl group relative to which the methyl group is in the α-position. Comparison of the structures described in this paper with the structure of *dl*-methylsuccinic acid obtained by sublimation at 70° shows that though, naturally, different conformations will cause different stackings, identical conformations do not always result in an identical stacking. Several structures are found which may support the assumption that the differences in the conformational energies of the molecules are compensated by the differences in the energies of the stacking. If this assumption applies, then there is a transition point; if not then one of the structures is

metastable So far we can only say that no transition point has been found.

References

ALLMANN, R. (1967). *Acta Cryst.* **22**, 432–433.

BERG, J. M. VAN DEN & RUTTEN-KEULEMANS, E. W. M. (1963). *An Algol Program for the Calculation of Cell Dimensions from Angles.*

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

KRYGER, L., RASMUSSEN, S. E. & DANIELSEN, J. (1972). *Acta Chem. Scand.* **26**, 2339–2348.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

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

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

SCHOUWSTRA, Y. (1972). *Acta Cryst.* B**28**, 2217–2221.

SCHOUWSTRA, Y. (1973). *Acta Cryst.* B**29**, 1–4.

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

Acta Cryst. (1973). B**29**, 1641

The Crystal and Molecular Structure of Uracil-β-D-arabinofuranoside

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The crystal structure of uracil-β-D-arabinofuranoside ($C_9H_{12}N_2O_6$) has been determined from data collected on a Hilger and Watts linear diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$, with cell dimensions: $a=6{\cdot}810$ (5), $b=6{\cdot}870$ (5), $c=20{\cdot}98$ (1) Å. The structure was solved by Patterson interpretation methods. The final R for 1164 observed reflexions is 0·058. The glycosidic torsion angle defined for the sequence of atoms O(1′)–C(1′)–N(1)–C(6) is 34·0°. The sugar ring pucker is C(2′) *endo* and, relative to the least-squares plane through the five-atom sugar ring, it is C(2′) *endo*–C(1′) *exo*. The orientation of the C(5′)–O(5′) bond is *gauche* to both the C(4′)–O(1′) and C(4′)–C(3′) bonds. There is an intramolecular hydrogen bond between atoms O(2′) and O(5′), in which O(2′) is the donor.

Introduction

The structure determination of uracil-β-D-arabinofuranoside (ara U) was undertaken as part of a series of structure determinations of nucleosides and nucleotides. Ara U was first isolated from sponges of the species *Cryptotethya crypta* (Bergmann & Feeney, 1950, 1951), and for this reason is also referred to as spongouridine. We were particularly interested in comparing the conformation of ara U with those of related ribose and deoxyribose nucleosides. A preliminary account of the conformational parameters of ara U has been given recently (Tollin, Wilson & Young, 1973).

Experimental

Crystals of ara U ($C_9H_{12}N_2O_6$) (Fig. 1) were obtained by evaporation from aqueous solutions. The unit-cell dimensions, obtained from Weissenberg photographs with Cu $K\alpha$ radiation, are

$$a=6{\cdot}810\ (5),\quad b=6{\cdot}870\ (5),\ c=20{\cdot}98\ (1)\ \text{Å}$$

(λ Cu $K\alpha_1=1{\cdot}54050$ Å, λ Cu $K\alpha_2=1{\cdot}54434$ Å)

and the space group is $P2_12_12_1$. The calculated density, with one molecule per asymmetric unit, is 1·652 g cm^{-3}.

The intensities of 1165 unique reflexions were measured on a Hilger and Watts linear diffractometer with Mo K radiation and balanced filters. The data were collected to a $\sin\theta$ value corresponding to the radius of the limiting sphere for Cu $K\alpha$ radiation. Two crystals were used, one mounted along **a** and the other along **b**. Both were about 0·5 mm long and 0·15 × 0·15 mm in cross section. No absorption corrections were applied.

Structure determination

The structure amplitudes were sharpened and used to calculate the $I(\theta\varphi)$ function (Tollin & Cochran, 1964) in order to determine the orientation of the plane of the base. This function showed two large peaks of comparable height, one at (90°, 0°) of height 154 on an arbitrary scale, the other at (90°, 90°) of height 138. In order to distinguish between these two possibilities, and to determine the azimuthal angle which defines the orientation of the base in its plane, the function $I(\theta_1\theta_2\theta_3)$ was calculated (Munns, 1971; Tollin & Munns, to be published). This function rotates a model of the base in its plane until the best fit with the Patterson function is obtained. The peak at (90°, 90°) was shown to be the correct one, the height of the peak in the $I(\theta_1\theta_2\theta_3)$ function being 364. The largest peak in