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Crystal Structures of Mesotartaric Acid

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Triclinic mesotartaric acid monohydrate crystallizes in $P\bar{1}$ with $Z=2$ and $a=5\cdot516$, $b=9\cdot220$, $c=7\cdot330$ Å and $\alpha=115\cdot11$, $\beta=93\cdot62$, $\gamma=93\cdot64°$; the monoclinic monohydrate in $P2_1/c$ with $Z=4$ and $a=5\cdot215$, $b=5\cdot019$, $c=25\cdot92$ Å and $\beta=99\cdot72°$; the triclinic anhydrous modification in $P\bar{1}$ with $Z=2$ and $a=9\cdot459$, $b=6\cdot464$, $c=5\cdot396$ Å and $\alpha=68\cdot99$, $\beta=76\cdot36$, $\gamma=75\cdot77°$; and the orthorhombic anhydrous modification in $Pbn2_1$ or $Pbnm$ with $Z=16$ and $a=19\cdot05$, $b=9\cdot88$, $c=12\cdot16$ Å. The first three structures were solved by application of the correlation method to projections and refined by three-dimensional least squares.

The molecules are not centrosymmetric but have the staggered conformations as found earlier in mesotartrates. In the monoclinic modification the carbonyl group in one of the planar halves of the molecule is, surprisingly, not at the side of the α-hydroxyl group. The other intramolecular bond lengths and angles are approximately the same for the three structures. In the networks of hydrogen bonds, carboxylic acid dimers and hydrated links are of primary importance.

Introduction

The object of this investigation was to determine the conformation of the mesotartaric acid molecule in several crystal modifications. Moreover, the structure determinations of these substances, containing only light atoms, served as test cases for the correlation method (de Vries, 1965).

In the literature, three modifications of mesotartaric acid are described, namely a triclinic hydrate (Longchambon, 1926) and two anhydrous forms, one of which is orthorhombic (Longchambon, 1926) and the other triclinic (Schneider, 1928).

By recrystallization of the triclinic hydrate from water at different temperatures, the three modifications mentioned in the literature were obtained, as well as a monoclinic monohydrate (Bootsma & Schoone, 1964). Though no thermodynamic data are available it is reasonable to assume that at room temperature the monoclinic hydrate is not the stable modification.

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Experimental

In the determination of cell-dimensions 2θ values were measured on the single-crystal diffractometer. For the intensity measurements spherical crystals (diameter $\sim 0\cdot3$ mm), ground by the technique described by Schuijff & Hulscher (1965), were used. The intensities were recorded on integrated Weissenberg photographs or collected with a General Electric diffractometer provided with a single-crystal orienter and a scintillation counter. Each reflexion was counted once and the background was measured for 15 seconds at both ends of the scanning region (3–4°). Copper radiation was used in all cases.

The intensities were corrected for Lorentz–polarization and absorption factors and for non-linearity of the counter.

Cell data

The cell dimensions were refined by a least-squares treatment of $\sin^2\theta$ values. In Table 1 our values are compared with those reported by Longchambon and Schneider.

For the orthorhombic crystal the systematic absences are $0kl$ for k odd and $h0l$ for $h+l$ odd, giving $Pbn2_1$ or $Pbnm$ as the space group. All reflexions with h odd, however, are weak and the $hk0$ reflexions with h twofold are very weak. If the intensities of these reflexions are supposed to be exactly zero and the a axis is halved, the space group of the crystal will be $Pbca$ (with $Z=8$). In that case there is one crystallographically independent molecule in the elementary cell as with the other three structures.

Structure determinations

The structure factors were converted to unitary structure factors by the method described by Woolfson (1961).

The correlation method uses sign relations $S_a = s(H)s(K)s(H+K)$ and correlation equations, coupling (four) sign relations (Woolfson 1961, page 80). The correlation equations are used quantitatively in the calculation of values of $P_a^* = P_{-a}^*/P_{+a}^*$, P_{+a}^* being the probability that S_a is positive.

The sign relation with the lowest value of P^* – the highest probability to be positive – is accepted as correct, substituted by a $+$ sign and eliminated from the set of data. If correlation equations simplify to a form in which only two sign relations remain, one of them can be eliminated as their signs have to be equal. After the elimination of sign relations from the correlation equations a new set of P^* values has to be calculated and so on. In this manner a list of successively accepted sign relations can be made. The process of calculation of P^* values, acceptance and elimination has been programmed for ZEBRA and X1.

Usually the correlation method yields a number of probable sets of signs $s(H)$. For the choice between the corresponding Fourier syntheses several criteria were applied, apart from *lower bound* (Vand & Pepinsky, 1956) and *zero-check* (Cochran & Douglas, 1957).

'*Origin-check*': Whenever it is known or can be expected that there is no atom at one of the possible origins (centres of symmetry), then there should be such a balance of positive and negative signs that only small peaks or holes at the centres of symmetry are found. A simple check of this sign balance is the difference between the maximum and the minimum found

at any of the possible origins. The Fourier synthesis with the lowest value for this difference is the most probable one.

Scale factor refinement: For sets of equal numbers of atoms placed at the centres of the strongest peaks found for each of the Fourier syntheses, a scale factor refinement is undertaken with the highest F_{obs} values, starting with the Wilson scale factor. The lowest values of

$$R_1(\Sigma |F_{obs} - F_{calc}|/\Sigma |F_{obs}|)$$
$$\text{and } R_2(\Sigma |F_{obs}^2 - F_{calc}^2|/\Sigma F_{obs}^2)$$

are indications for the correct possibility.

Triclinic mesotartaric acid monohydrate

The structure was determined from the [100] and [001] projections, with photometrically determined intensities.

Table 3 presents results of a calculation with the correlation method for the $0kl$ reflexions with $U \geq 0.26$ (Table 2). It seemed reasonable to accept them, inclusive of the 17th step. Three Fourier syntheses were constructed with the 21 structure factors. A least-squares refinement showed a model based on one of these syntheses to be correct.

In the case of the [001] projection two sets of data were treated with the sign relation program, one with 34 $hk0$ reflexions ($U \geq 0.22$), 74 sign relations, 55 correlation equations and the other with 30 reflexions ($U \geq 0.24$), 48 sign relations, 28 correlation equations. The joint results of these calculations, together with the known signs of the $0k0$ reflexions, were used for the construction of four Fourier syntheses (24 structure factors).

A criterion for the best set of signs was the following. The relative x coordinates of the atoms were approximately determined by projecting the molecule, fixed on the known [100] projection, on the (001) plane. The molecule was then shifted in the x direction so as to find the position where the residual had its minimal value. The signs calculated for this position agreed with those of one of the four sets. In Fig.1 the [001] electron density synthesis (108 reflexions) is given.

Monoclinic mesotartaric acid monohydrate

The structure determination was performed with photographically measured intensities of $0kl$ and $h0l$

Table 1. *Comparison of cell data*

a', b' etc.: notation of Longchambon (L) and Schneider (S); a, b, c: our axial system.

		a'	:	b'	:	c'	α'	β'	γ'
Triclinic hydrate	L	$\frac{1}{2}(b+c)$		$\frac{1}{2}(b-c)$		a			
	L	0·6424	:	1	:	0·7925	90·27°	96·51°	75·77°
	B–S	0·6442	:	1	:	0·7878	90·50	96·67	75·66
Anhydrous triclinic	S	a		b		c			
	S	1·461	:	1	:	0·861	70·5	78·0	79·5
	B–S	1·462	:	1	:	0·835	68·99	76·36	75·77
Anhydrous orthorhombic	L	$\frac{1}{2}a$		b		c			
	L	0·9467	:	1	:	1·2265			
	B–S	0·9637	:	1	:	1·2299			

reflexions. Our first attempts to solve the [010] projection, using U values calculated from $h0l$ intensities only, failed. A comparison of the values of φ in

$$|U(H)| = \varphi(\sin\theta) \cdot |F_{obs}(H)|,$$

for the $h0l$ reflexions with those averaged for the $0kl$, $h1l$ and $h2l$ reflexions – all on the same scale – revealed a remarkable difference for $\sin\theta < 0.4$ (Fig. 2). The U values of the $h0l$ reflexions with $\sin\theta < 0.4$ were therefore redetermined, using the lower φ's. Although the

number of reflexions with corrected U's is small, the influence of this correction on the process of sign determination is considerable (Table 5, cases 4 and 5). The results of the calculation with corrected values for U were accepted up to a situation with seven sets of signs for 24 reflexions. For the choice between the Fourier syntheses several criteria were applied (Table 4).

The scale factor refinement was performed for sets of eight oxygen atoms with 71 highest F_{obs} values, starting with a scale factor of 0·46, the zero-check for

Table 2. *List of $0kl$ reflexions with $U \geq 0.26$*

k=even l=even			k=even l=odd			k=odd l=even			k=odd l=odd		
k	l	100U	k	l	100U	k	l	100U	k	l	100U
8	$\bar{2}$	42	4	$\bar{3}$	43	5	$\bar{6}$	44	11	$\bar{3}$	57
8	$\bar{6}$	39	10	$\bar{3}$	37	7	0	42	7	1	48
4	$\bar{2}$	37	2	$\bar{3}$	35	3	$\bar{6}$	33	3	$\bar{5}$	43
4	6	36	4	1	30	7	$\bar{6}$	33	1	3	39
0	4	34	10	$\bar{1}$	29	1	$\bar{4}$	31	3	5	37
2	$\bar{2}$	27				3	0	31	7	$\bar{7}$	30
4	$\bar{4}$	27				11	$\bar{2}$	31	9	3	32
10	$\bar{4}$	27				5	$\bar{8}$	28	1	1	31
2	0	26				5	$\bar{2}$	28	7	3	28
4	2	26				5	4	27			
8	0	26				9	0	27			

Tabel 3. *Results of the application of the correlation method for 36 $0kl$ reflexions, 78 sign relations and 52 correlation equations*

Arbitrary choice: $s(2,\bar{3}) = s(1,\bar{3}) = +$. P_a^* in floating point notation.

		S_a accepted			Reflexions	
Step	H	K	H+K	P_a^*	included	Possibilities
1	7,1	1,$\bar{3}$	8,$\bar{2}$	0·35-5	4	2
2	2,$\bar{3}$	1,$\bar{3}$	3,$\bar{6}$	0·17-3	5	2
3	2,$\bar{2}$	2,$\bar{3}$	4,$\bar{5}$	0·23-3	7	4
4	4,6	3,$\bar{6}$	7,0	0·25-3	9	8
5	4,6	3,$\bar{5}$	7,1	0·10-3	10	8
6	8,$\bar{2}$	2,$\bar{3}$	10,$\bar{5}$	0·72-4	11	8
7	8,$\bar{6}$	0,4	8,$\bar{2}$	0·36-3	13	16
8	1,$\bar{3}$	1,1	2,$\bar{2}$	0·47-3	14	16
9	3,5	1,1	4,6	0·39-3	15	16
10	4,$\bar{4}$	3,5	7,1	0·14-3	16	16
11	2,2	2,$\bar{2}$	4,$\bar{4}$	0·22-3	16	8
12	2,$\bar{2}$	3,$\bar{6}$	5,$\bar{8}$	0·64-3	17	8
13	4,2	3,$\bar{5}$	7,$\bar{3}$	0·66-3	19	16
14	1,1	7,$\bar{3}$	8,$\bar{2}$	0·59-4	19	8
15	1,$\bar{3}$	7,3	8,$\bar{6}$	0·24-3	19	4
16	4,$\bar{2}$	4,$\bar{4}$	8,$\bar{6}$	0·36-3	20	4
17	7,$\bar{7}$	1,1	8,$\bar{6}$	0·50-3	21	4
18	4,$\bar{5}$	7,0	11,$\bar{5}$	0·10-2	22	4
19	4,$\bar{2}$	7,$\bar{3}$	11,$\bar{5}$	0·18-2	22	2
20	2,$\bar{2}$	9,$\bar{3}$	11,$\bar{5}$	0·18-2	23	2
21	4,$\bar{2}$	4,2	8,0	0·42-2	24	2
22	8,$\bar{2}$	2,$\bar{2}$	10,$\bar{4}$	0·72-2	23	2
23	2,$\bar{2}$	1,$\bar{4}$	3,$\bar{6}$	0·73-2		

Table 4. *Criteria used for the choice between the Fourier syntheses*

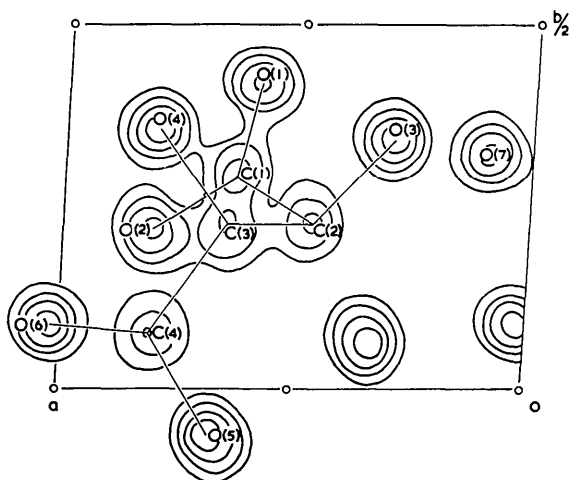| Set	Lower bound	Origin check	Scale-factor refinement			Zero check
			Scale factor	R_1 (%)	R_2 (%)	
A	−250	458	0·62	52	74	1·6
B	−204	140	0·56	48	65	1·7
C	−171	252	0·61	53	70	2·1
D	−182	260	0·79	60	79	2·1
E	−229	74	0·50	44	66	1·6
F	−193	246	0·60	51	71	1·7
G	−166	122	0·56	47	67	3·3

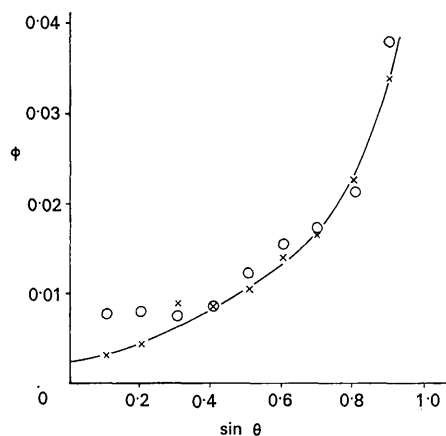Fig. 1. Electron density projection on (001) of triclinic mesotartaric acid monohydrate.

Fig. 2. Graph of φ against $\sin \theta$. Circles: $h0l$; crosses: $0kl$, $h1l$ and $h2l$.
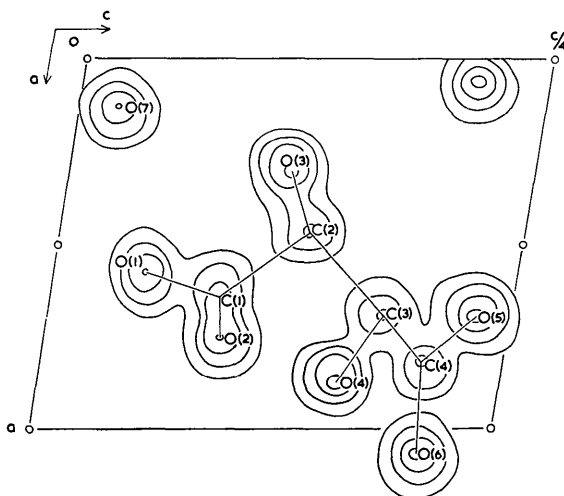

Fig. 3. Electron density projection on (010) of monoclinic mesotartaric acid monohydrate.

the 30 $h0l$ reflexions with $U(H) \leq 0.05$. The results of the application of these criteria together with the general appearance of the Fourier syntheses suggested case E as the most probable. From a second Fourier synthesis, calculated with 37 high F_{obs} values with signs controlled by the contribution of the eight oxygen atoms, a model was derived that did refine successfully by least-squares. The final electron density projection (169 $h0l$ reflexions) is given in Fig. 3.

The [100] projection was solved by using the correlation method (Table 5, case 8), inserting the known signs of the 00l reflexions.

Triclinic anhydrous mesotartaric acid

For the calculation of the U values we used the intensities of all $hk0$ and $h0l$ reflexions, measured with the counting technique. For 35 $hk0$ reflexions ($U \geq 0.27$) 69 sign relations and 56 correlation equations were found. Three reflexions could not be included in any of the sign relations.

The results of the application of the correlation method were accepted up to a situation with 29 eliminated sign relations, 17 reflexions, 4 possibilities (13 steps). The next step would have implied a doubling of the number of possibilities. This number is reduced again to 4 in the 25th step.

One of the three Fourier syntheses constructed with the 17 structure factors showed high peaks on three out of four centres of symmetry and seemed therefore the least plausible. The two remaining Fourier syntheses showed an arrangement of peaks similar to that of the [100] projections of the triclinic and monoclinic hydrates (projection axes: 5·40, 5·52 and 5·22 Å respectively). The model of the known projections fitted in best with one of the Fourier synthesis. The final [001] Fourier synthesis is given in Fig. 4.

Attempts to solve the [010] projection with the correlation method were not successful. Once the [001] projection has been solved, the [010] projection is known in principle: the two molecules in the unit cell are evidently connected by one of their carboxyl groups through a centre of symmetry [in Fig. 4 at $(\frac{1}{2},0)$]. The z coordinates of the atoms were approximated by projecting the molecule, fixed on the [001] projection, onto (010). A Fourier synthesis was made with 35 structure factors with signs calculated for the projected model. The coordinates from this Fourier synthesis could be refined by least squares.

Results of the correlation method

In Table 5 the results of the application of the correlation method are summed up as the optimal number of correctly eliminated sign relations together with the number of included reflexions and possible sets of signs.

For several projections we operated with different sets of structure factors, corresponding sign relations and correlation equations, the difference being the cut-off limit for the U values.

Success was scored for the three analogous projections triclinic hydrate [100], monoclinic [100] and triclinic anhydrous [001], all with two overlapping atoms (Fig. 4). Two cases (7 and 9) passed off correctly to the very end. The monoclinic [010] projection could be solved only after correction of the U values of some low-order reflexions (5–7).

Solution of the [001] projection of the triclinic hydrate and of the [010] projection of the triclinic anhydrous modification with the correlation method alone would have been hardly possible. Where the method failed, a wrong sign relation whose sign in previous steps was found equal to the signs of other (wrong) sign relations was taken as correct. The effect of an equality of signs of two sign relations (both positive or both negative) makes for a greater probability that the signs are positive.

For the choice between the probable Fourier syntheses the lower bound criterion appeared to be of no value in these cases of syntheses constructed with only 15% of the total available number of reflexions. The origin-check gave the correct indication in all cases. Correct indications were also obtained by the scale factor refinement and zero-check criteria.

Refinement of the structure

For the further refinement of the structures three-dimensional sets of structure factors were used, starting with the parameters obtained for the projections. The scattering factors for the atoms were taken from *International Tables for X-ray Crystallography* (1962, page 202). After refinement of coordinates, scale and overall temperature factors we continued with individual isotropic temperature factors as additional parameters, on ZEBRA and X1, using diagonal and block diagonal approaches. From difference Fourier syntheses, using only low-order reflexions, provisional locations of the hydrogen atoms could be derived, which were kept unaltered in the subsequent stages of refinement, including that of anisotropic temperature parameters.*

Triclinic mesotartaric acid monohydrate

For the three-dimensional refinement 1429 intensities out of a total of 1535 reflexions within the copper sphere were measured with the counting technique. The calculations were carried out, attributing equal weights to all reflexions. When anisotropic temperature parameters were introduced and a full-matrix program (Busing, Martin & Levy, 1962; ORFLS on IBM 7090) was used the R index dropped from 11·4 to 5·5%. Finally two cycles of refinement of the coordinates of the hydrogen atoms were carried out. The final value was 4·8%. The differences between the hydrogen locations so obtained and those determined from a difference Fourier synthesis (at $R = 5·5\%$) were insignificant for all hydrogen atoms except H(5), whose provisional coordinates were not good enough to permit the complete adjustment in two cycles. The results of the refinement are given in Table 6; for H(5) the Fourier coordinates have

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* The final sets of structure factors, $|F_o|$ and $|F_c|$, have been put on microfilm and deposited in this laboratory. Prints are available on request.
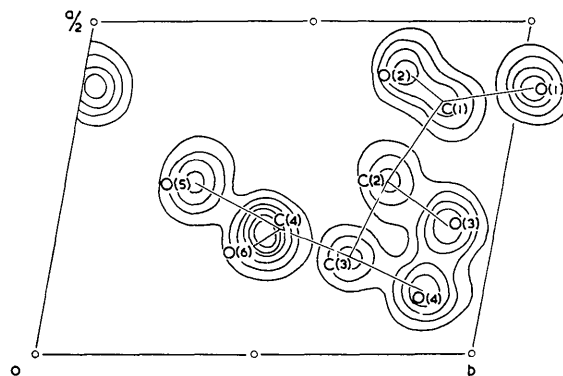

Fig. 4. Electron density projection on (001) of triclinic anhydrous mesotartaric acid.

Table 5. *Results obtained with the correlation method*

Triclinic hydrate	Case	U	Reflexions	Number of Sign relations	Correlation equations	Number of Reflexions	Possibilities
[100]	1	≥0·26	36	78	52	25	2
[001]	2	≥0·22	34	74	55	12	8
[001]	3	≥0·24	30	48	28	27	16
Monoclinic							
[010]	4	≥0·25	38	98	114	9	4
[010]	5	corr.	38	98	114	30	8
[010]	6	≥0·25	31	51	30	27	8
[010]	7	≥0·24	37	67	44	37	2
[100]	8	≥0·20	30	52	32	25	4
Triclinic anhydrous							
[001]	9	≥0·27	32	69	56	32	1
[010]	10	≥0·24	33	81	79	15	16
[010]	11	≥0·27	30	55	26	17	16

been taken. The mean (maximal) values of the e.s.d.'s for the coordinates of the oxygen and carbon atoms are 0·0027 (0·0033) and 0·0036 (0·0039) Å. The maximal e.s.d. in the bond lengths is 0·006 Å and in the bond angles 0·4°.

Monoclinic mesotartaric acid monohydrate

The intensity measurements were performed with two different techniques, using two crystals. The reflexions $0kl$, $h0l$, $h1l$ and $h2l$ were recorded on Weissenberg photographs; the intensities of the remaining reflexions were counted. The intensities of the $00l$, $01l$ and $02l$ reflexions, already determined photographically, were remeasured for scaling purposes and for determining the α_1–α_2 splitting factor. The intensities of

1396 out of a total of 1531 reflexions within the copper sphere were determined.

The experimentally determined scale factors of the five separately measured groups of reflexions were introduced as adjustable parameters during the refinement; the differences between final and original values were all less than 4%. The calculations were carried out with equal weights for all reflexions, zero weight being given to 5 very strong ones. A considerable decrease in R, from 13·9 to 7·8%, was obtained by refinement of anisotropic temperature parameters, on the PASCAL and X1 computers.

From the final three-dimensional difference Fourier synthesis, using only low-order reflexions, the positions of the hydrogen atoms H(7) and H(8) on the water

Table 6. *Triclinic mesotartaric acid monohydrate: final parameters*

U's defined by the temperature factor:
$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{31}lhc^*a^*)\right]$$

	x	y	z	1000 U_{11}	1000 U_{22}	1000 U_{33}	2000 U_{12}	2000 U_{23}	2000 U_{31}
O(1)	+0·5859	+0·4184	+0·1277	40	39	59	12	70	14
O(2)	+0·8110	+0·2136	+0·0757	36	50	47	30	68	32
O(3)	+0·3112	+0·3436	+0·3627	23	28	51	14	39	18
O(4)	+0·8128	+0·3565	+0·5533	33	26	37	7	23	−9
O(5)	+0·6647	−0·0616	+0·2606	28	25	48	4	32	−2
O(6)	+1·0233	+0·0899	+0·3741	24	31	49	9	48	12
O(7)	+1·0917	+0·3214	−0·1393	32	27	33	2	28	5
C(1)	+0·6315	+0·3019	+0·1529	25	33	35	−4	40	−10
C(2)	+0·4851	+0·2357	+0·2741	21	25	37	5	35	3
C(3)	+0·6496	+0·2172	+0·4383	27	25	30	9	28	13
C(4)	+0·8031	+0·0769	+0·3535	30	26	32	5	41	3

	x	y	z	Bonded to	B
H(1)	+0·408	+0·126	+0·174	C(2)	3·0
H(2)	+0·537	+0·195	+0·524	C(3)	3·0
H(3)	+0·899	+0·255	+0·020	O(2)	3·5
H(4)	+0·742	−0·137	+0·213	O(5)	3·5
H(5)	+0·236	+0·314	+0·417	O(3)	3·5
H(6)	+0·736	+0·411	+0·604	O(4)	3·5
H(7)	+1·013	+0·322	−0·245	O(7)	3·5
H(8)	+1·189	+0·389	−0·094	O(7)	3·5

Table 7. *Monoclinic mesotataric acid monohydrate: final parameters*

	x	y	z	100 U_{11}	1000 U_{22}	1000 U_{33}	2000 U_{12}	2000 U_{23}	2000 U_{31}
O(1)	+0·5705	+0·0480	+0·2967	54	46	28	−43	−22	25
O(2)	+0·7548	+0·3885	+0·3443	51	30	40	−25	−20	27
O(3)	+0·2951	−0·1043	+0·3649	28	62	32	−42	−35	26
O(4)	+0·8579	−0·1804	+0·4085	26	23	36	−4	−24	26
O(5)	+0·6859	+0·3609	+0·4819	25	32	39	−4	−34	24
O(6)	+1·0692	+0·2404	+0·4612	21	29	32	−10	−20	19
O(7)	+0·8708	+0·1621	+0·2308	46	52	39	−21	−29	26
C(1)	+0·6114	+0·1968	+0·3384	32	26	28	−4	−8	10
C(2)	+0·4739	+0·1018	+0·3824	21	32	29	−7	−22	11
C(3)	+0·6799	−0·0060	+0·4267	21	25	25	−9	−12	23
C(4)	+0·8340	+0·2122	+0·4580	22	23	20	−2	−5	20

	x	y	z	Bonded to	B
H(1)	+0·394	+0·258	+0·397	C(2)	3·0
H(2)	+0·586	−0·083	+0·453	C(3)	3·0
H(3)	+0·700	+0·103	+0·269	O(1)	3·5
H(4)	+0·786	+0·508	+0·508	O(5)	3·5
H(5)	+0·156	−0·125	+0·382	O(3)	3·5
H(6)	+0·781	−0·311	+0·394	O(4)	3·5
H(7)	+0·79	+0·25	+0·20	O(7)	3.5
H(8)	+0·96	+0·00	+0·23	O(7)	3·5

oxygen atom O(7) could not be established accurately, because the peaks were not clearly separated. The positions in Table 7 are the most reasonable ones, considering the difference Fourier synthesis and the hydrogen bond scheme.

The calculated mean (maximal) values of the e.s.d.'s for the coordinates of oxygen and carbon atoms are 0·0027 (0·0033) and 0·0034 (0·0038) Å, so the maximal e.s.d. in the intramolecular bond lengths is 0·006 Å and in the bond angles 0·4°.

Triclinic anhydrous mesotartaric acid

The intensities of the reflexions were measured by the counting technique. A set of five reference reflexions was counted every 3 or 4 hours. During the course of our measurements there appeared to be a serious decline in the intensities, due to a disintegration of the crystal. Consequently out of a total of 1346 reflexions within the copper sphere only 632 reflexions (*k* and *l* positive) were counted.

The least-squares refinement was performed on the X1 computer. Equal weights were given to all reflexions, except for six very strong ones, which were apparently subject to extinction. The final difference Fourier synthesis constructed with the contribution of the hydrogen atoms excluded from F_{calc} contained, notwithstanding the limited set of data, a correct number of peaks. Their coordinates, though not very reliable, are given in Table 8, together with the final parameters of the 'heavy' atoms. The final R value was 7·6%. The mean (maximal) values of the e.s.d.'s for the coordinates of the oxygen and carbon atoms are 0·0044 (0·0057) and 0·0057 (0·0072) Å. The maximal e.s.d. in the bond lengths is 0·01 Å and in the bond angles 0·7°.

Though the set of structure factors is incomplete, it can be argued that the introduction of anisotropic temperature parameters seems justified by the fairly accurate measurements.

It is of interest to find that the results of the three analyses with different ways of refinement compare rather well.

Discussion of the structures of mesotartaric acid

The lack of optical activity of mesotartaric acid was usually ascribed to intramolecular compensation. The two halves of the molecule were supposed to be mutually related either by a mirror plane [Fig. 5(a)] or by a centre of symmetry [Fig. 5(b)], the second possibility being accepted as the more probable one on account of the steric interactions.

From cell dimensions and experimental densities of crystals of anhydrous triclinic mesotartaric acid and of potassium mesotartrate dihydrate Schneider (1928) concluded that the cell contents comprised two non-symmetrical molecules related by a centre of symmetry. These premature conclusions were confirmed by Kroon, Peerdeman & Bijvoet (1965) for the mesotartrates and by our determination of the structures of different mesotartaric acid modifications. The two mesotartaric acid molecules in the unit cell, related by a centre of symmetry, have the staggered conformations of Fig. 6 and not the generally assumed centrosymme-
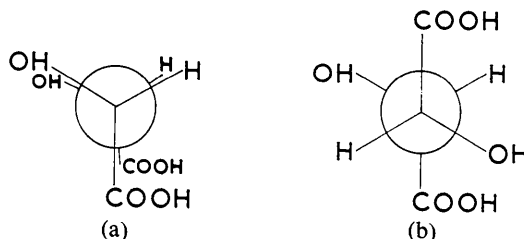

Fig. 5. Newman projections of mesotartaric acid. (a) Eclipsed conformation. (b) Centrosymmetrically staggered conformation.
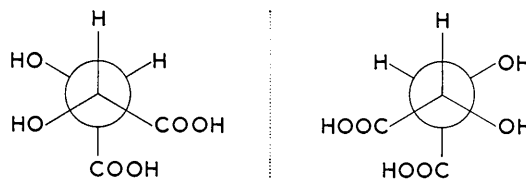

Fig. 6. Conformations of mesotartaric acid in the solid state.

Table 8. *Triclinic anhydrous mesotartaric acid: final parameters*

	x	y	z	1000 U_{11}	1000 U_{22}	1000 U_{33}	2000 U_{12}	2000 U_{23}	2000 U_{31}
O(1)	+0·4035	+1·0303	+0·2730	35	27	29	−28	17	−27
O(2)	+0·4268	+0·7357	+0·6502	33	31	29	−24	17	−32
O(3)	+0·1967	+0·8946	+0·1604	40	26	24	−14	−3	−33
O(4)	+0·0921	+0·8700	+0·7185	30	31	41	8	−26	−24
O(5)	+0·2601	+0·2967	+0·7875	76	29	40	−3	−18	−11
O(6)	+0·1676	+0·4763	+1·0925	48	38	20	−18	−2	−10
C(1)	+0·3720	+0·8511	+0·4295	21	26	21	−9	−2	−2
C(2)	+0·2625	+0·7387	+0·3805	27	19	20	−12	5	−15
C(3)	+0·1436	+0·6809	+0·6272	28	27	29	−16	−11	−14
C(4)	+0·1931	+0·4794	+0·8605	33	26	36	−14	−14	−21

	x	y	z	Bonded to	B				
H(1)	+0·317	+0·600	+0·367	C(2)	3·0				
H(2)	+0·061	+0·647	+0·572	C(3)	3·0				
H(3)	+0·472	+0·786	+0·689	O(2)	3·5				
H(4)	+0·289	+0·292	+0·850	O(5)	3·5				
H(5)	+0·162	+0·839	+0·097	O(3)	3·5				
H(6)	−0·036	+0·936	+0·731	O(4)	3·5				

tric conformation of Fig. 5(b). The crystals are race-mates and their lack of optical activity is caused by intermolecular compensation of the 'conformational antipodes'.

The assumption that the diastereoisomeric tartaric acids exist in solution predominantly in the same ethane conformations as found in crystals provides a simple explanation of experimental data reported in the literature (Bootsma, 1964).

In the following paragraphs the results of the determinations of the mesotartaric acid structures are compared.
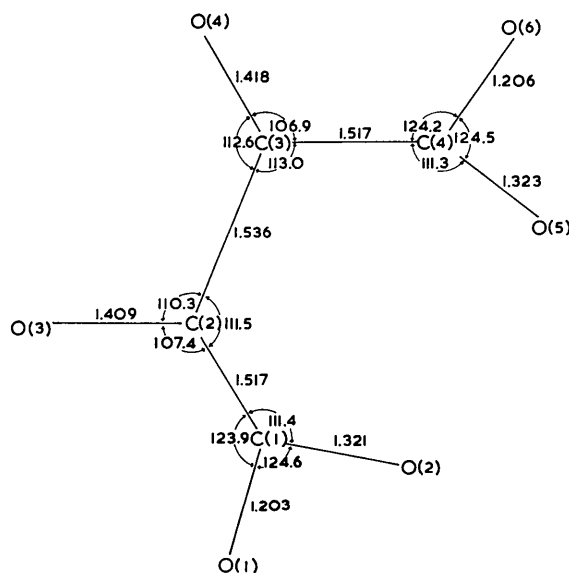
Fig. 7. Bond distances (Å) and bond angles (°) in the molecule of mesotartaric acid as determined in the structure of the triclinic hydrate.

Geometry of the mesotartaric acid molecule

The configuration of the molecule in the three modifications is the same as that found by Kroon, Peerdeman & Bijvoet (1965) in crystals of mesotartrates. The bond distances and bond angles are given in Table 9 and for the triclinic monohydrate also in Fig. 7.

The limits of accuracy stated in Table 9 are twice the maximal e.s.d. in the bond lengths and angles.

The distances of the central C–C bond (mean value 1·533 Å) are in good agreement with the distance accepted for an sp^3-sp^3 bond (1·533 Å; Lide, 1962). The mean value of the other C–C distances (1·517 Å) is slightly larger than the value suggested for an sp^2-sp^3 bond (1·505 Å; Lide, 1962). The mean values of the bond length and angles for the aliphatic hydrogen atoms are 0·99 Å (C–H), 107° (C–C–H) and 114° (O–C–H). For the other hydrogen atoms the corresponding values are 0·85 Å (O–H) and 110° (C–O–H).

A comparison of the intramolecular bond distances (Table 9) reveals one anomaly: in the carboxyl group C(1)O(1)O(2) of the monoclinic hydrate the carbonyl oxygen atom and the α-hydroxyl group lie evidently at different sides of the C(1)–C(2) bond. This interchange is confirmed by the corresponding bond angles and by the hydrogen bonds (Fig. 5). The most normal conformation of the molecule seems to be that found in the triclinic hydrate (Fig. 7) in which corresponding distances and bond angles in both halves are nearly equal. The angle between the planes of the two carboxyl groups is 57° (as in the mesotartrates). The same distances and angles, within the limits of accuracy, are found for the C(3)O(4)C(4)O(5)O(6) side of the monoclinic hydrate. The packing requirements of the molecules in the monoclinic structure were clearly of such

Table 9. *Bond distances and bond angles in mesotartaric acid*

	Triclinic hydrate	Monoclinic	Triclinic anhydrous
Bond			
C(1)–O(1)	1·203 ± 0·012 Å	1·302 ± 0·012 Å	1·222 ± 0·020 Å
C(1)–O(2)	1·321	1·213	1·307
C(4)–O(5)	1·323	1·304	1·341
C(4)–O(6)	1·206	1·223	1·212
C(2)–O(3)	1·409	1·415	1·413
C(3)–O(4)	1·418	1·414	1·414
C(1)–C(2)	1·517	1·521	1·520
C(2)–C(3)	1·536	1·534	1·523
C(3)–C(4)	1·517	1·511	1·520
Angle			
O(1)–C(1)–C(2)	123·9 ± 0·8°	114·2 ± 0·8°	121·8 ± 1·4°
O(2)–C(1)–C(2)	111·4	120·9	113·0
O(1)–C(1)–O(2)	124·6	124·8	125·3
O(5)–C(4)–C(3)	111·3	111·4	113·0
O(6)–C(4)–C(3)	124·2	123·8	124·3
O(5)–C(4)–O(6)	124·5	124·7	122·5
C(1)–C(2)–O(3)	107·4	111·0	106·9
C(3)–C(2)–O(3)	110·3	108·8	109·6
C(1)–C(2)–C(3)	111·5	108·3	110·6
C(4)–C(3)–O(4)	106·9	107·9	108·2
C(2)–C(3)–O(4)	112·6	112·6	108·6
C(4)–C(3)–C(2)	113·0	112·9	115·0

a nature that for the other side a compromise had to be found.

The analogy of the conformations in the three modifications is also demonstrated by the deviations of the atoms from the least-squares planes calculated for the two halves of the molecule (Table 10). The significant differences in this table can be explained as effects of small rotations of the carboxyl groups around the C–C bonds. The C(1)C(2)O(1)O(2) plane of the monoclinic form has been rotated towards the plane of the other carboxyl group, causing a decrease of the interplanar angle to 49°. In the anhydrous form the rotation of the C(4)C(3)O(6)O(5) plane is in the reverse direction and the angle between the planes is increased to 67°.

Thermal movement in the molecule

The anisotropic thermal parameters resulting from the refinement have been interpreted in terms of the ellipsoids of thermal motion. In Table 11 temperature factors corresponding to the root mean square displacements $(B = 8\pi^2 \overline{u^2})$ along the three principal axes of the ellipsoids of thermal motion are given for the three structures. The long principal axes of the ellipsoids of the carboxyl oxygen atoms coincide in all cases approximately with the normals on the planes of the carboxyl groups, indicating a libration of these groups around the C–C bonds.

The environment of the molecule in the triclinic hydrate structure

The packing of acid and water molecules is illustrated in Fig. 8. The water molecules play an essential part in the three-dimensional network of hydrogen bonds by which the molecules are held together. Each water oxygen atom O(7) is connected by hydrogen bonds to four different acid molecules, and each acid molecule in its turn forms four hydrogen bonds with surrounding water molecules. These bonds are close to linear, the angle H–O···O'*, being 6, 7, 7 and 24° for O(2)···O(7), O(5)···O(7'), O(7)···O(4'') and O(7)···O(1''') respectively. The angle H(7)O(7)H(8) is 111°.

The remaining two hydrogen atoms H(5) and H(6) do not take part in strong hydrogen bonds. Although the intermolecular distances O(3)···O(6^{iv}) (2·78 Å) and O(4)···O(3^{v}) (2·71 Å) seem almost conclusive, the valence angles C–O···O and the hydrogen locations are indications for the formation of bifurcated connexions of the hydroxyl oxygen atoms O(3) and O(4) to carbonyl and hydroxyl oxygen atoms of the same half of adjacent molecules; O(3)···O(4^{iv}) = 3·15 Å and O(4)···O(1^{v}) = 3·42 Å.

The environment of the molecule in the monoclinic hydrate structure

There are four acid and four water molecules in the monoclinic unit cell (Fig. 9). Single layers that contian molecules of the same antipode are formed parallel to

* As reference to symmetry-related atomic positions the following superscripts are used.

' atom at	2−x, −y, −z	^{vii} atom at	2−x, 1−y, 1−z
''	x, y, z−1	^{viii}	1−x, ½+y, ½−z
'''	2−x, 1−y, −z	^{ix}	x, y−1, z+1
^{iv}	x−1, y, z	^{x}	1−x, 2−y, 1−z
^{v}	1−x, 1−y, 1−z	^{xi}	−x, 2−y, 1−z
^{vi}	x, y−1, z		

Table 10. *Distances to carboxyl planes* (Å)

	Plane C(1)C(2)O(1)O(2)				Plane C(4)C(3)O(6)O(5)		
	Triclinic hydrate	Monoclinic	Triclinic anhydrous		Triclinic hydrate	Monoclinic	Triclinic anhydrous
C(1)	+0·007	−0·017	+0·002	C(4)	+0·011	+0·008	+0·023
C(2)	−0·002	+0·005	−0·001	C(3)	−0·003	−0·002	−0·006
O(1)	−0·003	+0·006	−0·001	O(6)	−0·005	−0·003	−0·009
O(2)	−0·002	+0·007	−0·001	O(5)	−0·004	−0·003	−0·007
O(3)	+0·112	−0·183	+0·199	O(4)	−0·137	−0·189	+0·200
O(4)	+2·396	+2·445	+2·313	O(3)	+1·027	+1·002	+0·719
O(5)	−0·143	+0·664	−0·297	O(2)	+2·680	+2·852	+2·744

Table 11. *Temperature factors* (Å²) *corresponding to the r.m.s. displacements along the principal axes of the ellipsoids of thermal motion*

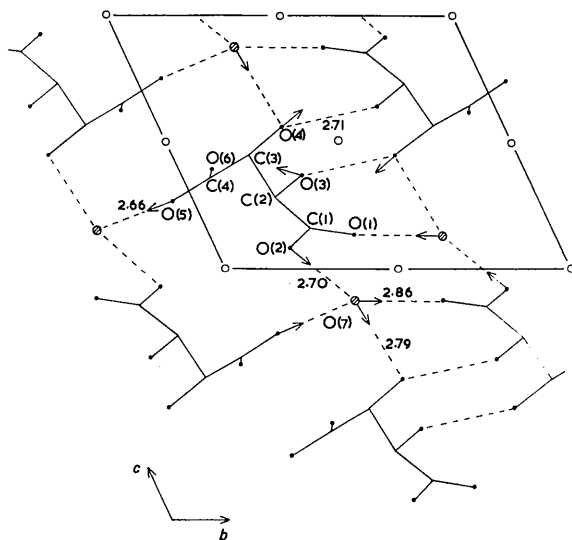|	Triclinic hydrate			Monoclinic			Triclinic anhydrous		
	B_I	B_{II}	B_{III}	B_I	B_{II}	B_{III}	B_I	B_{II}	B_{III}
C(1)	3·4	2·0	1·6	2·6	2·4	1·8	2·8	1·7	1·3
C(2)	3·0	1·7	1·6	3·2	1·6	1·4	2·6	2·0	1·0
C(3)	2·5	1·9	1·7	2·7	1·6	1·1	2·7	2·0	1·9
C(4)	2·8	2·4	1·2	2·2	1·7	1·0	3·2	2·2	2·0
O(1)	4·9	3·1	1·7	5·8	2·4	1·8	4·5	2·0	1·2
O(2)	4·9	2·4	2·0	4·7	2·9	1·8	4·6	2·0	1·2
O(5)	4·0	2·2	1·9	4·2	2·0	1·2	6·6	3·3	2·2
O(6)	3·9	1·9	1·8	3·3	1·6	1·5	3·8	3·5	1·4
O(3)	4·1	2·1	1·6	6·1	1·9	1·4	3·6	2·1	1·2
O(4)	3·6	2·2	2·0	3·6	1·8	1·1	3·5	2·8	1·8
O(7)	2·7	2·6	2·0	5·2	3·1	2·3			

Fig. 8. The arrangement of the molecules in the triclinic hydrate viewed along the a axis. Arrows: donor direction in the hydrogen bonds (dashed lines).
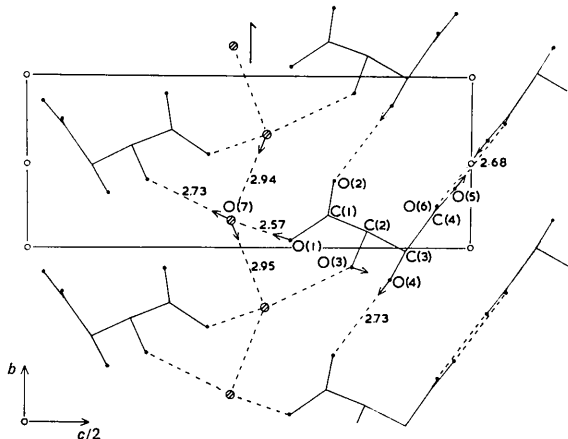

Fig. 9. The arrangement of the molecules in the monoclinic hydrate viewed along the a axis.
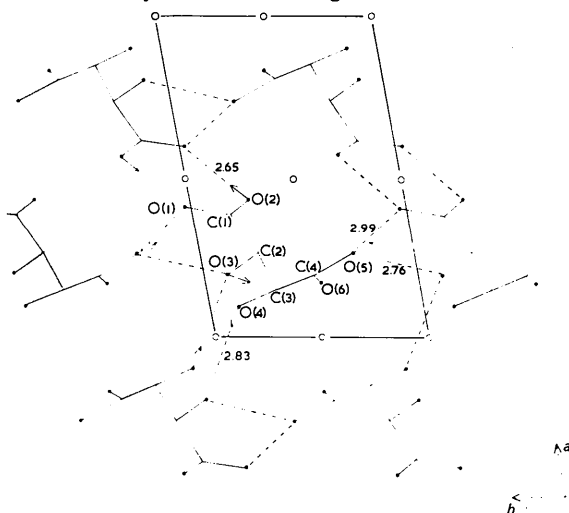

Fig. 10. The arrangement of the molecules in the triclinic anhydrous structure viewed along the c axis.

the (001) plane. Within these layers the molecules are linked by the hydrogen bonds $O(4)\cdots O(2^{vi})$ (2·73 Å, $\angle H(6)-O(4)\cdots O(2^{vi})=20°$) in the direction of the b axis and $O(3)\cdots O(4^{iv})$ (2·74 Å, $\angle H(5)-O(3)\cdots O(4^{iv})$ $=5°$) in the a-axis direction.

At one side the single layers are connected directly to single layers containing the opposite antipode by means of dimerization of the carboxyl groups $(O(5)\cdots O(6^{vii})=2·68$ Å, $\angle H(4)-O(5)\cdots O(6^{vii})=6°)$. The connection of these double layers by the action of the screw axis is through water molecules, resulting in the double layer sequence $(rl)(lr)(rl)$ etc. The four hydrogen bonds around the water oxygen atom are arranged in a roughly tetrahedral configuration. One hydrogen bond $[O(1)\cdots O(7)]$ is shorter than the other ones (2·57 Å, $\angle H(3)-O(1)\cdots O(7)=2°$).

The closest intermolecular approaches between nonbonded atoms are those between $O(5)$ and $O(5^v)$ (2·68 Å) and between $O(7)$ and $O(1^{viii})$ (3·00 Å). The distance between the planes of dimerized carboxyl groups is 0·03 Å. The separation of two $C(3)C(4)O(5)$-$O(6)$ planes related by translation along a is only 0·14 Å.

The environment of the molecule in the triclinic anhydrous structure

As in the structure of the monoclinic modification, alternating layers containing molecules of one of the antipodes are formed, here parallel to the (100) plane (Fig. 10).

There are six intermolecular $O\cdots O$ distances shorter than 3·00 Å. No stringent conclusions can be drawn on the basis of the peak locations of the three-dimensional difference Fourier synthesis constructed with the limited set of data. The hydrogen bonds between molecules of the same antipode are formed by the atoms $H(4)(O(5)\cdots O(1^{ix})=2·99$ Å, $O(5)\cdots O(3^{ix})=2·76$ Å) and

$H(5)(O(3)\cdots O(6^{ii})=2·94$ Å, $O(3)\cdots O(4^{ii})=2·86$ Å) and probably of a bifurcated type (for H(5) compare analogy in the triclinic hydrate structure).

The connexion between the layers is at the one side by dimerization of carboxyl groups $(O(2)\cdots O(1^x)=$ 2·65 Å, separation of the planes 0·21 Å) and at the other side by hydrogen bonds between the hydroxyl groups $(O(4)\cdots O(3^{xi})=2·83$ Å).

Comparison with the structure of racemic acid

The crystals of the mesotartaric acid modifications are racemates. It is therefore of interest to look for common features in the structures of meso- and DL-tartaric acid (Parry, 1951). The difference between a tartaric and a mesotartaric acid molecule lies in the arrangement about one of the asymmetric carbon atoms. Spatial models and also analogous projections of these molecules can be brought into coincidence with each other, with the exception of one of the carboxyl groups.

In the triclinic mesotartaric acid structures the relative positions of all but three 'heavy' atoms of the

molecule with regard to the centres of symmetry are approximately the same as those of the corresponding atoms of tartaric acid in the racemic acid structure.

According to Parry one of the important linkages in the racemic acid structure is a square system of hydrogen bonds between hydroxyl groups on four molecules, thus forming columns parallel to the, say, c' axis ($c' = c$ for racemic acid). Each hydroxyl group is supposed to take part in two bonds, one with a hydroxyl group of an antipode molecule and the other with a hydroxyl group of a molecule of the same configuration related by translation in the direction of c'.

Analogous squares are formed in the mesotartaric acid structures (see Figs. 8 and 10; in both Figures c' corresponds to the projection axis). From the high values of the valence angles and our findings with regard to the hydrogen bond formation it may be concluded that these *hydroxyl squares* are of secondary importance for the coherence of the structures compared with the links to be described next.

In the structure of racemic acid one carboxyl group of the molecule is directly linked with a carboxyl group of a centrosymmetrically related molecule, and the other carboxyl group is indirectly connected with a counterpart through water molecules. The first type of linkage (*carboxylic acid dimers*) is found at one side of the molecule in the anhydrous form (Fig. 10), the second type (*hydrated links*) at one side of the molecule in the structure of the triclinic hydrate (Fig. 8). In the monoclinic hydrate (Fig. 9) one side of the molecule takes part in a carboxylic acid dimer configuration, but the linkage through water molecules at the other side of the molecule is a less common mutation of the hydrated links found in other cases. Here a tetrahedral arrangement of close neighbours around the water oxygen atom O(7) is achieved by mutual hydrogen bonding of water oxygen atoms related by the twofold screw axis.

Evidently the geometry of the mesotartaric acid molecule does not permit an ideal three-dimensional arrangement with both types of intermolecular linkages present.

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A Neutron Diffraction Study of the Crystal Structure of Lithium Hydrazinium Sulphate

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A single-crystal neutron-diffraction investigation of lithium hydrazinium sulphate has been made in which the intensities of 215 reflexions in all the three prism zones were measured. The structure was refined by Fourier and least-squares techniques. The heavy-atom positions obtained agree very well with values from the X-ray determination. The hydrogen atoms of the NH_2–NH_3^+ ion are arranged tetrahedrally about the nitrogen atoms and the configuration was found to be staggered. The NH_2 groups of the ions are linked into infinite chains by hydrogen bonds pointing in the negative c direction. The hydrogen atoms of the NH_3 group are static and do not rotate along the N–N axis.

The interesting electrical properties of room temperature ferroelectric lithium hydrazinium sulphate ($LiN_2H_5SO_4$) have been the subject of a great deal of investigation. The proton and ^7Li nuclear magnetic resonance signals have been investigated in detail over a wide temperature range, $-180°C$ to $+210°C$, by Cuthbert & Petch (1963). From these experiments they concluded that (1) at the temperature region about