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Refinement of the Structure of D-Tartaric Acid by X-ray and Neutron Diffraction*

BY Y. OKAYA AND N. R. STEMPLE
IBM Watson Research Center, Yorktown Heights, New York, U.S.A.
AND M. I. KAY
Puerto Rico Nuclear Center, Mayaguez, Puerto Rico

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The crystal structure of D-tartaric acid determined by Stern & Beevers [*Acta Cryst.* **3**, 341 (1950)] was refined by using three-dimensional intensity data (Cu $K\alpha$) collected on a computer-controlled diffractometer operated by an IBM 1620 machine under a stored data collection program. The crystallographic data are: $a=7{\cdot}71_5\pm0{\cdot}003$, $b=6{\cdot}00_4\pm0{\cdot}003$, $c=6{\cdot}23_1\pm0{\cdot}003$ Å, $\beta=100{\cdot}1\pm0{\cdot}1°$, with space group $P2_1$. The parameters were refined by using a full-matrix least-squares program; all the hydrogen atoms were located by a difference Fourier synthesis and refined by the least-squares method. The results of this refinement are compared with a similar result obtained from neutron diffraction data.

The molecule is made of two –C*H . OH . COOH parts, each part consisting of a planar carboxyl group and a tetrahedral asymmetric carbon atom; the α-hydroxyl oxygen atom is also situated close to the carboxyl plane. There is a slight but interesting difference in the overall shape of these two parts; the angle between the planes of the carboxyl groups in these two parts is 54·6°.

The molecules are held in the structure by a three-dimensional network of O–H . . . O hydrogen bonds of usual strength. The hydrogen bond scheme in the crystal was unequivocally determined by the present analysis.

Introduction and experimental

The crystal structure of D-tartaric acid was determined some fifteen years ago by Stern & Beevers (1950) by elegant deconvolution of the Patterson function. Although their results revealed an interesting network of O–H . . . O hydrogen bonds and the general shape of the molecule, no attempt was made to refine the structure enough for the bond lengths and angles of this important oxyacid to be discussed with confidence. The present paper† deals with the refinement of the structure based on three-dimensional X-ray intensity data obtained by counter measurement on CCXD, a computer-controlled diffractometer (Cole, Okaya & Chambers, 1963) and on two projections of neutron diffraction data.

A single crystal of D-tartaric acid was ground into a sphere of approximately 0·5 mm in diameter and mounted on a General Electric Goniostat; the b axis of the crystal was set almost parallel to the φ axis of the Goniostat. Full three-dimensional intensity data within the range of $\sin\theta\leq0{\cdot}96$ for Cu $K\alpha$ (Ni-filtered) were then recorded by CCXD operated under a stored data-collection program in an IBM 1620 computer (Okaya, 1964). For each reflection, the crystal setting and the accuracy of the equipment were first tested by step-scanning around the ω and χ axes and then the integrated intensity data were recorded by (θ-2θ) step scanning. While the ω setting was studied, the maximum and minimum counts were recorded and if the difference between them did not exceed the statistical fluctuation, the reflection was then treated as non-observed. Out of 647 reflections recorded by the diffractometer there were fewer than five such reflections. The intervals between the steps were so chosen that the first three and the last three out of the total of twenty-four θ–2θ steps for each reflection could be taken to represent the background at the 2θ value of the reflection; they are 0·09° for 2θ less than 70°, 0·11° for $70°\leq2\theta<140°$ and 0·13° thereafter. The integrated intensity data were calculated from data on the 2θ step scan as a time-shared program on the IBM 1620 computer. The observed F values were corrected for the absorption effect ($\mu r=0{\cdot}8$). The crystal belongs to the monoclinic system with space group $P2_1$, and the cell dimensions measured on the diffractometer are $a=7{\cdot}71_5\pm0{\cdot}003$, $b=6{\cdot}00_4\pm0{\cdot}003$, $c=6{\cdot}23_1\pm0{\cdot}003$ Å, $\beta=100{\cdot}1\pm0{\cdot}1°$; these values agree well with the values given in the previous paper.

Starting from the atomic coordinates given by Stern & Beevers the refinement of the structure was made in the usual manner by using a full-matrix least-squares program on an IBM 7094 computer. After several cycles of refinement with only the contribution of the non-hydrogen atoms, the positions of the hydrogen atoms were obtained by an $F_o-F_{(c+o)}$ synthesis. The atomic coordinates thus obtained for the hydrogen atoms were then subjected to the least-squares treatment; only isotropic temperature factors were used for the hydrogen atoms. The atomic coordinates, their standard devi-

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Table 1(*a*). *Atomic coordinates in fractions of cell edges and their estimated standard deviations*

Standard deviations are in units of 10^{-4} Å for C and O, and 10^{-3} Å for H atoms.

Atoms	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
O(1)	0·3382	26	0·0343	25	0·5102	21
O(2)	0·4296	27	−0·0325	27	−0·0219	23
O(3)	0·6084	24	0·0050	26	0·3005	22
O(4)	0·3063	25	0·4173	25	0·2335	22
O(5)	−0·0765	28	0·0792	32	0·1790	28
O(6)	−0·0217	27	0·4072	33	0·3496	29
C(1)	0·2941	33	0·0159	34	0·2832	30
C(2)	0·4640	34	−0·0068	35	0·1911	31
C(3)	0·2003	32	0·2273	33	0·1811	29
C(4)	0·0219	35	0·2528	35	0·2496	31
H(1)	0·241	36	−0·116	36	0·236	29
H(2)	0·182	33	0·207	35	0·028	31
H(3)	0·253	93	0·037	85	0·555	72
H(4)	0·515	81	−0·046	69	−0·090	57
H(5)	0·342	54	0·438	64	0·367	56
H(6)	−0·182	85	0·049	67	0·203	54
Neutron diffraction results						
H(1)	0·2101	21	−0·1385	28	0·2256	34
H(2)	0·1699	15	0·1993	45	0·0032	18
H(3)	0·2359	14	−0·0177	35	0·5724	19
H(4)	0·5360	15	−0·0427	26	−0·0931	23
H(5)	0·3470	21	0·4329	46	0·3900	22
H(6)	−0·1928	12	0·0725	27	0·2315	24

Table 1(*b*). *Anisotropic temperature factors*

The β's are used in the expression $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0·00695	0·02355	0·01149	−0·00006	0·00568	0·00578
O(2)	0·00725	0·02713	0·01412	0·00372	0·00814	−0·00598
O(3)	0·00578	0·02374	0·01634	0·00233	0·00606	0·00881
O(4)	0·00648	0·01708	0·01018	−0·00400	0·00343	0·00116
O(5)	0·00640	0·02688	0·02362	−0·00763	0·01023	−0·01724
O(6)	0·00920	0·02641	0·02492	−0·00004	0·01310	−0·01773
C(1)	0·00510	0·01411	0·01266	0·00222	0·00388	0·00336
C(2)	0·00665	0·01161	0·01502	−0·00024	0·00557	0·00333
C(3)	0·00442	0·01532	0·00954	−0·00009	0·00284	0·00067
C(4)	0·00496	0·01802	0·01203	0·00164	0·00052	−0·00043

Isotropic temperature factors for hydrogen atoms, in 10^{-16} cm^2

H(1)	H(2)	H(3)	H(4)	H(5)	H(6)
−1·3	−1·2	6·4	4·4	1·8	5·3

ations and thermal parameters after five cycles of further refinement are shown in Table 1. The final conventional error index $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ is 0·043 including unobserved reflections (as $F_o=0$). Comparison between the observed and calculated structure factors is shown in Table 2(*a*). The atomic scattering factors used in the computation were those values listed in *International Tables for X-ray Crystallography* (1962). The parameter shifts at the last stage were negligible in comparison with the standard deviations. The weighting scheme used in the refinement procedure was: $\sqrt{w}=1·0$ for $F_{obs}<10·0$, $\sqrt{w}=10·0/F_{obs}$ for $F_{obs}\geq 10·0$, and zero weight for unobserved reflections. As shown in Table 1, the isotropic temperature factors of two hydrogen atoms have become negative; although it is doubtful that any real significance can be attributed to such a result, one notices that these two hydrogen atoms are those bonded to the carbon atoms.

Table 1(*c*). *Anisotropic temperature factors from neutron diffraction**

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}
O(1)	0·0082	0·0157	0·0054	0·0021	0·0039
O(2)	0·0055	0·0164	0·0083	0·0037	−0·0009
O(3)	0·0060	0·0174	0·0178	0·0017	0·0048
O(4)	0·0047	0·0121	0·0142	−0·0019	0·0045
O(5)	0·0049	0·0214	0·0277	−0·0012	0·0028
O(6)	0·0058	0·0182	0·0252	0·0037	0·0056
C(1)	0·0034	0·0137	0·0057	0·0112	0·0005
C(2)	0·0043	0·0090	0·0094	−0·0013	0·0001
C(3)	0·0049	0·0113	0·0046	0·0013	0·0009
C(4)	0·0021	0·0157	0·0096	0·0000	0·0020
H(1)	0·0136	0·0142	0·0232	−0·0022	0·0100
H(2)	0·0089	0·0288	0·0125	−0·0033	0·0001
H(3)	0·0080	0·0298	0·0225	−0·0004	0·0023
H(4)	0·0079	0·0146	0·0308	−0·0016	0·0085
H(5)	0·0192	0·0377	0·0155	0·0014	0·0008
H(6)	0·0068	0·0230	0·0343	0·0014	−0·0019

* Since only $h0l$ and $hk0$ data were used, no β_{23} was calculated.

Table 2(*a*). *Observed and calculated structure factors from X-ray diffraction* (×10)

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
0	0	1	10	17		1	3	32	33	7	3	0	59	58		6	1	20	18		1	-3	61	61		3	-3	27	26
	0	2	324	342		1	4	49	50		3	1	9	9		6	2	18	17		1	-4	44	46		3	-4	40	41
	0	3	36	35							3	2	28	29		6	3	32	31		1	-5	10	7		3	-5	21	22
	0	4	198	196	8	1	0	14	16		3	3	14	15							1	-6	36	35					
	0	5	34	28		1	1	29	27						5	6	0	9	8						8	3	-1	51	55
	0	6	60	63		1	2	46	46	8	3	0	30	29		6	1	21	20	7	1	-1	15	14		3	-2	6	7
	0	7	15	16		1	3	27	29		3	1	19	19		6	2	6	5		1	-2	26	19		3	-3	67	64
											3	2	25	25							1	-3	25	28		3	-4	20	24
1	0	0	103	107	9	1	0	42	41						0	7	1	48	45		1	-4	18	16					
	0	1	242	239		1	1	45	44	0	4	0	170	173		7	2	21	20		1	-5	46	45	1	4	-1	27	26
	0	2	239	225							4	1	59	61		7	3	28	29		1	-6	109	103		4	-2	39	42
	0	3	96	90	0	2	1	63	57		4	2	46	45												4	-3	29	26
	0	4	67	66		2	2	67	53		4	3	59	59	1	7	0	16	13	8	1	-1	43	43		4	-4	68	72
	0	5	0	0		2	3	139	138		4	4	79	81		7	1	52	50		1	-2	6	6		4	-5	37	38
	0	6	50	47		2	4	107	102		4	5	45	46		7	2	35	33		1	-3	60	59		4	-6	47	50
	0	7	14	13		2	5	48	50		4	6	22	21							1	-4	55	56					
						2	6	58	58						2	7	0	13	12						2	4	-1	126	126
2	0	0	137	132		2	7	11	14	1	4	0	125	124		7	1	3	1	9	1	-1	30	27		4	-2	100	103
	0	1	167	173							4	1	148	146		7	2	18	16		1	-2	67	66		4	-3	64	64
	0	2	70	62	1	2	0	390	345		4	2	50	41							1	-3	46	54		4	-4	54	57
	0	3	44	42		2	1	227	256		4	3	49	49	3	7	0	8	10							4	-5	50	51
	0	4	118	119		2	2	70	53		4	4	39	39		7	1	41	38	1	2	-1	106	105		4	-6	38	38
	0	5	18	16		2	3	116	119		4	5	51	51							2	-2	58	57					
	0	6	40	40		2	4	126	126		4	6	40	39	1	0	-1	112	119		2	-3	75	68	3	4	-1	64	54
	0	7	26	27		2	5	53	65							0	-2	93	93		2	-4	136	135		4	-2	53	54
						2	6	10	5	2	4	0	22	11		0	-3	181	188		2	-5	30	29		4	-3	38	42
3	0	0	340	316		2	7	30	31		4	1	40	37		0	-4	178	185		2	-6	17	18		4	-4	31	31
	0	1	38	37							4	2	32	31		0	-5	60	60		2	-7	55	56		4	-5	81	83
	0	2	82	79	2	2	0	80	72		4	3	42	42		0	-6	20	6							4	-6	38	39
	0	3	9	5		2	1	205	211		4	4	30	29		0	-7	45	43	2	2	-1	94	98					
	0	4	117	117		2	2	106	107		4	5	24	23							2	-2	152	151	4	4	-1	52	54
	0	5	71	68		2	3	75	73		4	6	22	25	2	0	-1	15	14		2	-3	123	121		4	-2	74	77
	0	6	28	26		2	4	131	136							0	-2	78	78		2	-4	45	46		4	-3	45	45
						2	5	49	48	3	4	0	36	16		0	-3	188	185		2	-5	97	100		4	-4	80	82
4	0	0	27	35		2	6	82	89		4	1	44	38		0	-4	30	28		2	-6	52	49		4	-5	51	49
	0	1	9	8		2	7	9	15		4	2	52	52		0	-5	80	78		2	-7	17	16		4	-6	52	53
	0	2	37	28							4	3	36	34		0	-6	2	1										
	0	3	69	69	3	2	0	189	175		4	4	80	79		0	-7	36	36	3	2	-1	252	256	5	4	-1	91	93
	0	4	107	105		2	1	33	28		4	5	53	52							2	-2	58	58		4	-2	60	59
	0	5	45	43		2	2	131	133						3	0	-2	117	120		2	-3	59	58		4	-3	41	39
	0	6	11	9		2	3	64	65	4	4	0	50	49		0	-3	118	118		2	-4	81	78		4	-4	31	31
						2	4	91	91		4	1	51	51		0	-4	59	59		2	-5	106	106		4	-5	12	13
5	0	0	36	32		2	5	49	49		4	2	33	31		0	-5	105	106		2	-6	65	64		4	-6	36	40
	0	1	6	5		2	6	13	14		4	3	36	36		0	-6	33	31		2	-7	17	9					
	0	2	19	24							4	4	47	45		0	-7	54	64						6	4	-1	22	17
	0	3	118	118	4	2	0	121	123		4	5	28	26						4	2	-2	72	56		4	-2	50	48
	0	4	7	5		2	1	102	106						4	0	-1	38	29		2	-3	40	41		4	-3	38	39
	0	5	11	13		2	2	79	81	5	4	0	60	63		0	-2	182	182		2	-4	74	74		4	-4	28	29
						2	3	35	34		4	1	27	24		0	-3	65	53		2	-5	75	67		4	-4	48	29
6	0	0	29	28		2	4	83	84		4	2	33	31		0	-4	131	132		2	-6	39	37		4	-5	10	11
	0	1	14	12		2	5	22	22		4	3	18	16		0	-5	165	174		2	-7	20	11					
	0	2	53	51		2	6	4	6		4	4	27	29		0	-6	57	51						7	4	-1	78	79
	0	3	79	78												0	-7	74	71	5	2	-1	29	24		4	-2	30	32
	0	4	49	44	5	2	0	84	85	6	4	0	19	15							2	-2	109	109		4	-3	11	11
	0	5	14	12		2	1	14	4		4	1	11	12	5	0	-1	21	7		2	-3	114	115		4	-4	25	24
						2	2	69	74		4	2	55	54		0	-2	26	25		2	-4	84	87					
7	0	0	31	28		2	3	87	87		4	3	51	51		0	-3	86	85		2	-5	48	46	8	4	-1	38	43
	0	1	94	88		2	4	17	18							0	-4	60	62		2	-6	33	32					
	0	2	46	48		2	5	8	10	7	4	0	47	45		0	-5	26	25		2	-7	29	28	1	5	-2	29	30
	0	3	152	149							4	1	37	36		0	-6	2	2							5	-3	85	85
	0	4	48	45	6	2	0	57	55		4	2	12	10		0	-7	8	6	6	2	-1	226	230		5	-4	48	49
						2	1	89	90												2	-2	70	68		5	-5	21	22
8	0	0	75	75		2	2	66	66	0	5	1	146	147	6	0	-1	217	227		2	-3	46	46					
	0	1	38	38		2	3	100	106		5	2	40	37		0	-2	50	52		2	-4	23	25	2	5	-1	47	48
	0	2	3	2		2	4	31	33		5	3	77	77		0	-3	18	15		2	-5	47	46		5	-2	19	19
	0	3	58	51							5	4	10	7		0	-4	9	7		2	-6	27	24		5	-3	35	32
					7	2	0	82	81		5	5	16	15		0	-5	32	29							5	-4	42	41
9	0	0	21	18		2	1	29	16							0	-6	4	4	7	2	-1	79	73		5	-5	23	22
	0	1	13	10		2	2	28	23	1	5	0	92	93							2	-2	16	16					
						2	3	55	45		5	1	40	37	7	0	-1	132	138		2	-3	45	44	3	5	-1	67	67
0	1	2	104	107		2	4	18	18		5	2	59	56		0	-2	30	29		2	-4	20	23		5	-2	85	87
	1	3	162	162							5	3	58	59		0	-3	38	31		2	-5	65	62		5	-3	41	41
	1	4	47	43	8	2	0	40	35		5	4	53	52		0	-4	23	22		2	-6	20	21		5	-4	63	60
	1	5	52	52		2	1	15	12		5	5	12	11		0	-5	26	27							5	-5	37	36
	1	6	59	59		2	2	10	10							0	-6	39	38	8	2	-1	54	51					
	1	7	15	20						2	5	0	18	20							2	-2	10	7	4	5	-1	56	58
					0	3	1	180	186		5	1	35	35	8	0	-1	61	60		2	-3	27	27		5	-2	44	45
1	1	0	157	168		3	2	66	63		5	2	38	38		0	-3	28	25		2	-4	61	70		5	-3	41	42
	1	1	262	265		3	3	91	91		5	3	37	37		0	-4	57	60							5	-4	63	65
	1	2	378	386		3	4	35	34		5	4	26	24		0	-5	2	6	9	2	-1	19	21		5	-5	34	35
	1	3	92	92		3	5	19	21		5	5	39	39															
	1	4	19	25		3	6	33	32						9	0	-1	8	10	1	3	-1	113	116	5	5	-1	25	25
	1	5	17	14		3	7	5	6	3	5	0	59	61		0	-2	84	86		3	-2	74	72		5	-2	39	34
	1	6	59	59							5	1	68	65		0	-3	23	24		3	-3	103	103		5	-3	33	32
	1	7	14	13	1	3	0	56	52		5	2	11	6		0	-4	0	3		3	-4	77	81		5	-4	13	11
						3	1	129	128		5	3	61	59							3	-5	49	49		5	-5	55	54
2	1	0	137	138		3	2	58	69		5	4	24	23	1	1	-1	190	191		3	-6	34	35					
	1	1	90	94		3	3	59	58							1	-2	68	69		3	-7	36	37	6	5	-1	25	23
	1	2	79	82		3	4	54	56	4	5	0	44	43		1	-3	72	71							5	-2	34	32
	1	3	57	53		3	5	87	88		5	1	13	14		1	-4	124	124	2	3	-1	68	67		5	-3	24	24
	1	4	147	149		3	6	41	41		5	2	17	20		1	-5	94	97		3	-2	139	140		5	-4	6	7
	1	5	27	24							5	4	33	32		1	-6	12	13		3	-3	50	63					
	1	6	27	27	2	3	0	201	187							1	-7	8	9		3	-4	25	24	7	5	-1	24	25
	1	7	10	11		3	1	44	46	5	5	0	31	32							3	-5	58	60		5	-2	17	19
						3	2	94	94		5	1	31	32	2	1	-1	120	118		3	-6	47	49					
3	1	0	129	126		3	3	150	157		5	2	24	25		1	-2	344	345		3	-7	29	27	1	6	-1	43	47
	1	1	47	50		3	4	97	97		5	3	21	19		1	-3	197	208							6	-2	40	45
	1	2	127	131		3	5	74	77							1	-4	76	80	3	3	-1	142	142		6	-3	17	16
	1	3	37	35		3	6	6	7	6	5	0	63	61		1	-5	44	41		3	-2	120	120		6	-4	0	1
	1	4	93	93							5	1	38	35		1	-6	59	58		3	-3	25	25					
	1	5	54	52	3	3	0	143	137		5	2	51	52		1	-7	30	29		3	-4	47	43	2	6	-1	45	44
	1	6	34	37		3	1	126	130												3	-5	55	56		6	-2	7	7
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4	1	0	87	82		3	3	59	59							1	-2	190	184		3	-7	14	16		6	-4	33	34
	1	1	259	263		3	4	52	51	0	6	0	40	40		1	-3	90	90										
	1	2	96	94		3	5	62	63		6	1	39	37		1	-4	50	47	4	3	-1	71	74	3	6	-1	42	43
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	1	4	63	72							6	3	29	28		1	-6	64	62		3	-3	56	57		6	-3	15	13
	1	5	77	77	4	3	0	68	67		6	4	4	5		1	-7	49	46		3	-4	53	64		6	-4	54	54
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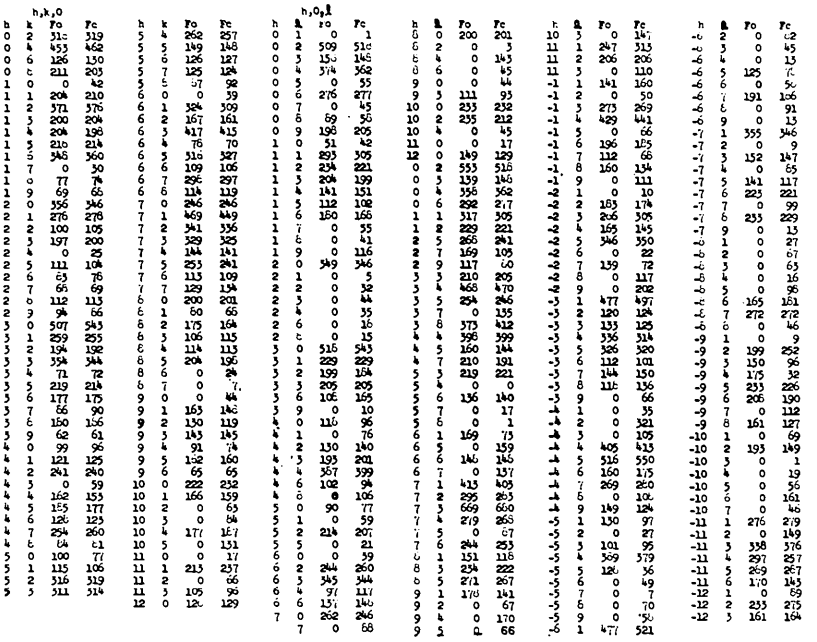
5	1	0	72	71		3	3	16	12		6	1	19	17		1	-2	48	48							6	-2	14	16
	1	1	69	68		3	4	60	61		6	2	50	50		1	-3	70	68	5	3	-1	114	119		6	-3	5	6
	1	2	62	60		3	5	47	44		6	3	18	19		1	-4	75	74		3	-2	83	85		6	-4	10	10
	1	3	42	42							6	4	16	16		1	-5	173	181		3	-3	70	71					
	1	4	10	4	5	3	0	107	114							1	-6	51	48		3	-4	89	90	5	6	-1	31	30
	1	5	46	47		3	1	90	92	7	6	0	31	36		1	-7	13	10		3	-5	46	45		6	-2	16	16
						3	2	59	68		6	1	17	14							3	-6	21	22		6	-3	10	11
6	1	0	59	58		3	3	79	82		6	2	7	6	5	1	-1	76	80										
	1	1	114	118		3	4	25	21		6	3	22	22		1	-2	30	30	6	3	-1	22	21	6	6	-1	19	25
	1	2	47	49		3	5	28	30		6	4	9	9		1	-3	155	160		3	-2	131	134					
	1	3	48	48												1	-4	14	11		3	-3	34	34	1	7	-1	32	31
	1	4	11	11	6	3	0	128	133	7	6	0	38	40		1	-5	14	12		3	-4	48	46		7	-2	5	3
	1	5	26	28		3	1	26	26		6	1	21	20		1	-6	43	40		3	-5	11	12		7	-3	18	19
						3	2	71	72		6	2	10	10		1	-7	41	39		3	-6	40	40					
7	1	0	107	109		3	3	10	10		6	3	9	10											2	7	-1	32	36
	1	1	70	69		3	4	14	14						6	1	-1	53	50	7	3	-1	37	41		7	-2	15	12
	1	2	73	72						4	6	0	21	22		1	-2	22	16		3	-2	33	32					

Table 2(*b*). *Observed and calculated structure factors from neutron diffraction* (×100)



To confirm and refine the hydrogen positions, two (*h*0*l* and *hk*0) zones of neutron diffraction data were taken by the (θ–2θ) scan method. Because of an accident, the *h*0*l* data had to be collected on two different crystals.

Refinement with the neutron data was carried out by means of least-squares analysis, starting with the X-ray parameter set. The carbon and oxygen positional parameters (as given in Table 1) were held constant. Refinement was carried out on all the hydrogen parameters, the carbon and oxygen temperature parameters and three scale factors. The refinement proceeded with isotropic temperature factors, followed by six rounds of least squares with anisotropic temperature factors. The weights are $\sqrt{w}=1/(\sigma(F)+0{\cdot}025F)$ where $\sigma(F)$ is

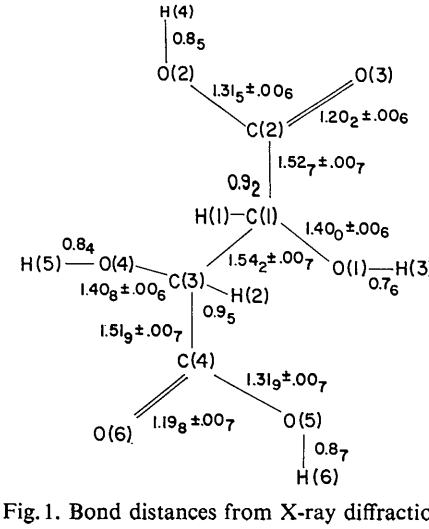


Fig. 1. Bond distances from X-ray diffraction.

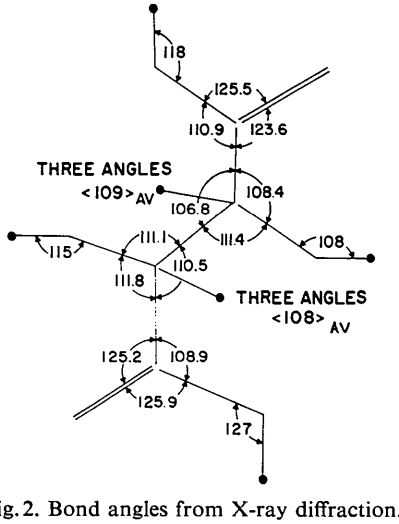


Fig. 2. Bond angles from X-ray diffraction.

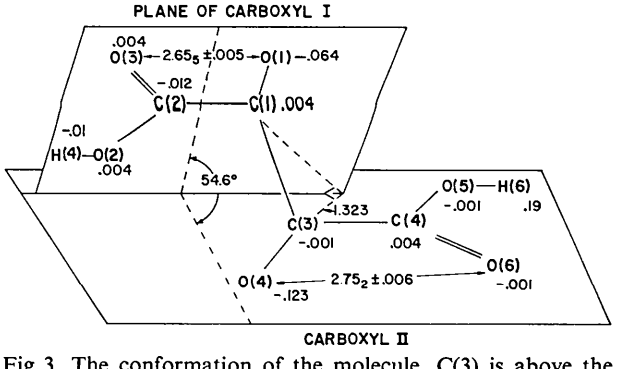


Fig. 3. The conformation of the molecule. C(3) is above the plane of carboxyl I by 1·323 Å. The deviations (Å) of atoms from the group plane are also shown for each part. Note the difference between the O(1)–O(3) and O(4)–O(6) distances.

based on counting statistics. Non-observed reflections were given zero weight. The resultant parameters are given in Table 1. The final R was 0·059 (omitting unobserved reflections). The observed and calculated structure factors (multiplied by 100) are given in Table 2(*b*). Both X-ray and neutron least squares minimized $\Sigma w(F_o - F_c)^2$.

Discussion

Bond distances and angles have been calculated from the X-ray atomic coordinates in Table 1(*a*); they are shown in Figs. 1 and 2 respectively. Around C(1) and C(2), only the average of the three angles involving the hydrogen atom is shown for each atom. The results of the hydrogen determination by neutron diffraction are given in Table 4 for comparison. The molecule consists of two $-C^*H \cdot OH \cdot COOH$ parts, each part containing a planar carboxyl group and a tetrahedral $-C^*H \cdot OH-$ configuration. In each of the two parts, the α-hydroxyl oxygen atom stays close to the carboxyl plane; it is interesting to note that a similar situation also exists in the mesotartaric ion (Kroon, Peerdeman & Bijvoet, 1965). It may be seen from the Figures that although these two parts are similar in over-all shape, there exist slight differences. The carboxyl group of part I, C(1), C(2), O(2), and O(3), is less planar than that of part II and the O(1)–O(3) distance is much shorter than the corresponding O(4)–O(6) distance in part II; this is mainly due to the large C(4)–C(3)–O(4) angle. It is interesting to notice that such seemingly

Table 3. *Hydrogen-bond system in the* D-*tartaric acid crystal*

The second values for H–O, H · · · O and angles around hydrogen atoms are those obtained by the neutron study

Bonds	*A*	*B*	*C*	*D*
From	O(1)	O(4)	O(2)	O(5)
to	O(6)	O(3)	O(4)	O(3)
of	$(-x, -\frac{1}{2}+y, 1-z)$	$(1-x, \frac{1}{2}+y, 1-z)$	$(1-x, -\frac{1}{2}+y, -z)$	$(-1+x, y, z)$
Hydrogen involved	H(3)	H(5)	H(4)	H(6)
Distances (Å)	2·839	2·909	2·633	2·707
O–H	0·8, 0·98	0·8, 0·97	0·9, 1·00	0·9, 1·00
H...O	2·1, 1·86	2·1, 1·95	1·8, 1·64	1·9, 1·71
Angles around hydrogen atoms	157°, 171°	172°, 169°	176°, 172°	152°, 168°
Separations listed by Stern & Beevers (1950)	O(1)–O(10)	O(7)–O(5)	O(4)–O(7)	O(5)–O(9)

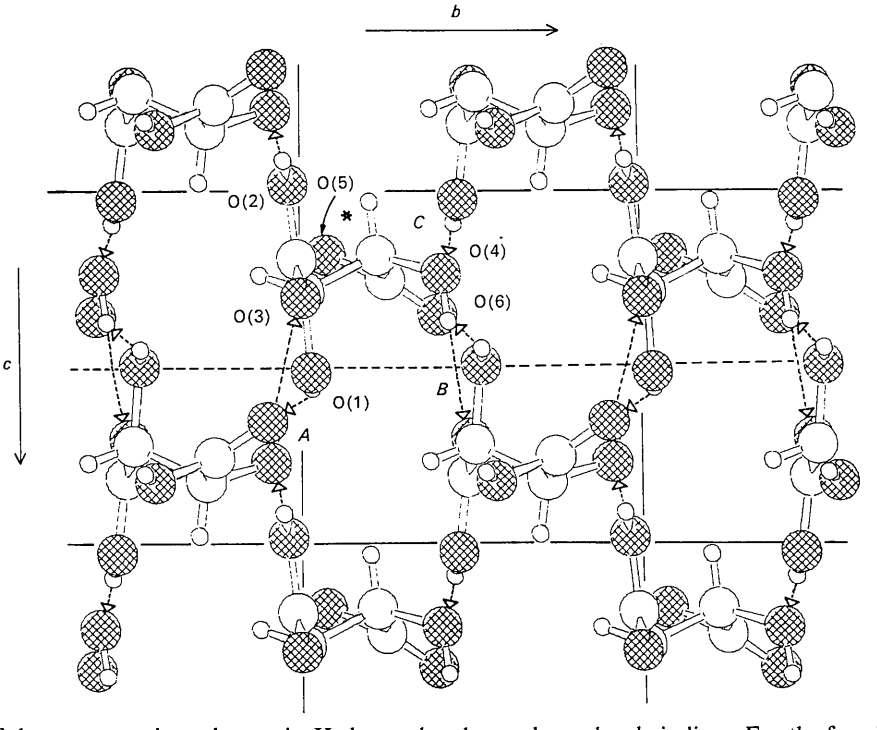


Fig. 4. Projection of the structure along the *a* axis. Hydrogen bonds are shown by chain lines. For the four hydrogen bonds, *A* to *D*, see Table 3. *Bond *D* is formed from O(5) to O(3) of the tartrate ion which is one unit cell below in the *a* direction.

equivalent groups start to take slightly different configurations. It is difficult to decide whether this asymmetry of the molecule is due only to differences in the hydrogen-bond formation or is inherent in the tartrate ion itself. The question might be answered by accurate crystal structure analyses of various crystals with tartaric as well as mesotartaric ions. The planes of the two parts make an angle of 54·6° (Fig. 3). In these two carboxyl groups, which retain their protons, there are two distinct C–C–O angles; a C–C–OH angle of around 110° and a wider C–C=O angle of about 125°. The differences between the C–O and C=O distances are about 0·1 Å for the two groups. This situation is found in many crystal structures of molecules with carboxyl groups; when a carboxyl group loses its proton, the two C–C–O angles become almost equivalent and are about 118°. The dependence of the shape of carboxyl groups upon the state of ionization has been exhibited by various acid salts of dicarboxylic acids, *e.g.* ammonium hydrogen D-tartrate (Bommel & Bijvoet, 1958), dipotassium ethylenetetracarboxylate (Kumra & Darlow, 1965), potassium acid phthalate (Okaya, 1965) and others.

The structure consists of a complicated network of O–H · · · O hydrogen bonds. Figs. 4 and 5 are the structures projected down the *a* and *b* axes, showing the hydrogen-bond scheme which is essentially the same as that given by Stern & Beevers (1950); the fifth contact given in their paper is ruled out as a hydrogen bond. Donohue (1952) discussed the hydrogen-bond system in the crystal and proposed two possible schemes; the difference between these two schemes is based on the position of the proton on carboxyl I, *i.e.* the choice between O(2) and O(3) for the hydroxyl oxygen of this group. The difference in the two C–C–O angles given by Stern & Beevers indicates conclusively the position of the proton without locating its position; therefore, the hydrogen-bond system could have uniquely been assigned (Scheme A of Donohue) if the relation between the shape of carboxyl groups and proton positions had been fully understood at that

Table 4.

(*a*) Bond distances involving hydrogen atoms from coordinates determined by the neutron study

O(1)–H(3)	0·98 ± 0·02 Å
O(2)–H(4)	1·00 ± 0·02
O(4)–H(5)	0·97 ± 0·02
O(5)–H(6)	1·00 ± 0·02
C(1)–H(1)	1·15 ± 0·03
C(3)–H(2)	1·14 ± 0·02

(*b*) Bond angles

around oxygen atoms

C(1)–O(1)–H(3)	108 ± 3°
C(2)–O(2)–H(4)	115 ± 3
C(3)–O(4)–H(5)	112 ± 3
C(4)–O(5)–H(6)	115 ± 4

around C(1)

H(1)–C(1)–O(1)	114 ± 3
H(1)–C(1)–C(2)	107 ± 3
H(1)–C(1)–C(3)	110 ± 3

around C(2)

H(2)–C(3)–O(4)	111 ± 4
H(2)–C(3)–C(1)	107 ± 4
H(2)–C(3)–C(4)	105 ± 4

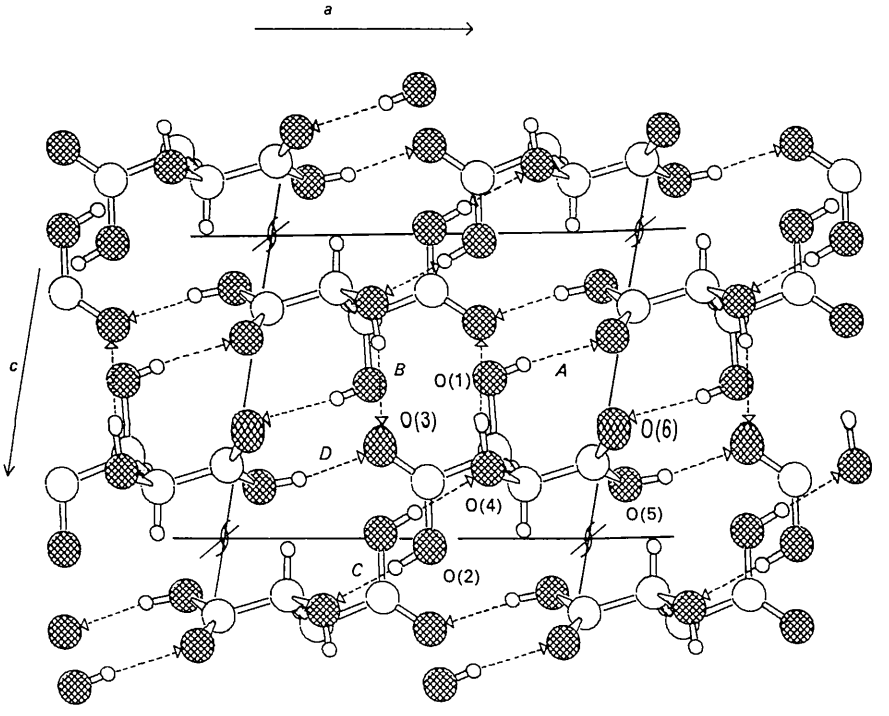


Fig. 5. Projection of the structure along the *b* axis showing the hydrogen bond scheme. Figs. 4 and 5 have been drawn on an IBM 1627 *X*–*Y* plotter based on calculation done on an IBM 7094 machine (Okaya, 1966).

time. As is evident from the Figures and Table 3, the two carboxyl groups do not have identical surroundings; possible implications of the situation in relation to the asymmetry of the tartrate ion have been discussed in the previous paragraph.

The neutron diffraction data confirm the hydrogen-bonding scheme deduced from the X-ray data. As has been noted in previously determined compounds, the values of the O–H and C–H bond distances (Table 4) from neutron data are about 0·15 Å longer than those determined from X-ray data (Fig. 3). This discrepancy is due to an inadequate description of the X-ray scattering from a bound hydrogen atom (for form factors of bonded hydrogen atoms, see Stewart, Davidson & Simpson, 1965). The bond distances derived from the neutron diffraction data are closer to accepted values. In addition, the two O–H–O hydrogen bond angles (Table 3) which were found to be less than 160° by X-rays are shown to be closer to 170°. We note that the expected inverse relationship between O–H and O–O distance in hydrogen bonds seems to hold in this compound, although the accuracy of the determination is not really high enough to be certain about it.

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References

BOMMEL VAN, A. J. & BIJVOET, J. M. (1958). *Acta Cryst.* **11**, 1961.
COLE, H., OKAYA, Y. & CHAMBERS, F. W. (1963). *Rev. Sci. Instrum.* **34**, 872.
DONOHUE, J. (1952). *J. Chem. Phys.* **56**, 502.
International Tables for X-ray Crystallography (1962). Birmingham: Kynoch Press.
KROON, J., PEERDEMAN, A. F. & BIJVOET, J. M. (1965). *Acta Cryst.* **19**, 293.
KUMRA, S. K. & DARLOW, S. F. (1965). *Acta Cryst.* **18**, 98.
OKAYA, Y. (1964). *Control Programs for Computer-Controlled Diffractometers.* IBM Internal Report.
OKAYA, Y. (1965). *Acta Cryst.* **19**, 879.
OKAYA, Y. (1966). ACA Meeting, Austin, Texas. B-5.
STERN, F. & BEEVERS, C. A. (1950). *Acta Cryst.* **3**, 341.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). ACA 1965 Spring Meeting, A-5, Suffern, N.Y.

Acta Cryst. (1966). **21**, 243

X-ray Diffraction Study of Cold-worked α-CuIn and α-CuSn Alloys

BY K.N. GOSWAMI, S.P. SEN GUPTA AND M.A. QUADER
Indian Association for the Cultivation of Science, Calcutta 32, *India*

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X-ray diffraction line profiles from filings of copper-indium and copper-tin alloys in the solid solution range were recorded by a Geiger counter X-ray diffractometer. Information regarding stacking fault densities α and β was obtained from peak-position and peak-asymmetry measurements and both parameters were found to increase with increasing solute concentration. The same general behaviour of the stacking-fault parameter α with respect to solute concentration was observed in the two systems and α increases in the order Cu–In, Cu–Sn. The broadening of the powder peaks was studied by Fourier analysis of line shapes, and the anisotropic values of the effective particle sizes $[D_e]_{hkl}$ and the root mean squared strains $[\langle \varepsilon_L^2 \rangle]_{hkl}^{1/2}$ were obtained in all cases. The measured effective particle sizes are primarily a consequence of deformation and twin faulting. A fair agreement was observed for the compound fault probability $(1{\cdot}5\alpha+\beta)$ obtained by two different methods.

1. Introduction

Cold working or plastic deformation of metals and alloys has been found to produce appreciable changes in the intensity distribution of diffracted X-rays. The changes in position, shape and width of X-ray powder diffraction line profiles from cold-worked metals and alloys are evidences of microstructural changes in the materials. The earlier X-ray studies in this field were usually confined to measurements of line-widths and it was suggested that line broadening is produced either by lattice strains or by lattice strains and small particle size simultaneously (Greenough, 1952). It was Barrett (1950), who first suggested that plastic deformation of face-centred cubic metals may introduce stacking faults on the (111) planes. Subsequently, Paterson (1952), Warren & Warekois (1955), and Wagner (1957*a*, *b*) developed the effects of deformation and twin stacking faults on the diffraction profiles of f.c.c. structures. If the normal stacking sequence of (111) planes is *ABCABC*, then a deformation fault is a break in this sequence *ABC'BCABC* where the prime indicates the fault plane. A reversal in the sequence *ABCACBA* represents a twin fault. Deformation faults give rise to a symmetrical broadening and peak-shift, while twin faults produce an asymmetrical broadening and a negligibly small peak-shift. In addition to the broadening due to faulting, the peaks of cold-worked