

Walden Inversion

I. The Crystal Structure and Absolute Configuration of (-)-Chlorosuccinic Acid

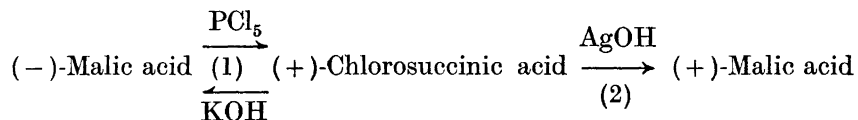
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(-)-Chlorosuccinic acid ($\text{HOOC}-\text{CH}_2-\text{CHCl}-\text{COOH}$) is orthorhombic with $a=9.202$, $b=8.699$, and $c=7.591$ Å. The space group is $P2_12_12_1$ (No. 19). There are 4 molecules per unit cell. The X-ray analysis was based on intensity data obtained from an automatic counter diffractometer using $\text{MoK}\alpha$ radiation. The structure was determined by direct methods. All atoms were located during refinement. The final R -factor is 0.027.

The absolute configuration of the (-)-chlorosuccinic acid was determined by the anomalous dispersion method. $\text{CrK}\alpha$ radiation was used. A comparison of 25 Friedel pairs gave an unequivocal determination.

The investigation of the crystal structure and absolute configuration of (-)-chlorosuccinic acid has been performed as part of an attempt to decide which reaction causes the inversion in the Walden cycle which historically although incorrectly is written in the following way:



The absolute configuration of (-)-malic acid is described in a following paper¹ with a discussion of the chemistry in this Walden cycle.

EXPERIMENTAL

Chemistry

The synthesis of (-)-chlorosuccinic acid was carried out according to a method given by Karrer, Reschofsky and Kaase.² The starting material was (+)-aspartic acid.

The specific rotation of the product was $[\alpha]_D = -23.2$. The crystal used for the X-ray work was ground while rotating it round its [001] direction. The final shape attained

was an elliptic cylinder with the great axis in the [100] direction, thickness 0.20 mm, and the small axis in the [010] direction, thickness 0.15 mm. The crystal was 0.80 mm long.

X-Ray intensity measurements

(a) *MoK α* data (graphite monochromatized radiation). A three-dimensional set of *MoK α* data was obtained using an equinclination Supper diffractometer which was controlled by a Hewlett-Packard 2114A computer using interface developed by Dr. G. Thirup for the commercial Pace controller originally delivered with the instrument. The program employed was written by J. Nyborg.³ A scintillation counter and a pulse height analyser were used. All reflections within a hemisphere in the reciprocal space were recorded out to a Bragg angle of 27° (*hk0* to *hk9*).

A total of 793 independent reflections was obtained. Of these 737 had intensities greater than $2\sigma_c(I)$, where $\sigma_c(I)$ is the total number of counts in an intensity measurement. Each intensity is the mean of the intensities of 4 symmetry related reflections. Data reduction was carried out by means of a program written by T. la Cour.⁴

(b) *CrK α* data (graphite monochromatized radiation). The intensities of a set of 25 non pinacoid Friedel related reflections were measured using an automatic 4-circle Picker diffractometer, equipped with a scintillation counter and a pulse height analyser. The set was selected by computing in advance the differences between the intensities of Friedel related reflections. The maximum Bragg angle was $\theta = 57^\circ$. The data were reduced using a program DRAM⁵ written by M. S. Lehmann.

CRYSTAL DATA

HOOC-CH₂-CHCl-COOH, *M* = 152.5. Orthorhombic.

a = 9.202 Å, $\sigma(a)$ = 0.005 Å.

b = 8.699 Å, $\sigma(b)$ = 0.004 Å.

c = 7.591 Å, $\sigma(c)$ = 0.004 Å.

*V*_c = 606 Å³, density (calc.) 1.667 g cm⁻³, found by P. Walden:⁶ 1.687 g cm⁻³, *n* = 4. Space group *P*2₁2₁2₁ (No. 19). Systematic absences: *h*00 for *h* = odd, 0*k*0 for *k* odd, and 00*l* for *l* odd.

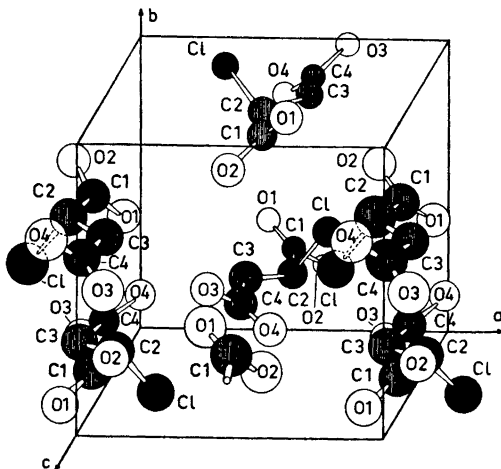


Fig. 1. Crystal structure of chlorosuccinic acid.

Single crystal oscillation, Weissenberg and precession photographs were obtained using $\text{CuK}\alpha$ radiation.

The colourless crystals are elongated in the [001] direction. They have a high tendency of twinning.

The linear absorption coefficients are $\mu = 155 \text{ cm}^{-1}$ for $\text{CrK}\alpha$ radiation and $\mu = 5.2 \text{ cm}^{-1}$ for $\text{MoK}\alpha$ radiation.

Atomic coordinates and thermal parameters, bond lengths and angles, dihedral angles, the observed and calculated structure factors, and the calculated phases are listed in Tables 1, 2, 3, 4, 5, and 6. The crystal structure is shown in Fig. 1, and the (-)-chlorosuccinic acid is shown in the absolute configuration in Fig. 2.

Table 1. Atomic coordinates as fractions of cell edges. The estimated standard deviations are multiplied by 10^4 . The isotropic temperature factors and their estimated standard deviations (in \AA^2) are also given for the hydrogen atoms.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Cl	0.6919	1	0.4677	1	0.3484	1		
O1	0.4351	2	0.4051	3	0.0578	2		
O2	0.6114	2	0.2302	2	0.0206	2		
O3	0.3720	2	0.4081	2	0.7140	2		
O4	0.5633	2	0.2544	2	0.6753	2		
C1	0.5301	3	0.3179	3	0.1134	2		
C2	0.5633	3	0.3128	3	0.3108	3		
C3	0.4294	3	0.3379	3	0.4208	3		
C4	0.4612	3	0.3315	3	0.6180	2		
H1	0.5886	42	0.2322	47	-0.0943	47	8.3	0.9
H2	0.3885	43	0.4029	44	0.8375	49	8.2	0.9
H3	0.3885	28	0.4348	28	0.3845	30	2.8	0.5
H4	0.3587	35	0.2532	36	0.3956	39	5.0	0.7
H5	0.6107	25	0.2267	26	0.3515	27	2.1	0.4

Table 2. Thermal parameters and their estimated standard deviations (in $\text{\AA}^2 \times 10^{-4}$).

	u_{11}	$\sigma(u_{11})$	u_{22}	$\sigma(u_{22})$	u_{33}	$\sigma(u_{33})$	u_{12}	$\sigma(u_{12})$	u_{13}	$\sigma(u_{13})$	u_{23}	$\sigma(u_{23})$
Cl	474	3	625	4	407	3	-193	3	-67	3	40	3
O1	658	13	859	14	253	6	303	13	-62	8	-9	9
O2	629	11	588	11	252	6	137	10	50	8	-17	8
O3	596	11	717	13	241	6	141	11	2	8	-56	8
O4	526	11	731	12	267	7	142	11	7	8	63	8
C1	374	11	414	11	217	7	6	10	7	8	-15	9
C2	375	12	414	11	259	8	-2	11	-33	9	19	9
C3	387	12	495	14	224	7	4	11	-29	9	3	9
C4	375	11	406	12	221	8	-19	10	20	9	7	9

Table 3. Interatomic distances and their estimated standard deviations ($\times 10^3$) in Å. A prime indicates a unit translation along the *c*-axis.

	<i>l</i>	$\sigma(l)$		<i>l</i>	$\sigma(l)$
C1—C2	1.815	3	C4—O4	1.234	3
C1—C2	1.530	3	C3—H3	0.964	25
C2—C3	1.504	3	C3—H4	1.001	32
C3—C4	1.527	3	C2—H5	0.917	22
C1—O1	1.232	3	O2—H1	0.897	36
C1—O2	1.280	3	O3—H2	0.951	37
C4—O3	1.284	3	O1—O3'	2.673	2
			O2—O4'	2.667	2

Table 4. Angles and their estimated standard deviations in degrees.

	v°	$\sigma(v)^\circ$		v°	$\sigma(v)^\circ$
O1—C1—O2	126.4	0.2	C2—C3—H3	106.8	1.5
O1—C1—C2	119.7	0.2	C2—C3—H4	108.7	1.8
O2—C1—C2	113.9	0.2	C4—C3—H3	112.7	1.4
Cl—C2—C1	105.2	0.2	C4—C3—H4	106.6	1.7
Cl—C2—C3	109.8	0.2	H3—C3—H4	109.6	2.3
Cl—C2—H5	104.3	1.4	O3—C4—C3	114.6	0.2
C1—C2—C3	112.1	0.2	O4—C4—C3	120.7	0.2
C1—C2—H5	116.6	1.3	O3—C4—O4	124.7	0.2
C3—C2—H5	108.4	1.4	C1—O2—H1	112.7	2.5
C2—C3—C4	112.5	0.2	C4—O3—H2	115.6	2.4

Table 5. Dihedral angles in degrees.

Atom sequence	Dihedral angle
O1—C1—C2—C1	−85.2
O1—C1—C2—C3	34.1
O2—C1—C2—C1	92.7
O2—C1—C2—C3	−148.0
C1—C2—C3—C4	179.5
Cl—C2—C3—C4	−64.0
C2—C3—C4—O3	153.9
C2—C3—C4—O4	−27.8

Table 6.

h	k	l	fobs	foalc	phase	h	k	l	fobs	foalc	phase	h	k	l	fobs	foalc	phase	
0	2	0	295	300	180	0	4	1	19	13	210	6	1	2	133	137	268	
0	4	0	219	223	0	0	6	1	194	194	0	8	2	2	45	48	163	
0	6	0	14	6	180	0	7	1	156	158	270	8	3	2	77	73	242	
0	8	0	58	55	180	0	8	1	116	119	0	8	4	2	110	108	20	
0	10	0	15	20	180	0	9	1	55	57	270	8	5	2	72	76	-80	
1	1	0	213	212	90	10	10	1	15	18	0	8	6	2	30	32	64	
1	2	0	943	961	90	1	1	1	138	146	270	8	7	2	19	22	244	
1	3	0	442	439	90	1	1	1	209	216	122	9	0	2	90	91	0	
1	4	0	39	39	270	1	1	2	163	160	-48	9	1	2	77	75	101	
1	5	0	217	219	90	1	1	3	337	334	73	9	2	2	93	96	-21	
1	6	0	54	52	90	1	1	4	134	133	-4	9	3	2	12	16	247	
1	7	0	44	44	90	1	1	5	218	221	143	9	4	2	64	66	-25	
1	8	0	85	89	90	1	1	6	194	190	-52	9	5	2	20	26	149	
1	9	0	39	36	270	1	1	7	120	118	100	10	1	2	104	102	128	
1	10	0	65	63	270	1	1	8	1	57	59	75	10	2	2	54	55	180
2	1	0	12	17	270	1	1	9	1	27	31	57	10	3	2	36	38	89
2	2	0	614	610	0	1	1	10	1	46	49	-23	10	4	2	16	12	100
2	3	0	240	240	180	1	1	11	1	20	28	64	10	5	2	37	39	180
2	4	0	738	743	180	2	0	1	1	51	59	90	11	1	2	38	36	169
2	5	0	959	956	0	2	1	1	482	468	0	11	2	2	23	28	170	
2	6	0	163	165	180	2	2	1	407	410	-86	0	8	2	38	37	243	
2	7	0	292	289	180	2	3	1	235	229	68	1	0	2	719	704	90	
2	8	0	29	27	0	2	4	1	209	200	182	1	1	2	380	370	0	
2	9	0	87	89	180	2	5	1	151	146	72	1	2	2	23	21	90	
2	10	0	69	69	180	2	6	1	81	81	178	1	3	2	161	157	0	
3	1	0	590	577	270	2	7	1	31	28	89	1	4	2	325	312	90	
3	2	0	17	11	90	2	8	1	67	68	192	1	5	2	54	52	90	
3	3	0	382	387	270	2	9	1	18	17	162	0	6	2	60	60	90	
3	4	0	61	61	270	2	10	1	37	42	200	1	7	2	314	309	-13	
3	5	0	27	25	90	3	0	1	167	184	90	1	8	2	37	36	230	
3	6	0	51	51	270	3	1	1	356	300	-1	1	9	2	131	127	-74	
3	7	0	21	25	90	3	2	1	175	169	103	1	10	2	149	144	158	
3	8	0	13	16	90	3	3	1	163	198	6	2	0	2	63	60	103	
3	9	0	53	49	180	3	4	1	254	252	86	2	1	2	147	142	157	
4	1	0	252	250	180	3	5	1	167	166	-71	2	2	2	48	49	74	
4	2	0	90	88	180	3	6	1	56	56	111	2	3	2	108	105	181	
4	3	0	65	65	0	3	7	1	38	36	149	2	4	2	40	37	128	
4	4	0	502	497	0	3	8	1	108	108	162	2	5	2	29	29	190	
4	5	0	39	40	180	3	9	1	70	72	-79	2	6	2	405	401	90	
4	6	0	110	111	0	3	10	1	40	44	-55	2	7	2	256	252	133	
4	7	0	130	128	0	4	0	1	217	221	90	2	8	2	169	165	-57	
4	8	0	79	77	180	4	1	1	295	299	200	2	9	2	241	246	-57	
4	9	0	73	76	0	4	2	1	182	175	25	2	10	2	340	337	92	
4	10	0	18	18	180	4	3	1	238	286	162	3	0	2	136	135	-36	
5	1	0	102	94	270	4	4	1	113	113	44	3	1	2	30	31	153	
5	2	0	80	79	270	4	5	1	55	53	-79	3	2	2	194	191	-68	
5	3	0	68	63	90	4	6	1	139	158	77	3	3	2	38	34	127	
5	4	0	14	11	270	4	7	1	35	34	128	3	4	2	44	44	252	
5	5	0	177	177	90	4	8	1	41	44	227	3	5	2	26	24	229	
5	6	0	83	83	270	4	9	1	27	29	233	3	6	2	152	151	90	
5	7	0	80	80	90	4	10	1	22	26	263	3	7	2	302	296	198	
5	8	0	79	82	90	5	0	1	275	269	270	3	8	2	192	190	21	
5	9	0	41	42	90	5	1	1	135	134	203	3	9	2	296	302	225	
6	1	0	115	115	180	5	2	1	213	217	265	4	0	2	130	129	14	
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6	3	0	246	244	0	5	4	1	173	172	-42	4	2	2	66	65	-5	
6	4	0	117	120	180	5	5	1	109	112	-72	4	3	2	19	24	158	
6	5	0	74	74	0	5	6	1	33	31	144	4	4	2	26	27	58	
6	6	0	124	126	180	5	7	1	91	92	113	4	5	2	15	11	-11	
6	7	0	73	72	0	5	8	1	61	63	174	4	6	2	139	143	270	
6	8	0	22	20	90	5	9	1	42	45	-79	4	7	2	223	220	220	
6	9	0	187	187	90	5	10	1	15	17	74	4	8	2	412	408	258	
6	10	0	139	136	270	6	0	1	179	184	270	4	9	2	82	82	118	
7	1	0	67	67	90	6	1	1	117	114	5	4	10	2	46	51	188	
7	2	0	97	96	90	6	2	1	87	91	244	5	0	2	29	33	-60	
7	3	0	80	75	270	6	3	1	69	68	-78	5	1	2	92	92	-60	
7	4	0	49	47	270	6	4	1	131	131	-64	5	2	2	48	49	89	
7	5	0	253	247	180	6	5	1	155	155	-23	5	3	2	17	18	90	
7	6	0	33	32	0	6	6	1	119	121	62	5	4	2	63	63	82	
7	7	0	64	66	180	6	7	1	20	13	86	5	5	2	172	168	4	
7	8	0	25	24	0	6	8	1	28	32	-37	5	6	2	55	55	-86	
7	9	0	69	69	180	6	9	1	44	47	204	5	7	2	157	154	-9	
8	1	0	60	57	0	7	0	1	146	150	90	5	8	2	72	71	-83	
8	2	0	83	79	180	7	1	1	61	60	46	5	9	2	90	89	-16	
8	3	0	117	118	270	7	2	1	112	113	102	6	0	2	34	37	-87	
8	4	0	61	58	270	7	3	1	33	36	132	6	1	2	17	9	37	
8	5	0	99	99	270	7	4	1	147	148	-22	6	2	2	38	35	21	
8	6	0	31	30	270	7	5	1	70	70	-44	6	3	2	15	14	-74	
8	7	0	23	19	270	7	6	1	26	26	38	6	4	2	143	144	90	
8	8	0	93	93	0	7	7	1	100	102	89	6	5	2	133	133	-57	
8	9	0	17	7	0	7	8	1	49	53	-64	6	6	2	157	156	105	
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9	2	0	39	37	270	8	1	1	93	93	84	6	8	2	63	66	90	
9	3	0	172	173	0	8	2	1	115	117	183	6	9	2	31	34	22	
9	4	0	115	117	270	8	3	1	86	86	210	6	10	2	41	45	-17	
10	1	0	55	51	0	8	4	1	70	69	213	6	11	2	44	43	97	
10	2	0	35	33	0	8	5	1	55	55	39	6	12	2	15	14	-74	
10	3	0	24	17	90	8	6	1	64	68	166	6	13	2	32	35	90	
10	4	0	17	13	0	8	7	1	61	63	64	6	14	2	116	113	148	
10	5	0	11	8	90	8	8	1	41	42	220	6	15	2	30	29	147	
10	6	0	3	3	0	8	9	1	49	44	81	6	16	2	33	33	109	
10	7	0	1	1	0	9	0	1	78	79	149	6	17	2	80	80	195	
10	8	0	1	1	0	9	1	1	38	40	256	6	18	2	44	45	207	
10	9	0	1	1	0	9	2	1	38	40	256	7	0	2	44	45	207	
10	10	0	1	1	0	9	3	1	38	40	256	7	1	2	44	45	207	

Table 6. Continued.

7	6	3	65	66	177	7	4	4	50	48	63	5	5	43	44	129	7	3	7	53	51	19		
7	7	3	50	53	59	7	5	4	49	51	238	7	0	5	20	20	90	2	4	7	23	22	216	
7	8	3	23	22	179	7	6	4	54	67	22	7	1	5	29	29	148	2	5	7	36	38	87	
8	0	3	105	103	270	7	7	4	31	33	217	7	2	5	56	59	90	2	6	7	41	39	218	
8	1	3	74	78	-60	8	0	4	155	156	0	7	4	5	37	36	244	2	7	7	66	67	79	
8	2	3	28	34	134	8	1	4	139	117	60	7	5	5	26	17	90	3	0	7	63	66	90	
8	3	3	71	71	203	8	2	4	45	49	-11	7	6	5	49	46	22	3	1	7	78	77	-28	
8	4	3	17	15	170	8	3	4	48	50	132	8	1	6	155	160	270	3	2	7	76	74	217	
8	5	3	69	71	-52	8	4	4	62	64	-34	8	2	6	12	12	0	3	3	7	85	83	-22	
8	6	3	19	13	158	8	5	4	70	16	176	8	3	6	204	204	270	3	4	7	68	65	123	
8	7	3	74	70	-77	8	6	4	26	24	-50	8	4	6	238	235	0	3	5	7	88	85	-15	
9	1	3	64	63	117	9	0	4	41	44	180	9	5	6	128	131	90	3	6	7	36	34	195	
9	2	3	85	84	17	9	1	4	53	56	77	9	6	6	42	42	180	3	7	7	20	17	4	
9	3	3	30	32	-61	9	2	4	48	48	159	9	7	6	23	20	0	4	0	7	156	154	90	
9	4	3	29	29	5	9	3	4	66	67	120	1	0	6	44	46	0	4	1	7	101	96	221	
9	5	3	79	78	228	9	4	4	29	32	201	1	1	6	189	188	87	4	2	7	104	100	80	
9	6	3	70	69	6	9	5	4	33	29	56	1	2	6	86	88	-80	4	3	7	30	31	259	
10	0	3	84	88	270	10	1	4	27	28	-79	1	3	6	109	108	39	4	4	7	53	53	78	
10	3	3	79	92	150	10	2	4	64	66	180	1	4	5	124	127	24	4	5	7	25	28	250	
10	4	3	31	30	-87	10	3	4	42	40	-80	1	5	6	134	134	14	4	6	7	20	24	21	
11	0	3	15	17	270	10	4	1	5	79	82	270	1	6	6	46	47	44	5	0	7	13	10	270
11	1	3	56	58	59	0	2	5	22	20	180	1	7	6	96	95	171	5	1	7	143	137	213	
11	2	3	16	8	-63	0	3	5	76	75	270	1	8	6	20	20	32	5	2	7	87	85	226	
0	1	4	205	214	270	0	4	5	96	96	180	2	0	5	179	127	180	5	3	7	60	60	153	
0	2	4	129	121	180	0	5	5	49	47	270	2	1	6	238	233	159	5	4	7	28	28	214	
0	3	4	114	109	270	0	6	5	152	153	180	2	2	6	153	181	214	5	5	7	37	35	211	
0	4	4	76	77	180	0	7	5	43	43	180	2	3	6	57	58	-84	6	0	7	20	22	-90	
0	5	4	57	56	270	0	8	5	40	44	90	2	4	6	19	20	13	6	1	7	33	33	-73	
0	6	4	189	182	180	1	0	5	115	128	270	2	5	6	130	128	124	6	2	7	38	35	246	
0	7	4	53	52	0	1	1	5	32	33	194	2	6	6	54	53	164	6	3	7	46	42	10	
0	8	4	23	25	90	1	2	5	159	161	85	2	7	6	29	27	145	6	4	7	49	42	-83	
0	9	4	22	23	0	1	3	5	172	169	-74	2	8	6	68	68	68	7	0	7	37	33	90	
1	0	4	294	286	0	1	4	5	97	101	162	3	0	6	92	92	180	7	1	7	84	80	-51	
1	1	4	267	267	-86	1	5	5	68	66	250	3	1	6	136	136	178	7	2	7	43	41	112	
1	2	4	189	194	-49	1	6	5	76	76	49	3	2	6	117	120	211	7	3	7	52	49	34	
1	3	4	159	163	-57	1	7	5	139	137	-56	3	3	6	119	112	256	8	0	7	22	16	90	
1	4	4	155	156	68	1	8	5	27	28	-48	3	4	6	78	77	-45	8	1	7	40	39	155	
1	5	4	55	55	263	1	9	5	42	45	234	3	5	6	18	23	243	8	2	8	123	146	90	
1	6	4	94	95	-66	2	0	5	10	9	-90	3	6	6	62	62	-80	9	0	8	34	35	244	
1	7	4	65	61	14	2	1	5	219	221	195	3	7	6	63	64	159	9	1	8	51	30	0	
1	8	4	66	67	244	2	2	5	156	169	34	3	8	6	61	60	-59	9	2	8	45	40	90	
1	9	4	29	29	201	2	3	5	68	67	112	4	1	6	146	146	151	0	5	4	45	40	90	
2	0	4	12	12	180	2	4	5	125	126	-2	4	2	4	94	96	-50	0	6	8	49	49	0	
2	1	4	63	60	132	2	5	5	91	93	199	4	3	6	110	107	-22	1	0	3	35	46	180	
2	2	4	267	269	24	2	6	5	115	115	-62	4	4	6	57	58	227	1	1	8	49	52	53	
2	3	4	220	215	36	2	7	5	14	16	161	4	5	6	71	67	-9	1	2	8	115	113	199	
2	4	4	112	110	14	2	8	5	67	68	34	4	6	6	60	63	264	1	3	8	79	80	151	
2	5	4	74	76	34	2	9	5	24	24	64	4	7	6	51	52	13	1	4	8	42	43	208	
2	6	4	70	71	138	3	0	5	261	254	270	5	0	6	42	45	180	1	5	8	20	16	-65	
2	7	4	43	44	32	3	1	5	48	51	12	5	1	6	68	72	166	3	1	6	3	51	179	
2	8	4	65	66	65	3	2	5	35	210	-68	5	2	6	76	76	99	2	0	8	44	45	180	
2	9	4	10	17	39	3	3	5	50	52	263	5	3	6	75	73	-67	2	1	8	80	82	240	
3	0	4	41	46	180	3	4	5	199	201	199	5	4	6	80	80	121	2	2	8	23	24	221	
3	1	4	55	60	97	3	5	5	156	155	107	5	5	6	24	26	-14	2	3	8	55	83	233	
3	2	4	114	117	211	3	6	5	57	59	-24	5	6	6	54	51	109	2	4	8	20	23	150	
3	3	4	74	75	40	3	7	5	19	23	-15	5	7	6	43	41	-19	2	5	8	15	11	186	
3	4	4	159	161	113	3	8	5	37	36	86	6	0	6	33	33	0	2	6	8	62	59	-59	
3	5	4	92	94	167	4	0	5	179	186	270	6	1	6	58	60	217	3	0	8	98	96	0	
3	6	4	117	118	43	4	1	5	88	86	-25	6	2	6	102	102	22	3	1	8	26	27	68	
3	7	4	52	50	132	4	2	5	132	136	88	6	3	6	58	56	214	3	2	8	33	21	56	
3	8	4	49	48	144	4	3	5	245	248	23	6	4	4	42	42	114	3	3	8	66	66	8	
3	9	4	71	73	181	4	4	5	17	14	115	6	5	6	61	61	223	3	4	8	70	70	-37	
4	0	4	210	211	180	4	5	5	63	64	-23	6	6	6	40	41	18	3	5	8	77	73	-44	
4	1	4	126	125	242	4	6	5	74	76	262	7	0	6	33	39	0	4	0	8	31	31	0	
4	2	4	105	103	-32	4	7	5	12	21	-46	7	1	6	68	68	79	4	1	8	23	24	-34	
4	3	4	95	100	163	4	8	5	34	34	118	7	2	6	71	73	-4	4	2	8	17	15	186	
4	4	4	180	185	-88	5	0	5	233	234	90	7	3	6	47	49	109	4	3	8	46	44	187	
4	5	4	50	51	177	5	1	5	84	85	-73	7	4	6	37	36	-78	4	4	8	80	78	117	
4	6	4	42	41	-69	5	2	5	163	167	29	7	5	6	47	46	120	4	5	8	28	27	54	
4	7	4	95	97	152	5	3	5	65	67	255	8	0	6	63	62	180	5	0	8	29	29	180	
4	8	4	28	29	0	5	4	5	129	127	135	8	1	6	47	47	37	5	1	8	65	63	186	
4	9	4	45	46	168	5	5	5	54	54	94	8	2	6	44	42	184	5	2	8	70	66	80	
5	0	4	132	130	180	5	6	5	31	31	34	8	3	6	54	55	76	5	4	8	59	57	-36	
5	1	4	91	94	67	5	7	5	30	31	197	8	4	6	58	62	190	6	0	8	99	93	0	
5	2	4	101	99	249	5	8																	

Table 7. Comparison of intensities used in the determination of absolute configuration. The ratio $q = I(hkl)/I(\bar{h}\bar{k}\bar{l})$ is given as observed and as calculated.

hkl	$q(\text{obs})$	$\sigma(q)$	$q(\text{calc})$	$\bar{h}\bar{k}\bar{l}$	$q(\text{obs})$	$\sigma(q)$	$q(\text{calc})$
$231/\bar{2}\bar{3}\bar{1}$	1.20	0.05	1.27	$451/\bar{4}\bar{5}\bar{1}$	1.59	0.34	2.50
$112/\bar{1}\bar{1}\bar{2}$	1.09	0.02	1.17	$451/\bar{4}\bar{5}\bar{1}$	1.93	0.34	2.50
$112/\bar{1}\bar{1}\bar{2}$	1.21	0.02	1.17	$132/\bar{1}\bar{3}\bar{2}$	0.64	0.04	0.59
$121/\bar{1}\bar{2}\bar{1}$	0.92	0.05	1.04	$132/\bar{1}\bar{3}\bar{2}$	0.66	0.03	0.59
$121/\bar{1}\bar{2}\bar{1}$	1.15	0.05	1.04	$142/\bar{1}\bar{4}\bar{2}$	0.57	0.04	0.62
$131/\bar{1}\bar{3}\bar{1}$	0.89	0.02	0.86	$142/\bar{1}\bar{4}\bar{2}$	0.60	0.03	0.62
$131/\bar{1}\bar{3}\bar{1}$	0.88	0.02	0.86	$621/\bar{6}\bar{2}\bar{1}$	0.74	0.04	0.70
$151/\bar{1}\bar{5}\bar{1}$	1.18	0.06	1.28	$621/\bar{6}\bar{2}\bar{1}$	0.69	0.05	0.70
$151/\bar{1}\bar{5}\bar{1}$	1.29	0.06	1.28	$442/\bar{4}\bar{4}\bar{2}$	1.41	0.04	1.39
$421/\bar{4}\bar{2}\bar{1}$	0.72	0.04	0.67	$442/\bar{4}\bar{4}\bar{2}$	1.32	0.03	1.39
$421/\bar{4}\bar{2}\bar{1}$	0.70	0.04	0.67	$133/\bar{1}\bar{3}\bar{3}$	0.75	0.03	0.68
$431/\bar{4}\bar{3}\bar{1}$	0.94	0.03	0.88	$133/\bar{1}\bar{3}\bar{3}$	0.82	0.03	0.68
$431/\bar{4}\bar{3}\bar{1}$	0.86	0.03	0.88	$143/\bar{1}\bar{4}\bar{3}$	0.88	0.03	0.76
$122/\bar{1}\bar{2}\bar{2}$	1.00	0.01	0.96	$143/\bar{1}\bar{4}\bar{3}$	0.79	0.02	0.76
$122/\bar{1}\bar{2}\bar{2}$	1.04	0.01	0.96	$153/\bar{1}\bar{5}\bar{3}$	1.24	0.22	1.52
$312/\bar{3}\bar{1}\bar{2}$	0.81	0.03	0.87	$153/\bar{1}\bar{5}\bar{3}$	1.05	0.20	1.52
$312/\bar{3}\bar{1}\bar{2}$	0.92	0.03	0.87	$334/\bar{3}\bar{3}\bar{4}$	0.55	0.09	0.53
$322/\bar{3}\bar{2}\bar{2}$	1.32	0.06	1.34	$334/\bar{3}\bar{3}\bar{4}$	0.62	0.12	0.53
$322/\bar{3}\bar{2}\bar{2}$	1.35	0.05	1.34	$342/\bar{3}\bar{4}\bar{2}$	0.93	0.02	0.96
$332/\bar{3}\bar{3}\bar{2}$	1.23	0.05	1.29	$151/\bar{1}\bar{5}\bar{1}$	1.23	0.03	1.29
$332/\bar{3}\bar{3}\bar{2}$	1.34	0.05	1.29	$322/\bar{3}\bar{2}\bar{2}$	1.22	0.02	1.35
$333/\bar{3}\bar{3}\bar{3}$	1.30	0.04	1.22	$332/\bar{3}\bar{3}\bar{2}$	1.26	0.02	1.29
$333/\bar{3}\bar{3}\bar{3}$	1.33	0.04	1.22				

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined using the $\text{MoK}\alpha$ data. The symbolic addition method was applied using the program system SYMBAD.⁷ 170 reflections with normalized structure factors, E , greater than 1.25 were used. A table was set up to list the reflections which entered into most combinations using the phase relationship $\phi(\bar{H}_1) + \phi(\bar{H}_2) + \phi(\bar{H}_3) = n \cdot 2\pi$ for $\bar{H}_1 + \bar{H}_2 + \bar{H}_3 = 0$. Four reflections were selected to define origin and enantiomorph and four others were assigned symbolic phases:

hkl	E	ϕ	
430	2.45	0	origin defining
120	2.46	$\pi/2$	origin defining
013	2.55	$\pi/2$	origin defining
505	2.22	$\pi/2$	enantiomorph defining
423	2.40	a	
216	2.14	b	
046	2.59	c	
243	2.04	d	

A phase combination carried out by hand gave the result that a could be assigned the phase $-\pi/2$ and c the phase value 0. The latter result was corroborated.

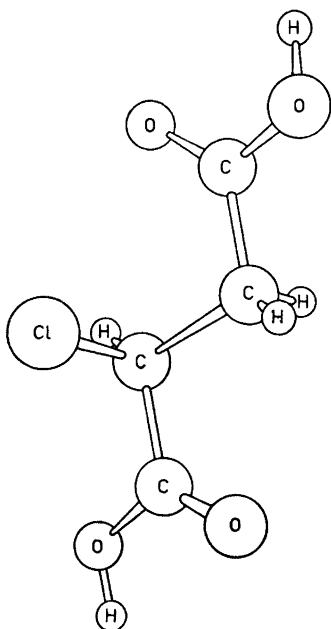


Fig. 2. (-)-Chlorosuccinic acid in absolute configuration.

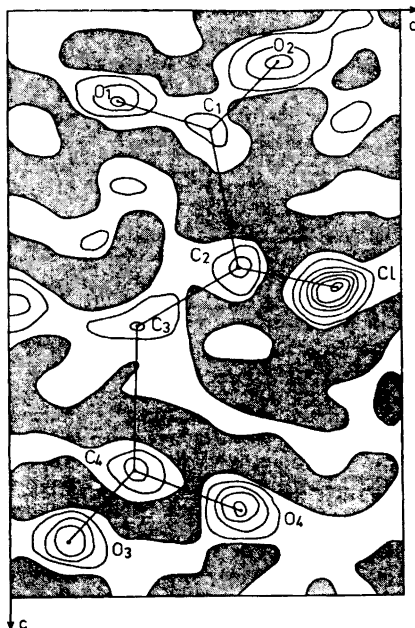


Fig. 3. Chlorosuccinic acid, bounded projection of Fourier (E -map). Computed on the basis of 170 phases found by tangent refinement.

orated by a \sum_1 criterion giving 046 the phase 0 with a probability of 0.98. The phase of b was indicated to be either 0 or π , and d was found to be $\pm \pi/2$. Phases were found for two more reflections, 209 and 053. These were added to the original basic set of eight reflections.

The four possible basic sets of 10 reflections were used for an automatic phase determination procedure using the tangent formula for refining multiply indicated phases. The reciprocal of the sum of the standard deviations was used as a figure of merit and the solution with the lowest figure of merit proved to be the correct one. Phases were assigned to all the 170 reflections used and a three-dimensional Fourier map computed using E -values revealed the positions of all atoms except the hydrogen atoms. A bounded projection (E -map) is shown in Fig. 3.

Coordinates and anisotropic temperature factors were refined using the methods of least squares in the block-diagonal approximation (program G 403⁸). The average discrepancy of the phases first found as compared with the phases of the refined structure is 16.3°.

Towards the end of the refinement all hydrogen atoms were found in difference-Fourier syntheses. They were assumed to have isotropic thermal parameters. The final R -factor attained was 0.027.

No corrections for absorption, extinction, or anomalous dispersion were made.

A constrained refinement was carried out assuming the molecule to vibrate and to librate as a rigid body. The method is described by Pawley⁹ and a program written by him was used. The hypothesis that the molecule moves as a rigid body could be rejected completely as the constrained refinement gave an R -value of 0.045 and the conventional refinement assuming independent atomic vibrations gave an R -value of 0.027. The ratio between the two R -values is so big that a statistical evaluation is unnecessary.

COMPUTATIONAL DETAILS

The atomic scattering curves used were for chlorine those given by Doyle and Turner.¹⁰ For oxygen and carbon the scattering curves given by Cromer and Mann¹¹ were used. The hydrogen scattering curves are given by Stewart, Davidson and Simpson.¹² Bassi¹³ polynomials were used to represent the scattering curves.

The weighting scheme used during the least squares refinement was: $1/w = (\sigma_c(F^2) + (1+a)F_o^2)^{1/2} - |F_o|^2$ for reflections with $F^2 > 2\sigma_c(F^2)$, otherwise zero, a was initially chosen to be 0.030. Its final value after refinement was 0.031. A weight analysis proved the quantity $\sum w_i (F_o^i - F_c^i)^2$ to be almost constant as a function of $|F_o^i|$ and of $(\sin \theta/\lambda)$. Bond lengths and angles were computed by an ALGOL program.¹⁴

The absolute configuration was found by comparing the intensities of the 25 Friedel pairs measured with $\text{CrK}\alpha$ radiation with those calculated for the arbitrarily selected enantiomorph. 16 of these comparisons gave indications on the correctness of the postulated enantiomorph. The ratio $I_o(hkl)/I_o(\bar{h}\bar{k}\bar{l})$ differed less than 3 standard deviations from $I_c(hkl)/I_c(\bar{h}\bar{k}\bar{l})$, but more than 3 standard deviations from its reciprocal value for these 16 Friedel pairs. The results are shown in Table 7.

None of the remaining 9 Friedel pairs were inconsistent with this determination. The ratios for these pairs are close to 1. They were selected for measurement as a check on the pairs showing large differences.

All calculations were carried out at Aarhus University's Computing Centre.

DISCUSSION

The four carbon atoms in the chain are almost coplanar and nearly coplanar with the two carboxyl groups. Dihedral angles are shown in Table 5. In the crystalline state, tartaric acid exhibits a structure with the four carbon atoms being approximately coplanar. The carboxyl groups are, however, not coplanar with the carbon chain. The heavy atoms of the two halves of the molecule lie in two planes which form an angle of 55° with each other. According to Peerde-mann, van Bommel and Bijvoet,¹⁵ (+)-tartaric acid has the $2R,3R$ configuration using the Cahn-Ingold notation. Our results expressed in this notation assign the S -configuration to (-)-chlorosuccinic acid. Thus (-)-tartaric acid and (-)-chlorosuccinic acid have similar configurations. The (-)-chloro-

succinic acid molecules are linked together by hydrogen bonds (2.67 Å) between the carboxyl groups. The chain of molecules extends along the direction of the *c*-axis. The bond distances show a good internal consistency. The model used for refinement: The use of spherically symmetric atomic scattering factors and independent linear vibrations, obscures, however, to some extent the physical meaning of the computed bond distances. The standard deviations obtained reflect better the internal consistency of our data than absolute uncertainties. Although it is of doubtful significance to discuss variations in bond lengths of the order of 3–4 times a standard deviation, variations of ten times a standard deviation may carry some significance. The bond length C(2)–C(3) is 0.03 Å shorter than C(3)–C(4) and C(1)–C(2). Thus a slight degree of double bonding is indicated. The difference in bond lengths between the C–OH and the C=O group in the carboxyl group is 0.05 Å. This is approximately half the difference found in most aliphatic carboxylic acids whereas it is close to the dimensions reported for aromatic carboxylic acids. The C(2)–Cl bond of 1.82 Å is longer than most other carbon-chlorine bonds in aliphatic systems. They range between 1.72 Å and 1.81 Å with an unbiased mean of 1.76 Å. The long distance is in accordance with the ease of substitution of the chlorine with a hydroxyl group. Other chemical aspects to be correlated with the structure, especially in connection with the Walden inversion, are discussed in the next paper.¹

Acknowledgements. The authors are indebted to Rita Grønbæk Hazell for the use of her programs and for helpful discussions, and to Mrs. B. Rasmussen for preparing the crystals and for shaping the specimen.

Statens almindelige Videnskabsfond is thanked for providing part of the Supper-Pace diffractometer used.

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Received October 25, 1971.

Acta Chem. Scand. **26** (1972) No. 6