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Determination of the Absolute Configuration of (−)-2-Bromosuccinamic Acid by X-Ray Diffraction Method

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Crystals of (−)-2-bromosuccinamic acid ($C_4H_6O_3NBr$) are orthorhombic, with space group $P2_12_12_1$ and lattice parameters $a=7.70, b=9.23, c=8.88$ Å, containing four molecules in the unit cell. The structure was solved by the heavy atom method coupled with three-dimensional Fourier and difference Fourier syntheses. The refinement was carried out by the full-matrix least-squares calculations. The final (R) value was 0.15. The absolute configuration was established to be (S) (−) by the anomalous dispersion method. The molecular and crystal structure were also discussed.

Introduction

In connection with our stereochemical studies, we became interested in the absolute configuration of the α-halo acid, which is prepared from the corresponding α-amino acid by treatment with nitrosyl halide. This reaction is very useful and interesting, because the α-halo acid is usually synthesized in high optical purity, and thereby the absolute configuration of the α-amino acid is supposed to be retained. However, the reaction mechanism was discussed only on the basis of stereochemical mechanism.[2]

To correlate the stereochemical relationship between these two compounds it is considered desirable to establish the absolute configuration of the α-halo acid on firm basis, that is, by X-ray diffraction method. For the configurational standard of α-halo acids bromosuccinic acid (II) seems to be most favorable, but it was difficult to obtain a single crystal of II suitable for X-ray work. The present X-ray diffraction study has therefore been undertaken on (−)-2-bromosuccinamic acid (I) utilizing the heavy atom and the anomalous dispersion method. The stereochemistry of I has already been correlated[3] to that of II.

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2) P. Brewster, F. Hiron, C.K. Ingold and P.A.D.S. Rao, *Nature*, **166**, 179 (1950).
3) P. Walden, *Chem. Ber.*, **28**, 2766 (1895).

Experimental

We synthesized (−)-2-bromosuccinamic acid (I) from L(−)asparagine monohydrate according to the reported method.[4] The crystals of I were recrystallized from water to give rods elongated along the *a*-axis, which was expected to be optically pure, because no further change in the specific rotation was observed by recrystallization. To confirm the direction of rotation a single crystal was cut into two pieces and one of them was used for X-ray analysis and the other was used for ORD measurement. The density was measured by the flotation method using the mixed solution of bromoform and carbon tetrachloride. The cell dimensions and space group were determined from rotation and Weissenberg photographs taken with Cu$K\alpha$ radiation.

Crystal data

(−)-2-Bromosuccinamic acid ($C_4H_6O_3NBr$)
Mol. wt. 196.0
mp 138—139.5° (decomp. uncorr.)
$[\alpha]_D^{18}$ −70.1° (c=1.007, EtOH)
orthorhombic
a=7.704±0.037, b=9.234±0.027, c=8.881±0.023 Å, V=631.8 Å^3
Dm=2.059 g·cm^{-3}, Dx=2.060 g·cm^{-3}, Z=4
Linear absorption coefficient for Cu$K\alpha$ radiation=88.2 cm^{-1}
$F(0\ 0\ 0)$=384
Absent reflexion : $h\ 0\ 0$ when h is odd
$0\ k\ 0$ when k is odd
$0\ 0\ l$ when l is odd
Space group $P2_12_12_1$

The three-dimensional reflexions of $0kl$—$3kl$ and $h0l$—$h2l$ were recorded with Cu$K\alpha$ radiation on equi-inclination Weissenberg photographs taken about the *a*- and *b*-axes using the multiple-film technique. The intensities of reflexions were visually estimated by using a standard scale. The *a*-axis X-ray specimen prepared for the intensity measurement was a cylindrical rod crystal elongated along the *a*-axis and 0.017 cm in diameter. No absorption correction was applied. All intensity data were corrected for Lorentz and polarization factors. The resulting values were put on a single scale by correlating various layers and a total of 530 structure factors were finally derived.

Determination of the Structure

The positions of the bromine atoms were determined by the calculation of the three-dimensional sharpened Patterson sections at u=1/2, v=1/2 and w=1/2. The first three-dimensional Fourier and difference Fourier syntheses utilizing the phase angles given by the

Table I. The Final Fractional Atomic Coordinates, Temperature Factors and Their Standard Deviations (To represent the correct absolute configurations, these coordinates should refer to the right-handed coordinate system.)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B(Å^2)	σ(B)
Br	0.1629	0.0006	0.1974	0.0005	0.0322	0.0006	see below	
O(1)	0.493	0.005	0.093	0.003	0.253	0.004	2.6	0.5
O(2)	0.433	0.004	−0.095	0.004	0.091	0.003	2.8	0.6
O(3)	−0.178	0.004	0.049	0.003	0.232	0.003	2.2	0.5
C(1)	0.387	0.006	0.007	0.005	0.169	0.005	2.3	0.8
C(2)	0.197	0.005	0.044	0.004	0.187	0.004	1.5	0.6
C(3)	0.083	0.006	−0.086	0.005	0.153	0.005	2.2	0.8
C(4)	−0.105	0.006	−0.044	0.005	0.153	0.005	2.2	0.8
N	−0.205	0.005	−0.140	0.004	0.061	0.004	3.0	0.8

Temperature factor of the bromine atom is given in the form of
$T=\exp.\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$

where,	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	0.0078	0.0069	0.0134	0.0032	0.0010	0.0029
$\sigma(\beta)$	0.0007	0.0005	0.0006	0.0010	0.0007	0.0005

4) P. Walden, *Chem. Ber.*, **28**, 2766 (1895); S. Kallenberg, *Chem. Ber.*, **50**, 94 (1917).

TABLE II. The Observed and the Calculated Structure Factors

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
0	0	2	41.55	44.94	1	2	4	46.17	42.88	2	1	A	24.72	23.55	3	2	A	12.49	6.92	4	2	9	5.47	2.95
0	0	4	61.12	57.87	1	2	5	38.13	35.84	2	1	7	16.98	16.58	3	2	7	35.65	33.10	4	2	10	4.24	2.83
0	0	A	11.42	8.28	1	2	A	33.74	31.51	2	1	8	5.71	5.17	3	2	8	9.02	8.39	5	0	1	14.54	12.43
0	0	10	15.76	16.63	1	2	7	16.57	13.23	2	1	9	5.37	4.43	3	2	9	12.32	13.68	5	0	2	7.83	13.70
0	1	1	63.43	78.87	1	2	8	17.30	16.69	2	1	10	6.54	5.18	3	2	10	3.34	4.11	5	0	3	26.32	22.07
0	1	2	92.49	107.55	1	2	9	9.94	10.11	2	1	11	5.03	7.71	3	3	0	16.12	18.78	5	0	4	31.76	32.46
0	1	3	68.34	77.24	1	2	10	13.13	18.08	2	2	0	49.93	44.47	3	3	1	73.60	75.14	5	0	5	23.61	23.15
0	1	5	42.68	46.41	1	2	11	3.04	3.74	2	2	1	83.98	83.24	3	3	2	29.77	26.24	5	0	6	33.32	32.73
0	1	6	22.77	21.84	1	3	0	59.62	60.26	2	2	2	57.80	54.29	3	3	3	62.95	59.52	5	0	7	18.01	17.35
0	1	7	6.52	6.80	1	3	1	48.18	47.28	2	2	3	45.21	49.20	3	3	4	51.47	48.27	5	0	8	22.67	24.61
0	1	8	14.50	13.43	1	3	2	50.17	51.22	2	2	4	46.94	43.15	3	3	5	24.44	17.97	5	1	0	5.15	5.45
0	1	11	4.19	6.21	1	3	3	43.47	37.70	2	2	5	26.94	22.74	3	3	6	24.57	17.78	5	1	1	22.09	20.56
0	2	1	16.29	20.70	1	3	4	46.87	41.87	2	2	6	24.81	24.44	3	3	7	7.63	7.26	5	1	2	26.60	26.77
0	2	2	98.02	130.08	1	3	5	35.35	36.04	2	2	7	15.78	12.84	3	3	8	18.97	16.09	5	1	3	36.20	36.28
0	2	3	40.89	39.85	1	3	6	13.30	10.84	2	2	8	15.59	13.34	3	3	9	7.08	7.77	5	1	4	11.80	11.94
0	2	4	36.63	40.95	1	3	7	10.39	8.78	2	2	9	7.44	4.82	3	3	10	4.26	4.59	5	1	5	31.24	30.25
0	2	5	43.86	46.48	1	3	8	17.71	23.56	2	2	10	9.34	7.84	3	4	0	54.04	49.46	5	1	6	17.49	17.48
0	2	6	7.85	7.04	1	3	9	10.71	13.23	2	2	11	3.89	8.18	3	4	1	17.09	12.59	5	1	7	26.17	27.46
0	2	7	16.57	16.19	1	3	10	4.75	5.47	2	3	0	48.71	38.81	3	4	2	90.60	87.71	5	1	8	11.76	10.77
0	2	9	13.77	18.22	1	3	11	1.90	2.87	2	3	1	32.23	32.69	3	4	3	10.61	8.87	5	1	9	11.72	12.72
0	2	11	6.03	8.50	1	4	0	54.89	53.93	2	3	2	31.11	23.69	3	4	4	26.15	23.03	5	2	0	17.02	9.51
0	3	1	81.99	90.50	1	4	1	72.11	78.13	2	3	3	71.59	60.52	3	4	5	10.07	6.01	5	2	1	54.47	46.64
0	3	2	17.13	15.44	1	4	2	33.57	30.09	2	3	4	49.89	42.87	3	4	6	25.73	22.32	5	2	2	28.42	22.11
0	3	3	35.16	30.83	1	4	3	61.03	57.45	2	3	5	33.38	25.96	3	4	7	10.76	10.19	5	2	3	33.21	31.09
0	3	4	66.68	75.58	1	4	4	31.56	28.35	2	3	6	17.73	15.59	3	4	8	3.19	1.72	5	2	4	30.13	27.85
0	3	5	6.67	6.84	1	4	5	25.43	27.30	2	3	7	28.33	26.95	3	4	10	4.21	3.54	5	2	5	16.08	15.81
0	3	6	32.97	35.11	1	4	6	23.99	24.33	2	3	8	14.33	13.58	3	5	0	13.88	11.42	5	2	6	33.00	29.19
0	3	8	14.73	20.26	1	4	7	6.44	6.79	2	3	9	19.97	20.50	3	5	1	62.27	60.31	5	2	7	7.66	8.77
0	3	9	8.30	10.40	1	4	8	9.56	9.78	2	3	10	8.92	9.53	3	5	2	11.50	8.01	5	2	8	12.60	12.88
0	3	10	10.78	13.14	1	4	9	4.51	2.47	2	4	0	36.89	29.60	3	5	3	46.94	47.69	5	2	9	8.19	10.73
0	3	11	2.46	5.54	1	4	10	6.46	10.28	2	4	1	23.48	20.71	3	5	4	8.96	9.10	6	0	0	57.16	61.10
0	4	0	5.00	4.78	1	5	0	65.03	66.30	2	4	2	23.03	20.70	3	5	5	23.65	24.66	6	0	1	13.09	11.59
0	4	1	8.87	4.33	1	5	1	40.69	42.26	2	4	3	26.60	25.40	3	5	6	11.33	11.15	6	0	2	36.95	35.99
0	4	3	68.73	78.28	1	5	2	60.15	55.65	2	4	4	37.89	36.29	3	5	7	4.68	4.93	6	0	3	22.95	20.57
0	4	4	8.83	4.72	1	5	3	38.66	36.29	2	4	5	30.11	24.32	3	5	8	4.19	5.94	6	0	4	57.03	52.02
0	4	5	22.00	20.27	1	5	4	38.92	36.37	2	4	6	36.99	37.28	3	5	9	4.66	3.07	6	1	1	52.65	59.12
0	4	6	13.92	17.09	1	5	5	14.09	16.53	2	4	7	15.61	15.23	3	6	0	71.14	68.47	6	1	2	8.47	4.51
0	4	7	28.65	36.51	1	5	6	16.08	15.35	2	4	8	23.82	21.49	3	6	1	19.69	15.29	6	1	3	33.98	34.25
0	4	8	7.78	7.59	1	5	7	6.39	7.65	2	4	9	13.86	12.01	3	6	2	43.07	41.81	6	1	4	16.38	11.71
0	4	9	13.60	19.50	1	5	8	10.33	9.68	2	4	10	12.08	14.73	3	6	3	54.29	16.54	6	1	5	27.82	23.81
0	5	2	16.53	18.21	1	5	9	2.91	5.69	2	5	0	14.58	13.24	3	6	4	41.16	31.56	6	1	6	17.11	16.82
0	5	3	7.04	6.37	1	5	10	3.93	5.24	2	5	1	24.59	16.59	3	6	5	6.84	6.98	6	1	7	11.83	8.25
0	5	4	25.49	27.77	1	6	0	29.89	34.17	2	5	2	27.97	21.12	3	6	6	8.19	8.75	6	1	8	5.30	5.40
0	5	6	30.71	41.86	1	6	1	49.55	51.70	2	5	3	39.97	38.91	3	6	7	12.74	12.84	6	2	0	42.28	44.91
0	5	7	14.73	20.34	1	6	2	22.15	18.75	2	5	4	26.17	26.84	3	6	8	5.24	7.86	6	2	1	40.69	28.16
0	5	8	16.87	27.68	1	6	3	24.38	25.59	2	5	5	38.71	46.42	3	6	9	4.32	4.84	6	2	2	55.00	46.58
0	5	10	5.22	11.92	1	6	4	25.58	26.41	2	5	6	17.06	13.57	3	7	0	5.71	3.16	6	2	3	14.46	13.33
0	6	1	25.23	29.58	1	6	5	26.30	28.36	2	5	7	26.69	20.77	3	7	1	45.14	37.63	6	2	4	9.92	10.85
0	6	2	29.96	36.63	1	6	6	11.14	9.39	2	5	8	13.17	11.98	3	7	2	17.47	14.17	6	2	5	23.31	21.80
0	6	3	26.75	31.59	1	6	7	7.93	8.41	2	5	9	14.16	11.71	3	7	3	25.02	20.74	6	2	6	13.66	13.93
0	6	4	15.78	16.09	1	6	8	8.34	7.88	2	6	0	44.63	26.73	3	7	4	19.31	12.60	6	2	7	10.69	10.78
0	6	5	35.39	44.70	1	6	9	6.05	9.07	2	6	1	45.12	31.42	3	7	5	13.75	13.21	6	2	8	6.65	5.68
0	6	6	14.48	20.81	1	7	0	37.89	40.46	2	6	2	32.31	21.93	3	7	6	16.49	21.28	7	0	1	9.02	6.58
0	6	7	17.86	27.87	1	7	1	23.63	22.60	2	6	3	33.10	28.73	3	7	7	6.47	1.94	7	0	2	13.77	14.35
0	6	9	6.12	8.38	1	7	2	33.47	39.19	2	6	4	31.86	22.84	3	7	8	8.04	8.40	7	0	3	18.60	21.18
0	7	1	36.31	48.22	1	7	3	17.43	19.47	2	6	5	23.42	23.31	3	8	0	22.92	22.17	7	0	4	23.01	22.56
0	7	2	22.86	21.96	1	7	4	13.37	14.56	2	6	6	29.17	22.56	3	8	1	21.06	18.63	7	0	5	14.99	16.30
0	7	3	20.02	21.74	1	7	5	11.72	12.32	2	6	7	18.92	13.93	3	8	2	20.72	17.79	7	0	6	13.47	16.79
0	7	4	18.56	21.31	1	7	6	11.29	13.01	2	6	8	24.72	23.10	3	8	3	13.45	10.53	7	0	7	7.04	8.58
0	7	5	15.67	21.51	1	7	7	15.89	19.79	2	6	9	9.67	10.57	3	8	4	11.72	10.20	7	1	0	6.20	7.66
0	7	6	19.74	19.98	1	7	8	7.61	11.07	2	7	0	45.03	33.92	3	8	5	18.50	17.97	7	1	1	15.80	11.65
0	7	8	9.39	12.31	1	7	9	5.41	7.88	2	7	1	33.17	16.22	3	8	6	2.69	3.30	7	1	2	16.94	16.36
0	8	0	37.91	48.37	1	8	0	9.77	7.44	2	7	2	44.39	29.24	3	8	7	13.34	17.42	7	1	3	25.25	24.55
0	8	2	28.80	27.73	1	8	1	17.34	16.54	2	7	3	29.21	23.68	3	9	0	8.62	3.91	7	1	4	14.61	15.46
0	8	3	12.83	12.20	1	8	2	18.58	22.52	2	7	4	25.81	16.97	3	9	1	6.48	5.38	7	1	5	22.82	20.89
0	8	4	23.12	27.79	1	8	3	21.98	20.39	2	7	5	28.27	20.53	3	9	2	17.68	14.50	7	1	6	13.79	15.77
0	8	5	18.35	22.10	1	8	4	19.40	22.64	2	7	6	30.71	24.68	3	9	3	10.99	8.37	7	1	7	14.97	16.97
0	8	6	11.46	11.68	1	8	5	3.51	7.54	2	7	7	28.16	22.60	3	9	4	23.24	23.60	7	2	0	11.46	16.91
0	9	1	30.52	35.49	1	8	6	17.62	18.63	2	7	8	8.32	5.85	3	9	5	9.41	11.21	7	2	1	26.54	22.85
0	9	2	13.49	5.32	1	8	7	10.61	12.98	2	8	1	63.66	39.57	3	9	6	10.52	17.42	7	2	2	27.35	27.05
0	9	3	25.51	36.64	1	8	8	7.08	14.14	2	8	2	21.34	10.32	3	10	0	6.82	6.45	7	2	3	23.57	16.57
0	9	4	12.53	13.72	1	9	0	11.59	14.08	2	8	3	49.18	33.60	3	10	2	10.59	10.58	7	2	4	18.50	18.91
0	9	5	9.02	12.63	1	9	1	6.33	4.04	2	8	4	34.73	22.23	3	10	3	14.07	17.83	7	2	5	11.42	11.55
0	10	0	18.28	30.62	1	9	2	10.22	10.18	2	8	5	27.71	17.52	3	10	4	7.66	7.80	7	2	6	19.29	20.70
0	10	1	11.65	2.81	1	9	3	13.42	11.34	2	8	6	20.85	13.22	3	10	5	2.52	18.98	7	2	7	10.69	12.30
0	10	2	24.10	29.56	1	9	4	11.59	15.00	2	8	7	12.96	9.68	3	11	0	10.18	14.12	8	0	0	23.57	20.87
0	10	4	12.27	13.83	1	9	5	18.09	21.18	2	9	2	44.05	30.27	3	11	1	5.88	7.55	8	0	1	39.95	40.19
0	11	1	18.47	22.81	1	9	6	10.16	12.23	2	9	3	22.45	13.73	3	11	2	5.62	8.45	8	0	2	16.55	12.60
0	11	3	8.81	13.90	1	9	7	7.40	10.91	2	9	4	35.16	22.49	4	0	0	60.47	54.83	8	0	3	27.12	28.87
1	0	1	10.69	5.54	1	10	0	3.29	3.47	2	9	5	12.79	7.73	4	0	1	64.45	70.60	8	0	5	7.55	11.18
1	0	2	46.10	47.99	1	10	1	5.67	7.43	3	0	1	83.93	75.69	4	0	2	41.16	43.31	8	1	0	25.40	32.22
1	0	3	35.28	30.90	1	10	2	16.19	17.39	3	0	2	35.82	28.99	4	0	3	42.96	38.79	8	1	1	8.19	9.35
1	0	4	36.61	32.67	1	10	3	10.39	12.90	3	0	3	33.17	26.39	4	0	4	9.05	6.84	8	1	2	28.03	31.29
1	0	5	13.66	9.86	1	10	4	12.21	17.55	3	0	4	17.60	15.25	4	0	5	16.87	16.70	8	1	3	14.86	13.23
1	0	6	39.07	34.77	1	10	5	8.32	8.72	3	0	5	74.57	72.85	4	0	6	24.10	25.88	8	1	4	14.26	17.83
1	0	7	35.10	34.22	1	10	6	4.44	14.94	3	0	6	4.36	2.28	4	0	7	7.36	4.58	8	1	5	6.31	7.93
1	0	8	28.93	30.19	1	11	0	11.93	17.25	3	0	7	31.28	27.49	4	0	8	5.94	5.80	8	1	6	9.69	10.75
1	0	9	13.54	15.13	1	11	1	3.59	7.30	3	0	9	25.30	22.33	4	1	0	24.66	27.88	8	2	0	11.89	9.74
1	0	10	7.42	5.64	1	11	2	7.55	10.11	3	0	10	3.55	1.27	4	1	1	41.46	44.45	8	2	1	26.67	26.86
1	0	11	3.66	4.43	1	11	3	11.16	13.77	3	1	0	48.48	36.72	4	1	2	62.76	60.96	8	2	2	12.44	13.50
1	1	0	40.03	34.47	1	11	4	4.34	11.12	3	1	1	52.65	47.64	4	1	3	38.51	41.45	8	2	3	21.19	21.86
1	1	1	35.01	28.83	2	0	0	48.03	43.04	3	1	2	29.08	27.26	4	1	4	33.57	31.93	8	2	4	7.89	10.01
1	1	2	34.86	33.95	2	0	1	41.14	44.93	3	1	3	23.89	19.40	4	1	5	15.87	15.76	8	2	5	8.90	10.78
1	1	3	63.06	54.48	2	0	2	56.65	53.36	3	1	4	43.38	37.43	4	1	6	12.23	15.32	8	2	6	5.67	9.60
1	1	4	34.98	33.96	2	0	3	72.42	75.76	3	1	5	16.49	15.37	4	1	7	13.81	11.70	9	0	1	12.19	10.21
1	1	5	52.37	52.25	2	0	4	53.36	50.26	3	1	6	45.18	41.23	4	1	8	13.02	11.92	9	0	2	9.80	9.82
1	1	6	34.32	33.08	2	0	5	35.63	35.73	3	1	7	13.79	4.98	4	1	10	6.59	7.85	9	0	4	6.86	6.53
1	1	7	39.22	39.04	2	0	6	14.01	12.47	3	1	8	28.70	25.24	4	2	0	24.95	21.11	9	1	0	5.67	2.44
1	1	8	13.17	10.33	2	0	7	11.38	12.30	3	1	9	3.10	4.15	4	2	1	49.78	43.66	9	1	1	5.98	7.14
1	1	9	15.93	14.02	2	0	8	13.60	11.90	3	1	10	13.32	13.61	4	2	2	44.99	34.89	9	1	2	12.27	14.42
1	1	10	8.44	9.00	2	1	0	104.48	104.30	3	2	0	68.54	70.95	4	2	3	47.64	46.70	9	1	3	5.98	6.61
1	1	11	6.18	9.11	2	1	1	59.83	57.72	3	2	1	34.34	22.80	4	2	4	36.59	31.55	9	1	4	11.98	19.17
1	2	0	15.72	17.47	2	1	2	97.23	92.81	3	2	2	15.70	18.75	4	2	5	25.44	22.85	9	2	0	20.52	27.26
1	2	1	47.10	49.46	2	1	3	23.43	20.45	3	2	3	58.02	54.37	4	2	6	24.42	20.80	9	2	2	9.84	13.33
1	2	2	54.89	57.63	2	1	4	39.07	34.70	3	2	4	56.09	49.78	4	2	7	15.59	15.27	9	2	3	16.23	17.18
1	2	3	57.69	51.11	2	1	5	19.59	14.20	3	2	5	32.38	30.97	4	2	8	18.01	19.73	9	2	4	8.65	11.26

contributions of the bromine atoms revealed six light atoms(R=0.36). These six atoms were then included in the next structure factor calculation assuming that all were carbon atoms, and in the second Fourier and difference Fourier maps, it was found that one of them to be false and two predominant peaks to be new atoms. The third set of calculations indicated that several atoms were improperly located. The fourth set of calculation (R=0.24) revealed out all atoms except C_1 (Fig. 3). The position of C_1 was then determined by assuming the plane structure of this compound.

Refinement of the Structure

The structure, which was obtained by Fourier and difference Fourier syntheses, was subjected to least-squares refinement using the block-diagonal matrix approximation. In the first step, all the atoms except bromine were treated as isotropic and the R value dropped to 0.16 after three cycles.

Further refinement of the structure was carried out using the full-matrix least-squares program ORFLS[5] with unit weight for each reflexion. As in the case of the block-matrix least-squares refinement, all the atoms except bromine were treated as isotropic, but for bromine atoms anisotropic thermal vibrations were allowed for. After four cycles, the R value reduced to at 0.15.

The final atomic parameters and the standard deviations are listed in Table I, and the observed and the calculated structure factors are given in Table II. The composite projection

Table III. The Intramolecular Bond Distances and Their Standard Deviations

		σ			σ
Br-C(2)	1.99Å	0.03Å	C(1)-C(2)	1.51Å	0.05Å
O(1)-C(1)	1.37Å	0.05Å	C(2)-C(3)	1.52Å	0.05Å
O(2)-C(1)	1.22Å	0.05Å	C(3)-C(4)	1.50Å	0.05Å
O(3)-C(4)	1.25Å	0.05Å	C(4)-N	1.43Å	0.05Å

Table IV. The Intramolecular Bond Angles and Their Standard Deviations

		σ			σ
C(2)-C(1)-O(1)	113°	3°	Br-C(2)-C(1)	103°	2°
C(2)-C(1)-O(2)	121°	4°	C(4)-C(3)-C(2)	111°	3°
O(1)-C(1)-O(2)	125°	4°	N-C(4)-O(3)	120°	4°
C(3)-C(2)-Br	111°	2°	N-C(4)-C(3)	111°	3°
C(3)-C(2)-C(1)	111°	3°	O(3)-C(4)-C(3)	128°	4°

Table V. The Intramolecular Rotational Angles

C(3)-C(2)-C(1)-O(2)	23°	C(4)-C(3)-C(2)-Br	−60°
Br-C(2)-C(1)-O(2)	−96°	C(4)-C(3)-C(2)-C(1)	−173°
C(4)-C(3)-C(2)-Br	−60°	N-C(4)-C(3)-C(2)	154°
C(3)-C(2)-C(1)-O(2)	23°	O(3)-C(4)-C(3)-C(2)	−34°
C(4)-C(3)-C(2)-C(1)	−173°	N-C(4)-C(3)-C(2)	154°
Br-C(2)-C(1)-O(2)	−96°	O(3)-C(4)-C(3)-C(2)	−34°

The definition of the rotational angle is given in the paper (M. Morisaki, S. Nozoe and Y. Iitaka, *Acta Cryst.* **B24**, 1293 (1968)).

5) W.R. Busing, K.O. Martin and H.A. Levy (1962). ORFLS, A Fortran Crystallographic Least-squares programs, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

Table VI. Best Planes

(a) Coefficient of the planes (The equation of the plane is, $LX+MY+NZ=D$, where X, Y, Z are expressed in Å units.)

Plane	L	M	N	
1	0.0269	−0.6143	0.7886	(all atoms without bromine)
2	−0.0781	−0.6257	0.7762	(α-carboxyl group)
3	−0.1373	−0.6422	0.7542	(β-amide group)
4	−0.0080	−0.2335	0.9723	(carbon chain)

(b) Displacement of atoms from the planes (Å)

Plane 1		Plane 2		Plane 3		Plane 4	
O(1)	0.06	O(1)	0.005	N	0.013	C(1)	−0.042
O(2)	−0.02	O(2)	0.006	O(3)	0.017	C(2)	0.043
O(3)	0.03	C(1)	−0.016	C(4)	−0.043	C(3)	0.042
C(1)	−0.06	C(2)	0.005	C(3)	0.013	C(4)	−0.043
C(2)	−0.19						
C(3)	0.29						
C(4)	0.01						
N	−0.11						
Br[a]	−2.15						

[a] The bromine atom was not included in the evaluation of the equation of the plane.

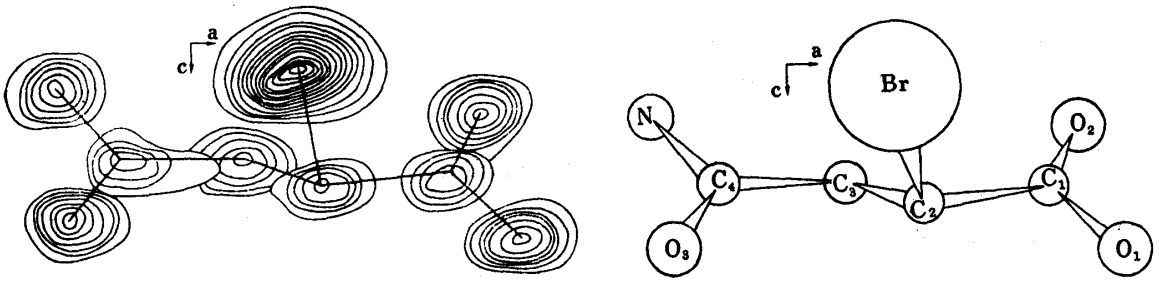


Fig. 1

(a) composite electron density map of the molecule viewed downwards along the b-axis

(b) a molecule viewed downwards along the b-axis

of the final three-dimensional electron density map is shown in Fig. 1. The atomic scattering factors in the calculations were taken from the "International Tables for X-ray Crystallography."[6]

Determination of the Absolute Configuration

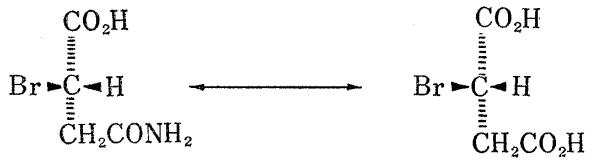
In order to establish the absolute configuration of (−)-2-bromosuccinamic acid (I), the anomalous dispersion effect[7] of Cu$K\alpha$ radiation for the bromine atom was used.

The dispersion correction for the bromine scattering factor for Cu$K\alpha$ radiation was given by Dauben & Templeton[8] as $\Delta f' = -0.9$ and $\Delta f'' = 1.5$. The structure factors were calculated from the out put atomic parameters of the block-matrix least-squares calculations, by assuming a right handed set of axes. Of the sixteen pairs of reflexions in $1kl$—$3kl$ and $h1l$—$h2l$ for which the intensity differences in $I(hkl)$ and $I(h\bar{k}l)$, $I(hkl)$ and $I(hk\bar{l})$ are expected to be mea-

6) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1962, p. 202.
7) J.M. Bijvoet, A.F. Peerdeman and A.J. van Bommel, *Nature*, **168**, 271 (1951).
8) C.H. Dauben and D.H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

Table VII. Comparison of the Observed and Calculated Intensity Differences used for the Establishment of Absolute Configuration

h	k	l	$\frac{F_c^2(hkl)}{F_c^2(\bar{h}\bar{k}\bar{l})}$	$\frac{I_0(hkl)}{I_0(\bar{h}\bar{k}\bar{l})}$	h	k	l	$\frac{F_c^2(hkl)}{F_c^2(\bar{h}\bar{k}\bar{l})}$	$\frac{I_0(hkl)}{I_0(\bar{h}\bar{k}\bar{l})}$
1	1	8	1.450	>1	3	2	2	0.710	<1
1	5	5	1.323	>1	3	6	5	1.513	>1
1	6	7	1.304	?	3	9	1	1.387	>1
1	7	5	0.735	<1	5	1	4	1.315	>1
11	0	1	0.762	?	6	1	2	0.515	<1
2	1	8	1.431	>1	2	2	9	1.537	?
2	2	9	1.537	>1	3	2	2	0.710	<1
3	1	7	1.311	>1	6	2	3	1.316	>1



(S)(−)(I)(EtOH) (S)(−)(II)(H2O)

Fig. 2. Fischer's Projection of (−)-2-Bromosuccinamic Acid (I) and (−)-Bromosuccinic Acid(II)

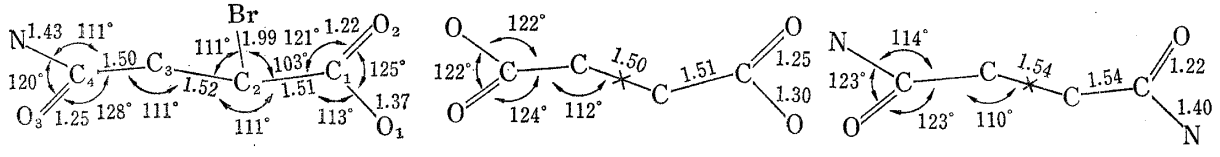
surable, thirteen pairs showed significant differences in the a- and b-axis Weissenberg photographs. These differences were confirmed by three observers. The results are shown in Table VII. A comparison of the observed and calculated intensity differences led to the absolute configuration shown in Fig. 1, 2. This configuration is also favored by Brewster, *et al.*[2] from their kinetic studies. Thus the deaminative bromination of L(−)Asp. NH_2 monohydrate by nitrosyl bromide was proved to give the corresponding (S)-bromo acids with retention of the configuration.

Result and Discussion

The Molecular Structure

Intramolecular bond distances, angles and rotational angles were calculated from the atomic coordinates given in Table I and shown in Tables III, IV, V, and the equations of the best planes of the several planar groups were evaluated, the latter listed in Table VI.

The molecular structure of (−)-2-bromosuccinamic acid may be compared with those of succinic acid (β-form)[9] and succinamide[10] (Fig. 3). As shown in Fig. 3 these three compounds have similar bond distances and angles. The carbon chain, C(1)-C(2)-C(3)-C(4), are coplanar and arranged in *trans* zigzag. Two carbonyl groups are transoid. Each of the carboxyl group and the amide group of (−)-2-bromosuccinamic acid (I) is coplanar within the limits of experimental error.



(−)-2-bromosuccinamic acid succinic acid (β-form) succinamide

Fig. 3. Interatomic Bond Distances(Å) and Angles

All four carbon atoms are coplanar.
× shows the center of symmetry.

9) J.D. Morrison and J.M. Robertson, *J. Chem. Soc.*, **1949**, 980.
10) R.A. Pasternak, *Acta Cryst.*, **6**, 808 (1953).

The angles between the best plane of the carbon chain and those of the carboxyl and the amide groups are 26° and 28°, respectively. These values differ from those of succinic acid, in which the carboxyl group rotates only 9° from the plane of the carbon chain. This may be due to the steric effect of the large bromine atom.

Hydrogen Bonds and Molecular Packing

As is seen in Fig. 4, the structural unit of the crystal consists of the bands of the molecules. Within the band the molecules are arranged head to tail to form a chain laying their long

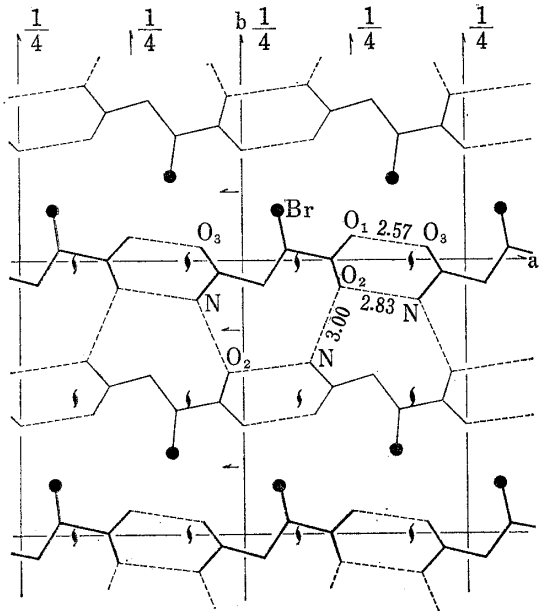


Fig. 4. A part of the structure shown in Fig. 5

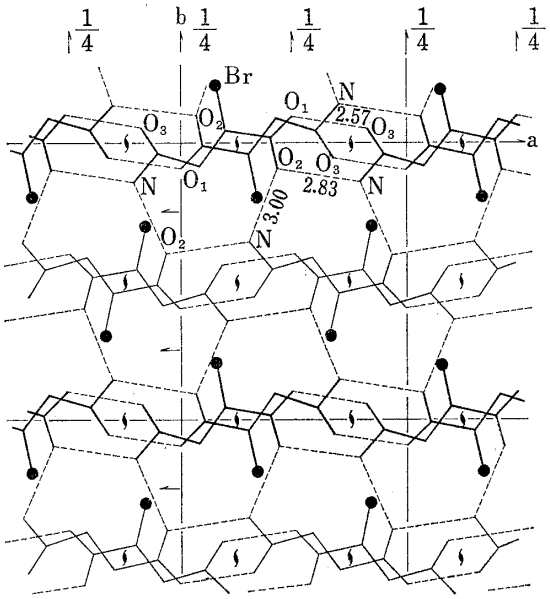


Fig. 5

Projection of the structure viewed downwards along the *c*-axis. Hydrogen bonds are shown by broken lines.

axis parallel to the *a*-axis. These molecules are bound together strongly through hydrogen bonds between amide nitrogen and carboxyl oxygen atoms (2.83 Å), and those between amide oxygen and carboxyl oxygen atoms (2.57 Å). There are two molecular chains contained in the band (Fig. 5). They are related by the two-fold screw axis parallel to ***a*** and joined together through rather weak hydrogen bonds between the amide nitrogen and caboxyl oxygen atoms (3.00 Å). These hydrogen bond distances can be compared with the reported hydrogen bond distances of β-form of succinic acid[9] (2.64 Å) and those of succinamide[10] (2.92 and 2.95 Å).

The bromine atoms are protruded out from the bands and arranged in zigzag form along the two-fold screw axis parallel to ***a***. The distance between the two bromine atoms is 4.02 Å and the arrangement of the bromine atoms seems to be determined mainly by van der Waals forces. The packing of the band is best represented in Fig. 6. It is seen that the planes

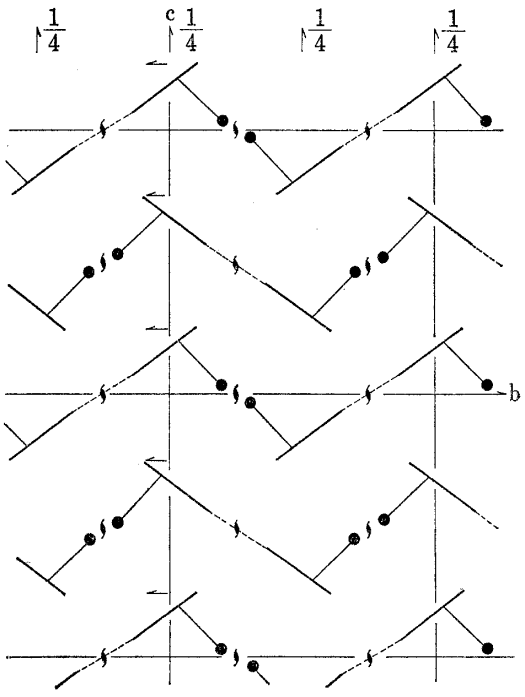


Fig. 6

Projection of the structure viewed downwards along the *a*-axis. All atoms of the molecule except bromine are sketched by a thick line. Hydrogen bonds are shown by broken lines.

of the molecular bands are mutually inclined and packed in the orthorhombic cell similar to the structure of the O⊥ packing of long chain compounds.[11] The crystal structure of the present type had not been observed in the crystals of amides of carboxylic acids, in which the hydrogen bonds are usually extended either in sheets (α-form of oxalic acid,[12] oxamide,[13] adipic acid[14] *etc.*) or in chains (longitudinal single chain, such as in β-form of oxalic acid[15] and transverse chain such as in benzamide[16]). Fig. 5 shows the projection of the structure along the *c*-axis.

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11) E. von Sydow, *Arkiv Kemi*, **9**, 231 (1956).
12) E.G. Cox, M.W. Dougill and G.A. Jeffrey, *J. Chem. Soc.*, **1952**, 4854.
13) E.M. Ayerst and J.R.C. Duke, *Acta Cryst.*, **7**, 588 (1954).
14) J.D. Morrison and J.M. Robertson, *J. Chem. Soc.*, **1949**, 987.
15) S.B. Hendricks, *Z. Krist*, **91**, 48 (1935).
16) B.R. Penfold and J.C.B. White, *Acta Cryst.*, **12**, 230 (1959).