BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2369—2378 (1966)

The Crystal Structures of L-Tryptophan Hydrochloride and Hydrobromide

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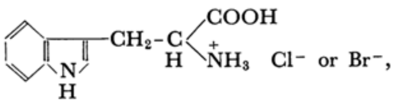
(Received April 26, 1966)

The hydrochloride and hydrobromide of L-tryptophan crystallize in the monoclinic space group $P2_1$. The cell dimensions of the hydrochloride are: $a=7.45$, $b=5.30$, $c=14.67$ Å, $\beta=98.80°$, and those of the hydrobromide are: $a=7.64$, $b=5.41$, $c=14.58$ Å, $\beta=100.47°$. There are two molecules in the unit cell. The two compounds are isomorphous. The crystal structure of the hydrobromide was first determined by the heavy atom method with two-dimensional data, and then that of the hydrochloride was refined by three-dimensional least-squares procedure. The molecular and crystal structure is mainly discussed for the hydrochloride here. The average of six C–C bond lengths in the benzene ring is 1.396 Å, that of C–N bond lengths in the indole ring is 1.384 Å. In the carboxyl group, one C–O bond length, 1.147 Å and two O–C–C angles, 106.8° and 125.7° are significantly different from those reported for amino and carboxyl acids so far investigated. The molecule consists of two planes of the carboxyl group and of the indole ring, the planes making an angle of 70.6° with each other. As to the conformation about the C(α)–C(β) bond, C(γ) lies at the gauche position with both of the carboxyl and the amino groups. The molecules are arranged in double layers parallel to the ab plane; the polar layer is held together by a network of the three N–H$\cdots$ Cl$^-$ hydrogen bonds, 3.17, 3.19 and 3.24 Å and one O–H$\cdots$Cl$^-$, 3.04 Å, and in the non-polar layer, the indole rings are packed mainly by van der Waals forces, the shortest C$\cdots$C and C$\cdots$N contacts being 3.74 and 3.42 Å respectively.

The three-dimensional structures of the amino acids have been studied by many authors to furnish the structural basis for protein research.[1] Out of twenty-odd naturally occurring amino acids, some seventeen compounds have been determined by X-ray analysis so far. Although the preliminary examination was reported for DL-tryptophan dihydrochloride by Dawson and Mathieson,[2] detailed X-ray analysis for tryptophan has not yet been published. This paper deals with X-ray analysis of the crystal structures of L-tryptophan hydrochloride and hydrobromide.

Experimental

L-tryptophan hydrochloride and hydrobromide,



were obtained in the form of needle-like crystals by dissolving L-tryptophan in concentrated hydrochloric and hydrobromic acid respectively at room temperature and by standing them at 5°C.

Rotation, Weissenberg and precession photographs showed the crystals to be monoclinic, the unique b being coincident with the needle axis. The unit-cell dimensions were determined from zero layer Weissenberg photographs taken about three crystallographic axes with standard aluminum powder reflections. The densities were measured by flotation in a benzene-carbon tetrachloride mixture.

Crystal data so obtained are:

For hydrochloride,

$a=7.45\pm0.02$, $b=5.30\pm0.01$, $c=14.67\pm0.02$ Å,
$\beta=98.80\pm0.07°$, $D_m=1.394$, $D_c=1.396$ g. cm^{-3},
$Z=2$,
$\mu=29.1$ cm^{-1} for Cu$K\alpha$ radiation.

For hydrobromide,

$a=7.64\pm0.02$, $b=5.41\pm0.01$, $c=14.58\pm0.02$ Å,
$\beta=100.47\pm0.10°$, $D_m=1.594$, $D_c=1.597$ g. cm^{-3}
$Z=2$,
$\mu=49.0$ cm^{-1} for Cu$K\alpha$ and 37.6 cm^{-1} for Mo$K\alpha$ radiation.

The only systematic absence in these two crystals is observed for ($0k0$) reflections with k odd. The space group was determined to be C_2^2-$P2_1$, an alternative centrosymmetric space group C_{2h}^2-$P2_1/m$ being excluded because of the asymmetry of the molecule.

Somewhat different crystal was obtained by dissolving L-tryptophan in dilute hydrobromic acid (1 N). The cell constants with less accuracy are $a=31.30$, $b=13.86$, $c=5.73$ Å, space group being $P2_12_12_1$. Density was measured to be 1.444 g. cm^{-3}. Elementary analysis and the crystal data indicated that the asymmetric unit consisted of 2tryptophan·HBr·1/2H$_2$O. No further study was attempted for this crystal.

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[1] e. g., A. Rich and D. W. Green, *Ann. Rev. Biochem.*, **30**, 93 (1961).

[2] B. Dawson and A. Mathieson, *Acta Cryst.*, **4**, 475 (1951).

For the hydrochloride, three-dimensional intensity data were collected by equi-inclination Weissenberg procedure with nickel-filtered Cu$K\alpha$ radiation. Photographs were taken for layers ($h0l$) to ($h4l$) and ($0kl$) to ($5kl$) by the multiple-film technique. Out of 1387 accessible reflections, 1258 non-zero reflections were observed and they amount to 80% of the reciprocal lattice points within the limiting sphere for Cu-$K\alpha$ radiation.

For the hydrobromide, only intensity data for ($h0l$) and ($0kl$) zones were recorded on Weissenberg and precession photographs respectively, the latter being taken with zirconium-filtered Mo$K\alpha$ radiation.

Intensities were estimated visually against the standard scale and they were corrected for Lorentz and polarization factors. For the equi-inclination Weissenberg data, a correction for spot-shape was made according to Phillips' equation.³⁾ Sizes of crystals used in the experiment were: $0.10\times0.15\times2.0$ mm. and $0.15\times0.15\times0.40$ mm. for the b and a axis photographs of the hydrochloride respectively, $0.15\times0.15\times2.5$ mm. for the b axis photographs of the hydrobromide.

Three-dimensional structure factors were put on a common scale by comparing data from photographs of the different axis. Estimated errors in the scaling were less than 10%.

Since the a axis data seemed to be less accurate than the b axis data, the former was only used, in the subsequent analysis, for reflections unaccessible by the b axis photographs.

Structure determination

Hydrobromide.—A modified Patterson projection along the b axis was constructed for the hydrobromide. From a heavy Patterson peak, the x- and z-coordinates of the bromide ion were determined to be 0.100 and 0.125 respectively. Based on the signs of the bromide ion, Fourier summation was carried out. Almost all the atoms were resolved on the resulting Fourier projection, and it was not difficult to give approximate coordinates even for a few overlapped atoms. Succesive Fourier refinement was made until the discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, became 0.19, the overall temperature factor $B=4.0$ Å² being applied. A least-squares refinement was then proceeded using 240 independent ($h0l$) reflections. Anisotropic temperature factors were applied only for the bromide ion. After three cycles of the refinement, the R factor dropped to 0.086.

In the a axis projection with the plane group pg, the y coordinate of the bromide ion was arbitrarily fixed at 1/4. On the Fourier projection based on the phases of the bromide ion only, much overlapping was observed, since it involved an additional mirror symmetry. With the aid of the molecular model of tryptophan and the b axis projection, the Fourier projection on (100) was interpreted reasonably and approximate y coordinates of all the atoms were obtained. Successive Fourier refinement decreased the R factor to 0.196. Further refinement was carried out by least-squares refinement, and after three cycles the R factor became 0.101.

Hydrochloride.—As seen from Fig. 1, the modified Patterson projections of hydrochloride and hydrobromide were similar to each other in general feature. This observation and approximately the same unit cell dimensions of the two crystals suggested that these two were isomorphous. The x- and z-coordinates of the chloride ion were determined to be 0.100 and 0.122 respectively from the Patterson projection. Fourier projections on (010), (100) and (001) were made with phases which were derived by assuming that the coordinates of the non-hydrogen atoms except the chloride ion were the same as those in the hydrobromide. The approximate coordinates of all the atoms were obtained from these Fourier projections and they were improved by three-dimensional Fourier synthesis.

The refinement of the structure was carried out by three-dimensional least-squares procedure. The least-squares program was constructed with the block-diagonal matrix approximation. In the earlier stage, temperature factor for each atom was taken as isotropic.

Three cycles of the refinement deduced the

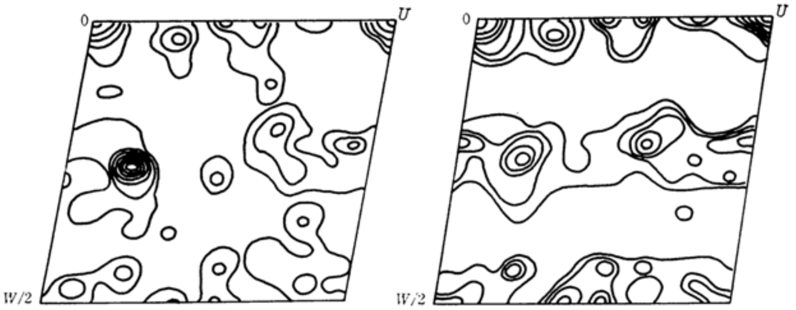

Fig. 1. Patterson projection on (010), modified by the factors of $M(\sin\theta)=\exp\{8(\sin\theta/\lambda)^2\}$
a) of the hydrobromide b) of the hydrochloride

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3) D. C. Phillips, Acta Cryst., **7**, 746 (1954).

R factor from 0.193 to 0.131. Disagreement between the observed and calculated structure factors increased with increasing *k* values. It was suggested that the anisotropic thermal vibration should be taken into account. Three cycles of least-squares refinement, with the anisotropic temperature factors for all the atoms, deduced the *R* factor to 0.117. Since the systematic disagreement remained, interlayer scales of the b axis data were adjusted by comparing the observed and

TABLE I. THE FINAL FRACTIONAL COORDINATES AND THE ESTIMATED STANDARD DEVIATIONS (in Å).

Atom	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
C(1)	0.5668	0.009	0.5872	0.010	0.1091	0.008
C(2)	0.6900	0.009	0.8211	0.009	0.1262	0.008
C(3)	0.7266	0.008	0.9126	0.010	0.2270	0.009
C(4)	0.8132	0.008	0.7138	0.011	0.2956	0.008
C(5)	0.7321	0.009	0.5178	0.010	0.3309	0.009
C(6)	1.0224	0.010	0.4963	0.011	0.3963	0.009
C(7)	1.0026	0.008	0.7009	0.009	0.3372	0.008
C(8)	1.1515	0.009	0.8579	0.011	0.3273	0.009
C(9)	1.3164	0.009	0.7833	0.014	0.3789	0.009
C(10)	1.3375	0.010	0.5813	0.011	0.4396	0.009
C(11)	1.1890	0.010	0.4255	0.011	0.4475	0.009
N(1)	0.8669	0.007	0.7554	0.011	0.0943	0.007
N(2)	0.8534	0.008	0.3816	0.009	0.3920	0.008
O(1)	0.4185	0.007	0.6361	0.009	0.1456	0.008
O(2)	0.5996	0.006	0.4068	0.008	0.0717	0.007
Cl	0.1130	0.002	0.2500	0.004	0.1202	0.002
H(1)	0.326	0.11	0.486	0.13	0.135	0.12
H(2)	0.647	0.09	0.949	0.11	0.074	0.09
H(3)	0.869	0.09	0.747	0.16	0.025	0.09
H(4)	0.947	0.10	0.581	0.13	0.105	0.10
H(5)	0.950	0.09	0.901	0.11	0.103	0.10
H(6)	0.642	0.09	1.051	0.11	0.249	0.09
H(7)	0.817	0.09	1.064	0.11	0.231	0.09
H(8)	1.136	0.10	1.013	0.11	0.280	0.10
H(9)	1.423	0.10	0.890	0.12	0.371	0.10
H(10)	1.467	0.12	0.506	0.13	0.481	0.11
H(11)	1.200	0.09	0.263	0.14	0.490	0.09
H(12)	0.826	0.10	0.213	0.14	0.429	0.10
H(13)	0.600	0.10	0.456	0.12	0.312	0.10

TABLE II. THE FINAL ANISOTROPIC TEMPERATURE FACTORS IN THE FORM OF

$$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$$

AND THEIR STANDARD DEVIATIONS ($\times 10^4$)

Atom	B_{11}	$\sigma(B_{11})$	B_{22}	$\sigma(B_{22})$	B_{33}	$\sigma(B_{33})$	B_{12}	$\sigma(B_{12})$	B_{13}	$\sigma(B_{13})$	B_{23}	$\sigma(B_{23})$
C(1)	177	19	255	34	34	4	−63	44	12	15	13	21
C(2)	157	17	284	40	35	4	12	40	−10	14	1	20
C(3)	150	17	236	32	44	5	−39	45	26	14	−43	22
C(4)	160	16	277	40	37	4	−15	46	50	13	−42	23
C(5)	157	18	347	41	47	5	−63	48	55	16	−39	25
C(6)	213	21	300	38	36	4	−12	48	59	16	−20	21
C(7)	188	17	245	40	27	4	−9	42	37	13	−50	19
C(8)	207	21	387	44	33	4	−42	52	28	15	−25	24
C(9)	176	19	526	58	53	5	−117	66	36	16	−13	34
C(10)	187	20	398	44	42	5	130	54	22	16	19	26
C(11)	226	22	357	42	32	4	170	55	8	16	11	25
N(1)	188	15	386	32	41	3	−24	54	44	11	13	27
N(2)	236	19	369	37	45	4	−45	48	53	14	−1	23
O(1)	181	15	523	40	77	5	−133	41	42	14	−82	24
O(2)	204	15	347	30	70	4	−31	40	57	13	−84	21
Cl	181	4	325	8	46	1	−118	15	33	3	22	7

caluculated structure factors. The contributions from hydrogen atoms were introduced at this stage. Hydrogen atoms were placed in such a way to give the bond distances, 1.09 Å for C–H, 1.01 Å for N–H and 0.97 Å for O–H, and bond angles in accord with the probable trigonal or tetrahedral arrangement of the bonds. Three hydrogens on the amino nitrogen and one on

Table III. The observed and the final caluculated structure factors

L	FO	FC
H,K=	0	0
3	57	59
4	856	863
5	445	419
6	168	185
7	85	88
8	132	143
9	247	243
10	57	57
11	92	88
12	75	78
13•	0	15
14	59	67
15	32	39
16	34	34
17•	0	3
18	89	78
H,K=	1	0
0	268	259
1	44	36
2	52	48
3•	8	0
4	109	107
5	45	57
6	149	150
7	28	40
8	25	28
9	21	22
10	51	41
11	18	19
12	70	72
13•	0	3
14	41	44
15	99	96
16	26	29
17	15	0
18	32	34
H,K=	2	0
0	145	143
1	65	69
2	243	240
3	124	131
4	342	328
5•	0	4
6	176	175
7	15	22
8	193	182
9	98	94
10	113	120
11	21	28
12	16	16
13	20	24
14	71	73
15	92	86
16•	0	16
17•	0	6
H,K=	3	0
0	75	75
1	312	295
2	70	77
3	125	129
4	64	76
5	337	330
6	129	138
7	49	50
8	18	29
9	114	118
10	177	191
11	40	47
12	53	58
13	23	29
14	69	72
15	25	30
16•	0	1
H,K=	4	0
0	245	249
1	230	236
2	40	49
3	14	15
4	111	112
5	88	99
6	56	58
7	25	20
8	72	74
9	17	22
10•	0	8
11	58	66
12	18	26
13	24	17
14•	0	2
15	13	11
H,K=	5	0
0	20	21
1	18	20
2•	0	5
3	60	68
4	87	88
5•	0	20
6	12	21
7•	0	7
8	153	169
9	71	45
10	41	49
11•	0	17
12	71	67
13	12	24
H,K=	6	0
0•	0	11
1	111	122
2	51	61
3	61	74
4	40	52
5•	0	5
6	27	34
7•	0	4
8	19	17
9•	0	1
10•	0	0
11	28	29
H,K=	7	0
0	108	129
1	34	53
2	58	74
3•	0	6
4	61	63
5	73	82
6	69	67
7	51	55
8	53	49
9	59	52
10	36	42
H,K=	8	0
0•	0	17
1	43	55
2•	0	19
3	35	35
4	18	14
5•	0	0
6•	0	10
7	38	40
H,K=	9	0
0	27	27
1•	0	15
2•	0	10
3	14	22
H,K=	1	0
-1	414	338
-2	210	174
-3	465	386
-4	578	496
-5	173	174
-6	175	176
-7	110	106
-8	116	122
-9	211	223
-10	145	152
-11	42	53
-12	36	49
-13	83	99
-14	77	91
-15	11	16
-16•	0	7
-17	29	24
-18•	8	20
H,K=	2	0
-1	373	338
-2	552	478
-3	31	42
-4	38	33
-5	70	80
-6	192	182
-7	30	48
-8	111	105
-9•	0	7
-10	190	191
-11	21	25
-12	50	66
-13	43	57
-14	129	140
-15	30	36
-16	26	35
-17	19	23
-18	53	44
H,K=	3	0
-1	152	147
-2	71	63
-3	26	38
-4	99	87
-5	47	61
-6	125	139
-7	91	93
-8	21	28
-9	75	98
-10	73	99
-11	19	21
-12	14	6
-13	14	24
-14	24	33
-15•	0	6
-16	16	14
-17	14	8
-18	36	34
H,K=	4	0
-1	177	175
-2	197	180
-3	293	263
-4	316	289
-5	248	222
-6	153	161
-7	217	205
-8	35	42
-9	76	109
-10	105	113
-11	59	68
-12	77	85
-13	17	23
-14	22	28
-15•	0	8
-16	90	84
-17•	0	10
H,K=	5	0
-1	114	117
-2•	0	17
-3	89	94
-4	64	67
-5	32	33
-6	84	86
-7	48	63
-8	38	47
-9	127	124
-10	126	130
-11	35	52
-12	20	24
-13	72	71
-14	42	47
-15	51	41
-16	31	33
-17	19	17
H,K=	6	0
-1	141	155
-2	35	48
-3	87	79
-4	25	35
-5	88	101
-6	51	59
-7•	0	15
-8	52	60
-9	40	47
-10•	0	0
-11•	0	5
-12•	0	6
-13	53	60
-14•	0	18
-15	16	19
-16	18	18
H,K=	7	0
-1•	0	19
-2	129	135
-3•	0	8
-4	97	107
-5	21	30
-6	105	108
-7	20	22
-8•	0	14
-9•	0	4
-10	26	31
-11	123	105
-12•	0	1
-13	24	27
-14•	0	2
H,K=	8	0
-1•	0	11
-2	19	29
-3	24	28
-4	24	37
-5	28	35
-6•	0	11
-7•	0	1
-8	51	50
-9	37	40
-10•	0	14
-11	36	30
-12•	0	15
H,K=	9	0
-1	19	22
-2	17	24
-3	29	35
-4	29	34
-5	15	19
-6	21	24
-7	19	29
-8	43	47
H,K=	0	1
1	308	412
2	230	240
3	436	514
4	169	168
5	122	117
6	85	90
7	126	120
8	72	61
9	55	56
10	33	25
11	56	62
12•	0	10
13	10	33
14	56	53
15	55	55
16	40	34
17	32	35
18	33	29
H,K=	1	1
0	236	228
1	492	458
2	302	306
3	373	354
4	275	281
5	415	414
6	209	210
7	94	82
8	169	173
9	257	256
10	149	154
11	95	98
12	77	92
13	109	112
14	43	41
15	91	78
16	19	26
17	73	64
H,K=	2	1
0	461	445
1	394	400
2	283	280
3	199	196
4	168	163
5	202	192
6	99	102
7	193	184
8	87	85
9	40	49
10	24	32
11	98	105
12	92	92
13	54	50
14	28	29
15	35	32
16	16	17
17	35	36
H,K=	3	1
0	82	78
1	51	58
2	140	138
3	215	216
4	31	16
5	11	14
6	120	118
7	138	127
8	93	96
9	52	59
10•	0	7
11	39	48
12	48	49
13	28	30
14	15	15
15	41	39
H,K=	4	1
0	113	117
1	21	35
2	114	110
3	142	135
4	83	88
5	84	83
6	96	94
7	72	78
8	55	66
9•	4	18
10	93	91
11	95	93
12•	0	4
13	16	18
14	59	49
15	57	54
H,K=	5	1
0	34	26
1	162	172
2	67	70
3	34	81
4•	0	9
5	155	156
6	77	87
7	39	38
8	25	32
9	29	42
10	54	54
11	36	35
12•	9	9
13	18	16
14	16	21
H,K=	6	1
0	92	96
1	174	180
2	45	55
3	44	43
4	87	89
5	100	109
6	53	62
7	10	14
8	38	34
9	62	57
10	24	27
11•	0	8
H,K=	7	1
0	54	56
1	45	47
2	31	35
3	24	29
4	26	28
5	43	39
6•	0	13
7•	0	3
8•	0	12
9	37	29
10	25	26
H,K=	8	1
0	32	35
1•	0	17
2	56	47
3	46	42
4	33	38
5•	0	9
6	48	44
7	38	40
H,K=	9	1
0•	0	6
1	28	27
2	32	32
H,K=	1	1
-1	220	213
-2	428	458
-3	514	553
-4	363	349
-5	198	215
-6	222	235
-7	350	339
-8	48	41
-9	64	59
-10	51	57
-11	132	130
-12	85	86
-13•	0	5
-14	40	52
-15	52	52
-16	28	37
-17	47	35
-18	25	27
H,K=	2	1
-1	188	188
-2	85	87
-3	178	168
-4	280	263
-5	299	287
-6	144	161
-7	152	152
-8	79	73
-9	80	86
-10	26	27
-11	17	23
-12	78	74
-13	24	25
-14•	0	13
-15•	0	19
-16	53	50
-17•	0	23
-18	16	15
H,K=	3	1
-1	268	254
-2	29	36
-3	108	104
-4	318	304
-5	229	215
-6	136	145
-7	72	67
-8	104	109
-9	202	215
-10	155	146
-11	53	52
-12	45	48
-13	104	124
-14	93	96
-15	57	58
-16	52	47
-17	33	24
-18	31	35
H,K=	4	1
-1	236	232
-2	125	123
-3	72	65
-4	134	123
-5	123	108
-6	79	76
-7	81	75
-8	39	43
-9	74	92
-10	54	57
-11	26	26
-12	18	20
-13	58	68
-14	85	77
-15•	0	12
-16•	0	13
-17	34	30
H,K=	5	1
-1	86	91
-2	93	96
-3	91	91
-4	64	69
-5	42	42
-6	110	117
-7	50	57
-8	32	39
-9	52	56
-10	68	78
-11	48	55
-12	29	41
-13	50	48
-14	73	71
-15	20	19
-16	29	27
-17	27	28
H,K=	6	1
-1	67	70
-2	91	95
-3	116	136
-4	158	161
-5	73	73
-6	23	24
-7	25	31
-8	98	102
-9	91	101
-10•	0	23
-11	27	29
-12	38	37
-13	45	41
-14	57	56
-15	30	23
-16	13	15
H,K=	7	1
-1	25	31
-2	25	27
-3	27	32
-4	82	88
-5	24	34
-6	25	26
-7	25	18
-8	104	106
-9	41	42
-10•	0	9
-11	18	13
-12	23	29
-13	68	57
-14	28	27
H,K=	8	1
-1	69	64
-2	40	41
-3	39	32
-4	42	37
-5	75	71
-6	52	46
-7	32	31
-8	55	50
-9	34	27
-10	28	22
-11	37	37
-12	11	13
H,K=	9	1
-1•	0	5
-2	29	23
-3	14	11
-4	22	27
-5	17	18
-6	28	26
H,K=	0	2
0	230	247
1	207	256
2	68	69
3	125	124
4	253	252
5	273	260
6	130	117
7	158	142
8	175	161
9	91	86
10	63	62
11	17	29
12	76	75
13	88	86
14•	0	13
15	25	32
16	31	30
17	29	36
H,K=	1	2
0	285	297
1	98	95
2	173	163
3	71	82
4	233	224
5	125	116
6	80	77
7	57	61
8	88	88
9	74	78
10	53	50
11	23	29
12	42	43
13	71	74
14	46	48
15	24	24
16•	6	11
17	17	22
H,K=	2	2
0	185	169
1	132	126
2	192	194
3	41	36
4	122	119
5	94	99
6	184	190
7	101	99
8	57	54
9	51	54
10	161	171
11	97	95
12	20	25
13	75	38
14	69	67
15	46	46
16•	0	14
H,K=	3	2
0	146	146
1	237	231
2	194	184
3	73	76
4	38	30
5	120	116
6	192	192
7	32	39
8	95	100
9	63	67
10	106	104
11	45	53
12	51	46
13	56	45
14	49	43
15	38	43
H,K=	4	2
0	164	179
1	135	133
2	48	54
3	126	132
4	108	108
5	87	96
6	88	88
7	57	62
8	65	69
9	55	57
10	48	50
11•	0	11
12	23	31
13	24	29
14•	8	18
H,K=	5	2
0	119	114
1	88	99
2	76	82
3	103	101
4	90	101
5•	0	10
6	69	71
7	50	56
8	74	77
9•	0	5
10	22	24
11	18	18
12	31	32
13	15	16
H,K=	6	2
0	28	32
1	44	53
2	25	30
3	82	81
4•	0	11
5	41	45
6	19	26
7	68	65
8	11	20
9•	0	18
10	27	29
11	27	29
H,K=	7	2
0	17	18
1	89	87
2	55	56
3	24	31
4	19	18
5	37	35
6	62	60
7	13	18
8•	0	3
9	17	25
H,K=	8	2
0	23	24
1	47	41
2	45	42
3•	0	11
4	28	24
5	38	33
H,K=	1	2
-1	318	342
-2	154	159
-3	210	206
-4	59	62
-5	403	394
-6	72	65
-7	226	220
-8	44	39
-9	207	207
-10	66	75
-11•	0	21
-12	44	39
-13	49	57
-14	62	69
-15	39	40
-16	17	14
-17	27	31
H,K=	2	2
-1	133	115
-2	184	178
-3	105	111
-4	120	112
-5	161	152
-6	146	138
-7	158	155
-8	97	106
-9	211	226
-10	71	78
-11	67	68
-12	57	64
-13	68	73
-14	83	79
-15	36	31
-16	32	35
-17	15	19
H,K=	3	2
-1	145	139
-2	159	188
-3	217	215
-4	65	64
-5	79	71
-6	83	81
-7	127	127
-8	17	10
-9	21	28
-10	89	99
-11	78	84
-12	38	49
-13	43	50
-14	31	34
-15	42	43
-16	27	33
-17	24	28
H,K=	4	2
-1	40	33
-2	43	41
-3	109	97
-4	184	188
-5	74	72
-6	53	58
-7	39	43
-8	135	145
-9	73	83
-10	84	99
-11	51	58
-12	83	87
-13•	8	12
-14	65	60
-15	20	20
-16	29	30
-17	23	24
H,K=	5	2
-1	83	80
-2	87	95
-3	109	123
-4	161	171
-5	67	65
-6	74	82
-7	83	85
-8	143	156
-9	58	64
-10	32	33

TABLE III (Continued)

L	FC	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FC	FC	L	FO	FC	L	FO	FC	L	FO	FC
-11	72	74	15	16	16	1	12	13	H,K=	6	3	2	45	48	-5	45	44	0	96	104	-6	45	39
-12	93	92	16•	0	9	2	11	11	-1	37	31	3	54	50	-6	39	36	1	56	66	-7	46	52
-13	21	33	H,K=	2	3	3	12	19	-2	47	51	4	59	52	-7	101	120	2	39	44	-8	14	23
-14	60	57	0	180	191	H,K=	1	3	-3	84	71	5	103	100	-8	22	33	3	43	56	-9	24	21
-15	17	18	1	130	135	-1	112	139	-4	80	79	6	76	68	-9	37	37	4	64	64	-10	54	51
-16	30	40	2	70	59	-2	74	82	-5•	0	7	7	38	33	-10	29	28	5	64	59	H,K=	5	5
H,K=	6	2	3	52	55	-3	63	60	-6	22	29	8•	0	8	-11	29	28	6	12	17	-1•	0	7
-1	68	77	4	167	189	-4	172	186	-7	93	91	9	30	27	-12	71	68	7•	8	19	-2	75	68
-2	28	32	5	136	143	-5	105	106	-8	64	58	10	33	28	-13	14	22	8	40	37	-3•	0	17
-3	36	45	6	110	112	-6	34	32	-9	19	22	11	62	55	-14	74	69	9	40	31	-4	40	39
-4	91	88	7	22	27	-7	98	105	-10•	0	18	12	42	35	H,K=	4	4	10	16	15	-5•	0	11
-5•	0	19	8	167	178	-8	52	54	-11	56	52	13	10	22	-1	53	58	11•	7	11	-6	34	40
-6	80	82	9	77	76	-9	37	37	-12	20	21	H,K=	4	4	-2	16	28	H,K=	3	5	-7	34	42
-7•	0	14	10	87	84	-10	47	52	-13	31	35	0	13	19	-3	85	86	0	91	89	-8	19	16
-8	61	57	11	20	16	-11	49	43	H,K=	7	3	1	126	134	-4	63	61	1	39	40	H,K=	0	6
-9	13	19	12	36	31	-12•	0	14	-1	75	73	2	21	17	-5	45	35	2	29	26	0	73	78
-10	63	56	13	60	53	-13•	0	9	-2	58	54	3	78	72	-6	20	16	3	66	62	1	59	54
-11	53	49	14	44	38	-14	46	44	-3	53	47	4	42	46	-7	38	38	4	71	68	2	33	28
-12	32	33	15	36	26	-15	45	36	-4	75	73	5	83	77	-8	60	59	5	37	41	3	64	67
-13	32	27	H,K=	3	3	-16	28	27	-5	57	49	6	42	47	-9	46	39	6	11	8	4	15	16
-14	39	33	0	186	198	H,K=	2	3	-6	47	45	7	25	25	-10	12	23	7	30	35	5	30	42
-15	22	32	1	72	72	-1	96	99	-7•	0	13	8	80	73	-11•	0	13	8	74	64	6	57	51
H,K=	7	2	2	67	69	-2	97	99	-8	36	33	9	67	57	-12	44	39	9	20	25	7	15	15
-1	46	50	3	93	106	-3	90	96	-9	48	38	10	24	25	-13	27	23	10	24	21	8	31	24
-2	30	29	4	131	136	-4	136	152	-10	35	31	11	14	11	-14	19	13	H,K=	4	5	H,K=	1	6
-3	66	65	5	64	64	-5	115	121	-11	29	29	H,K=	5	4	H,K=	5	4	0	30	24	0	25	28
-4	50	50	6	22	25	-6	44	50	H,K=	8	3	0	109	94	-1	66	68	1	49	50	1	28	22
-5	43	45	7	86	89	-7	92	107	-1	24	22	1	66	61	-2	35	38	2	59	52	2	31	35
-6	80	73	8	70	67	-8	122	128	-2•	0	4	2	35	42	-3	36	45	3•	0	15	3	54	64
-7	28	30	9	22	13	-9	77	77	-3	32	24	3	52	49	-4	86	78	4•	0	4	4•	0	11
-8	20	23	10	30	40	-10	134	154	-4•	0	18	4	73	73	-5	108	104	5	44	36	5•	0	4
-9	21	27	11	60	55	-11	117	128	-5•	0	14	5	21	22	-6•	0	12	6	62	42	6	49	51
-10	69	63	12•	0	12	-12	84	87	-6	32	25	6	12	17	-7	28	36	7	48	28	7	14	21
-11	22	21	13	27	23	-13	20	24	-7•	0	6	7	17	19	-8	67	57	8	18	21	8	20	18
-12	11	12	14	53	49	-14	86	77	-8	19	22	8	17	16	-9	80	68	H,K=	5	5	H,K=	2	6
-13	15	22	H,K=	4	3	-15	24	24	H,K=	0	4	9	15	22	-10	18	23	0	32	19	0•	0	10
H,K=	8	2	0	48	45	-16	18	22	0	58	68	H,K=	6	4	-11	12	16	1	27	28	1•	0	9
-1	27	31	1	29	25	H,K=	3	3	1	21	36	0•	0	5	-12	35	25	2	51	45	2	55	49
-2	41	39	2	20	17	-1	108	113	2•	9	16	1	39	36	-13	35	35	3	12	18	3	25	27
-3	65	60	3	93	102	-2	92	89	3	29	37	2	31	30	H,K=	6	4	4	9	4	4	24	29
-4	35	30	4	25	23	-3	41	42	4	83	93	3	18	26	-1	20	19	5	62	54	5	32	29
-5	18	17	5	73	76	-4	50	44	5	82	80	4	17	15	-2	57	53	6	41	37	6	43	41
-6	17	18	6	74	75	-5	148	163	6	27	6	5	32	31	-3	12	15	H,K=	1	5	7	30	32
-7	60	52	7	68	60	-6	61	55	7	42	46	6	42	40	-4	49	49	-1•	0	13	H,K=	3	6
-8•	0	11	8	35	29	-7	47	44	8	69	78	7	38	37	-5	30	28	-2	23	42	0	47	43
-9	51	44	9	47	42	-8	69	82	9	42	35	H,K=	7	4	-6	54	50	-3	73	69	1	19	22
-10	17	18	10	83	70	-9	98	103	10	44	50	0•	0	8	-7	41	29	-4	77	81	2	35	31
H,K=	9	2	11	21	22	-10	54	50	11•	0	8	1	23	18	-8•	0	5	-5	31	30	3	43	33
0	35	45	12	52	44	-11	68	70	12	37	34	2	57	51	-9	68	62	-6	28	34	4	60	55
-1	20	24	13	24	22	-12	58	66	13	55	49	3	11	15	-10	29	23	-7	27	35	5	25	24
-2	14	15	H,K=	5	3	-13	16	22	14	24	26	H,K=	1	4	-11	35	32	-8	39	49	H,K=	4	6
-3	19	21	0	105	114	-14	92	75	15•	0	12	-1	100	147	H,K=	7	4	-9	27	31	0	54	50
-4	33	30	1	99	109	-15	26	29	H,K=	1	4	-2	77	98	-1	16	17	-10	16	16	1	45	36
-5	22	27	2	27	31	-16•	8	18	0	145	164	-3	38	46	-2	44	35	-11	23	27	2	45	45
H,K=	0	3	3	32	38	H,K=	4	3	1	65	83	-4	145	150	-3•	0	9	-12	20	29	H,K=	1	6
1	43	63	4	18	20	-1	47	44	2	64	77	-5	94	107	-4	18	14	H,K=	2	5	-1	40	43
2	207	211	5	66	60	-2	97	101	3	113	131	-6	54	54	-5	26	18	-1	36	41	-2•	0	9
3	49	44	6	90	85	-3	63	61	4	69	75	-7	62	68	-6	40	36	-2	20	31	-3	12	19
4	93	85	7•	0	3	-4	44	52	5	82	74	-8	53	59	-7	15	20	-3	40	41	-4	31	32
5	95	105	8	14	16	-5	113	125	6	73	80	-9	90	103	-8•	0	8	-4	71	74	-5	48	54
6	139	139	9	59	55	-6	126	135	7	127	139	-10	49	48	H,K=	0	5	-5	84	91	-6	34	41
7	64	67	10	69	64	-7	48	52	8	44	47	-11	43	43	1	43	38	-6	25	32	-7	21	27
8	43	46	11	17	17	-8	25	34	9•	0	13	-12	44	43	2	91	100	-7	30	33	-8	27	29
9	80	78	12•	0	11	-9	129	136	10•	0	18	-13	51	35	3	97	102	-8	18	26	H,K=	2	6
10	130	153	H,K=	6	3	-10	60	63	11	67	61	-14	50	45	4•	0	26	-9	52	48	-1	48	52
11	37	46	0	53	44	-11	40	48	12	34	26	-15	27	27	5	50	54	-10	18	16	-2	58	62
12	28	27	1	97	94	-12	40	43	13	18	27	H,K=	2	4	6	62	71	-11	14	18	-3	17	26
13	27	26	2	55	57	-13	86	71	14•	0	9	-1	23	30	7	31	39	-12	20	24	-4	14	16
14	57	47	3	37	35	-14	82	71	H,K=	2	4	-2	45	51	8•	0	3	H,K=	3	5	-5	37	46
15	52	47	4	64	61	-15	43	40	0	28	13	-3	78	84	9	35	50	-1	73	75	-6	19	16
16	47	41	5	75	70	-16	15	27	1	66	61	-4	95	96	10	66	54	-2	16	12	-7	13	21
H,K=	1	3	6	31	32	H,K=	5	3	2	44	50	-5	63	66	11	43	15	-3	30	32	-8	14	21
0	120	164	7•	0	12	-1	72	76	3	55	57	-6	95	108	12	18	28	-4	77	84	H,K=	3	6
1	98	113	8	22	20	-2	58	58	4	68	64	-7	60	58	H,K=	1	5	-5	54	58	-1	13	9
2	158	162	9	46	40	-3	53	57	5	126	121	-8	60	62	0	76	93	-6	60	56	-2	16	16
3	93	96	10	19	22	-4	92	91	6	17	21	-9	59	65	1	104	105	-7	42	41	-3	29	13
4	77	75	H,K=	7	3	-5	57	60	7	50	56	-10	71	76	2	50	39	-8	40	41	-4	34	30
5	142	146	0	63	56	-6	60	65	8	31	23	-11	43	44	3	28	31	-9	47	43	-5	16	17
6	67	57	1	23	19	-7	19	26	9	45	43	-12	38	36	4	49	44	-10	55	53	-6	15	9
7	47	45	2•	0	8	-8	54	55	10	41	38	-13	34	32	5	72	74	-11	19	13	-7	29	32
8	19	23	3	20	25	-9	49	57	11	61	58	-14	63	59	6	42	43	-12•	7	15	H,K=	4	6
9	50	55	4	54	46	-10	35	30	12•	0	15	-15	29	33	7•	0	14	H,K=	4	5	-1•	0	2
10	69	64	5	17	18	-11	30	24	13	26	24	H,K=	3	4	8	19	17	-1	64	72	-2	18	16
11	27	28	6•	0	4	-12•	8	11	14	25	27	-1	58	56	9	55	57	-2	44	37	-3	32	34
12	36	34	7•	0	10	-13	21	17	H,K=	3	4	-2	38	37	10	56	56	-3	37	39	-4	68	71
13	74	66	H,K=	8	3	-14•	8	5	0	38	37	-3	134	145	11•	0	12	-4	18	23	-5•	9	13
14	48	38	0	13	18	-15	17	12	1	125	134	-4	30	35	H,K=	2	5	-5	40	34			

the carboxyl group were put on the lines to the chloride ions with which they hydrogen-bonded. After three cycles of the least-squares refinement, average shifts in the coordinates of the non-hydrogen atoms were $\Delta x/a=0.0003$, $\Delta y/b=0.0006$ and $\Delta z/c=0.0001$ and their maximum shifts were 0.0008, 0.002 and 0.004 respectively, and the R factor dropped to 0.087. Additional two cycles of the least-squares were made in order to adjust the interlayer scale factors, leaving coordinates and temperature factors fixed. The R factor was 0.088 and $\sum|F_c|/\sum|F_o|$ for each k value converged fairly to the unity. The weights in the least-squares calculation were given systematically as a function of the absolute values of the structure factors. Damping factors for the shifts were as follows; 0.7 in the overall scale factor, 0.5 in the overall temperature factor, 0.7 in the coordinates of non-hydrogen atoms, 0.5 in the anisotropic temperature factors of non-hydrogen atoms, and 0.1 in the coordinates and isotropic temperature factors of hydrogen atoms. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.⁴⁾

The final atomic coordinates with their standard deviations are listed in Table I and the anisotropic temperature factors are given in Table II. The estimated standard deviations were caluculated by the Cruickshank's formula.⁵⁾ A list of the observed and the final caluculated structure factors is given in Table III, in which reflections with asterisk were omitted in the least-squares refinement. The final superimposed sections of electron density distribution cut through the every atomic centers are shown in Fig. 2.

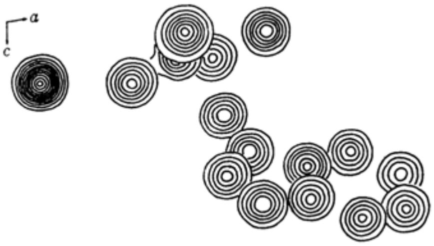

Fig. 2. The final three-dimensional Fourier synthesis. Sections passing approximately through the center of the atoms are superimposed on (010). Contour intervals of 1.5 e.Å^{-3} for light atoms and 3.0 e.Å^{-3} for the chloride ion ; the first contour begins at 1.5 e.Å^{-3}.

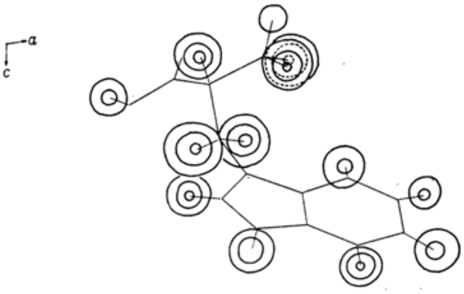

Fig. 3. The three-dimensional (F_o-F_c) synthesis. Sections passing approximately through the center of the hydrogen atoms are superimposed on (010). Contour intervals of 0.2 e.Å^{-3}, the first contour begins at 0.2 e.Å^{-3}. The dotted contours are in the lower section.

TABLE IV. THE COORDINATES AND PEAK HEIGHTS OF HYDROGEN ATOMS OBTAINED FROM THE THREE-DIMENSIONAL (F_o-F_c) SYNTHESIS

Atom	x/a	y/b	z/c	peak heights (in e.Å^{-3})
H(1)	0.347	0.479	0.126	0.36
H(2)	0.642	0.956	0.080	0.59
H(3)	0.897	0.760	0.037	0.22
H(4)	0.939	0.608	0.118	0.60
H(5)	0.947	0.908	0.106	0.69
H(6)	0.637	1.033	0.236	0.64
H(7)	0.798	1.050	0.238	0.68
H(8)	1.133	1.008	0.296	0.51
H(9)	1.400	0.900	0.377	0.44
H(10)	1.440	0.513	0.472	0.46
H(11)	1.189	0.268	0.486	0.58
H(12)	0.834	0.246	0.427	0.45
H(13)	0.623	0.450	0.319	0.60

Bond lengths (in Å)			
O(1)-H(1)	1.01	C(8)-H(8)	0.91
C(2)-H(2)	1.01	C(9)-H(9)	0.88
N(1)-H(3)	0.90	C(10)-H(10)	0.90
N(1)-H(4)	0.98	C(11)-H(11)	1.00
N(1)-H(5)	1.00	N(2)-H(12)	0.91
C(3)-H(6)	0.97	C(5)-H(13)	0.90
C(3)-H(7)	0.90		

TABLE V. INTRAMOLECULAR DISTANCES BETWEEN NON-BONDED ATOMS (in Å)

O(1)···O(2)	2.22
O(1)···C(2)	2.30
O(2)···C(2)	2.40
O(2)···N(1)	2.70
C(1)···C(3)	2.60
C(1)···N(1)	2.45

A three-dimensional (F_o-F_c) synthesis was then caluculated where F_c did not include the contributions from the hydrogen atoms, and phase was that of F_c. Fourier synthesis in this manner gives somewhat modified electron density distribution for hydrogen atoms.

In the resulting map as shown in Fig. 3, peaks were found in positions which could associate with the thirteen hydrogen atoms, their coordinates and heights being shown in Table IV. Maximum difference between the coordinates from the difference synthesis and those from the least-squares is 0.23 Å.

All the numerical computations were done on a NEAC 2101 of this laboratory, a NEAC 2206 of the computing center of Osaka University, a HITAC 5020 of the computing center of the University of Tokyo and an IBM 7090 of Japan IBM Co. Ltd. Main programs used are 'NLP-W-01-T' for Lorentz polarization and spot shape correction written by Nobuo Tanaka, 'FR-S-01-T' for the two-dimensional Fourier synthesis by Tsunehiro Takano and Yoriko Nishi, 'HBLS' for the least-squares by Tamaichi Ashida and 'SFFR' for three-dimensional Fourier synthesis by Yoshio Sasada.

Discussion of the structure

The present structure determination of L-tryptophan hydrohalides has revealed that the

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4) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

5) ibid., Vol. II, Kynoch Press, Birmingham (1959), p. 330.

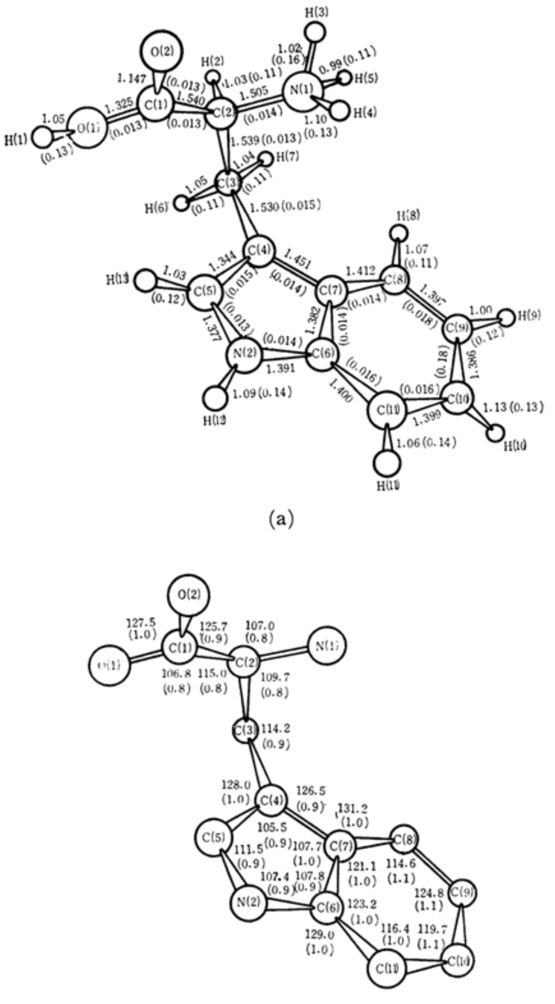

Fig. 4. (a) Bond lengths and their standard deviations in parentheses (in Å).
(b) Bond angles and their standard deviations in parentheses (in degree).

crystals of the hydrochloride and hydrobromide are isomorphous with each other and conformation of the tryptophan cations is essentially the same in both crystals. As the accuracy of the analysis of the hydrobromide is not so high, the crystal and molecular structure of the hydrochloride will be mainly discussed here.

All the interatomic bond distances and angles caluculated from the final coordinates are shown in Fig. 4, together with their standard deviations. Some of the important intramolecular distances between non-bonded atoms are given in Table V.

Carboxyl and Amino Group.—The planarity of the carboxyl group with α-carbon atom has been established in many investigations. For the present molecule, the equation for this median plane is determined to be

$$1.112X - Y + 2.090Z = 3.522$$

where X, Y and Z in Å refers to the crystallographic a^*, b and c axes respectively and coefficients were obtained by the least-squares method. The deviations of all the atoms from the least-squares plane are less than 0.0001 Å and they are strictly coplanar. The amino nitrogen is 0.154 Å out of the plane, the C–N bond making an angle of 6° with the plane.

The deviations of the amino nitrogen range from 0.00 to 0.82 Å for the amino acids so far investigated. The C–N distance 1.505 Å coincides well with those in, e. g., histidine hydrochloride monohydrate⁶⁾ (1.495 Å). Two C–O bond lengths are 1.325 and 1.147 Å and three angles around the C(1) atom are O(1)–C(1)–O(2) = 127.5°, O(1)–C(1)–C(2) = 106.8° and O(2)–C(1)–C(2) = 125.7°. This short C–O bond length 1.147Å and two O–C–C angles, 106.8° and 125.7° differ significantly from those reported for amino acids so far. Hahn's treatment⁷⁾ for the relation between bond lengths and angles of the carboxyl groups can not be applied in the present case.

Indole Ring.—The median plane through the atoms in the indole ring with the methylene carbon attached to it can be described by the equation,

$$0.3349X - Y - 1.3642Z = -6.3687$$

The plane forms a dihedral angle of 70.6° with that of the carboxyl group described above. The deviations of the atoms from the least-squares plane are listed in Table VI. The maximum deviation from the plane is 0.019 Å and the average 0.009 Å. It is concluded that the atoms are on nearly the same plane within the limit of error, as in the related compounds, glycyl-L-tryptophan dihydrate⁸⁾ and 3-indolylacetic acid⁹⁾. Bond lengths in the indole ring are tabulated in Table VII-a with those of the compounds quoted above. The average of six C–C bond lengths in the benzene ring is 1.396 Å, while that of C–N bond lengths in the indole ring is 1.384 Å respectively. The bond lengths found in the present molecule are all in good agreement with those of 3-indolylacetic acid⁹⁾ within the limit of error.

Longuet-Higgins and Coulson¹⁰⁾ have determined the mobile bond orders of the indole molecule by the molecular orbital treatment. Theoretical bond lengths derived from the bond orders by the empirical equation (Coulson,¹¹⁾ Cox and

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6) J. Donohue and A. Caron, *Acta Cryst.*, **17**, 1178 (1964).
7) T. Hahn, *Z. Krist.*, **109**, 438 (1957).
8) R. A. Pasternak, *Acta Cryst.*, **9**, 341 (1956).
9) I. L. Karle, K. Britts and P. Gum, ibid., **17**, 496 (1964).
10) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).
11) C. A. Coulson, *Proc. Roy. Soc.*, **A 207**, 91 (1951).

TABLE VI. DEVIATION FROM THE LEAST-SQUARES PLANE (in Å)

Atom	
C(3)	−0.020
C(4)	−0.001
C(5)	+0.000
C(6)	−0.004
C(7)	+0.006
C(8)	−0.008
C(9)	+0.014
C(10)	−0.019
C(11)	+0.015
N(2)	−0.003
Mean	0.009

TABLE VII. THE DIMENSIONS OF THE INDOLE GROUP

a) Bond lengths (in Å)

	I	II	III	IV	V
C(3)-C(4)	1.530	1.514	1.534		
C(4)-C(5)	1.344	1.342	1.338	1.36	0.812
C(4)-C(7)	1.451	1.470	1.418	1.42	0.498
C(5)-N(2)	1.377	1.401	1.430	1.36	0.412
N(2)-C(6)	1.391	1.385	1.307	1.37	0.381
C(6)-C(7)	1.382	1.407	1.388	1.41	0.565
C(7)-C(8)	1.412	1.434	1.405	1.41	0.574
C(8)-C(9)	1.397	1.409	1.411	1.38	0.709
C(9)-C(10)	1.386	1.396	1.353*	1.40	0.626
C(10)-C(11)	1.399	1.409	1.390*	1.38	0.699
C(11)-C(6)	1.400	1.422	1.399	1.40	0.604
σ (mean)	0.015	0.018	0.014		

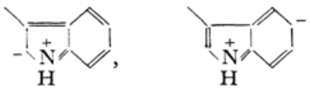
b) Bond angles (in degree)

	I	II	III
C(2)-C(3)-C(4)	114.2	114.7	115.1
C(3)-C(4)-C(5)	128.0	127.2	127.3
C(3)-C(4)-C(7)	126.5	125.2	124.7
C(5)-C(4)-C(7)	105.5	107.1	108.0
C(4)-C(5)-N(2)	111.5	110.3	106.9
C(5)-N(2)-C(6)	107.4	108.2	109.3
N(2)-C(6)-C(11)	129.0	128.2	127.9
N(2)-C(6)-C(7)	107.8	108.2	108.8
C(7)-C(6)-C(11)	123.2	123.5	123.1
C(4)-C(7)-C(8)	131.2	134.1	134.3
C(4)-C(7)-C(6)	107.7	106.1	106.9
C(6)-C(7)-C(8)	121.1	119.8	118.8
C(7)-C(8)-C(9)	114.6	116.7	117.4
C(8)-C(9)-C(10)	124.8	122.2	122.1*
C(9)-C(10)-C(11)	119.7	122.5	121.5*
C(6)-C(11)-C(10)	116.4	115.2	116.4*
σ (mean)	1.0	1.3	1.0

I ; L-tryptophan hydrochloride
II ; 3-indolylacetic acid[9]
III ; glycyl-L-tryptophan dihydrate[8]
IV ; theoretical value[10−12]
V ; mobile bond order[10]
* Pasternak points out that the coordinates of C(10) is less accurate than the other atoms.

Jeffrey[12]) are given in Table VII-a. The bond lengths in the indole ring of L-tryptophan hydrochloride agree well with the theoretical values within the limit of error.

But in glycyl-L-tryptophan dihydrate,[8] some bond lengths, especially C(6)–N(2), differ from those in L-tryptophan hydrochloride. Significantly short C(6)–N(2) bond, 1.307 Å of length, in glycyl-L-tryptophan dihydrate[8] may suggest that in this compound the contribution from the resonance of ortho- or para-benzoquinone type increases.



It will be interesting that the conformation changes as a result of introduction of glycyl residue, as shown in Fig. 5.

Bond angles in the indole ring are also shown in Table VII-b. Bond angles in the indole ring of the present molecule show the fairly good agreement with those of the related compounds and those in the benzene ring do not deviate from 120°.

Conformation about the C(α)-C(β).—Figure 5 shows the conformation about the C(α)–C(β) bond in the present molecule by the stereographic projections together with those in histidine hydrochloride monohydrate,[6] glycyl-L-tryptophan dihydrate[8] and L-tyrosine hydrobromide[13]. In the present molecule, C(γ) lies at gauche position with both of carboxyl and amino group. The same conformation has been found in the crystal of histidine hydrochloride monohydrate,[6] whose

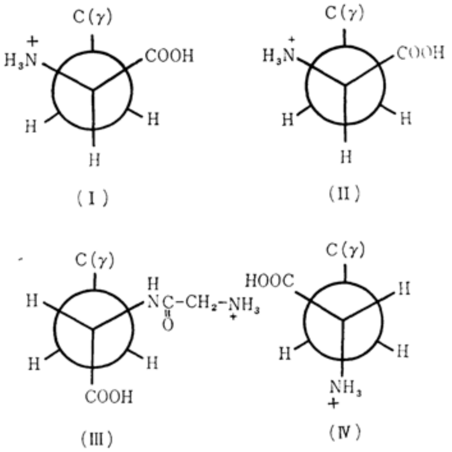


Fig. 5. Stereographic projection of the conformation about the C(α)-C(β) bond.
I; histidine hydrochloride monohydrate
II; L-tryptophan hydrochloride
III; glycyl-L-tryptophan dihydrate
IV; L-tyrosine hydrobromide

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12) E. G. Cox and G. A. Jeffrey, ibid., **A207**, 110 (1951).
13) R. Srinivasan, *Current Sci. (India)*, **27**, 46 (1958).

TABLE VIII. INTERMOLECULAR DISTANCES LESS THAN 4.0 Å

From atom in molecule M	to atom	in molecule	distance (in Å)	angle (in degree)	
a) Hydrogen bond					
O(1)	Cl	M	3.04	C(1)-O(1)···Cl	118.3
N(1)	Cl	M′	3.17	C(2)-N(1)···Cl	119.1
N(1)	Cl	A	3.24	C(2)-N(1)···Cl	131.5
N(1)	Cl	B	3.19	C(2)-N(1)···Cl	106.7
b) Other short contact					
C(4)	C(11)	M′	3.93		
C(5)	C(11)	M′	3.87		
N(2)	C(11)	M′	3.77		
C(6)	C(11)	M′	3.74		
C(7)	C(11)	M′	3.85		
C(9)	N(2)	M′	3.80		
C(10)	N(2)	M′	3.43		
C(11)	N(2)	M′	3.42		

Molecule M is at (x, y, z), M′ at $(1-x, 1/2+y, -z)$, A at $(1+x, y, z)$ and B at $(1+x, 1+y, z)$.

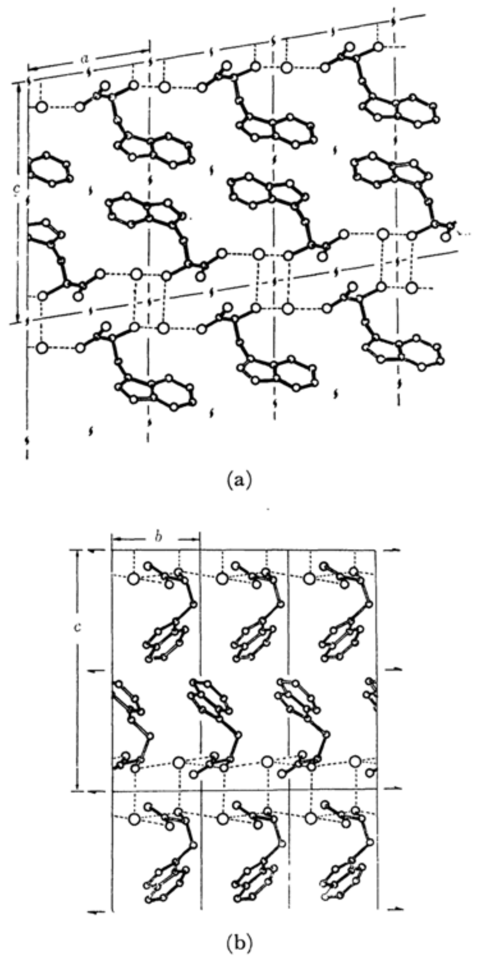

Fig. 6. (a) A projection of the structure along the *b* axis.
(b) A projection of the structure along *a* axis. Hydrogen bonds are indicated by the broken lines.

molecule also includes the five-membered ring next to C(β), while Ramachandran and Lakshminarayanan[14] have pointed out that in tyrosine and phenylalanine, both of which contain benzene ring, C(γ) goes only to the position at trans with the nitrogen and gauche with the carboxyl group.

The enviroment of the molecule.—Views of the crystal structure along the b and a axes are shown in Fig. 6 and intermolecular distances less than 4.0 Å and angles including hydrogen bonds are given in Table VIII. An amino nitrogen atom forms three N–H···Cl$^-$ hydrogen bonds, in lengths of 3.17, 3.19 and 3.24 Å; three acceptor halogen atoms are approximately at three vertices of regular tetrahedron centered around the nitrogen atom, with the α-carbon atom directed toward the fourth vertex. The fourth hydrogen bond is O–H···Cl$^-$ in length of 3.04 Å. Similar hydrogen bond distances are reported for N–H···Cl$^-$, 3.08, 3.25 and 3.27 Å, and for O–H···Cl$^-$, 2.98 Å in L-cystine hydrochloride.[15]

In L-tryptophan hydrobromide, the corresponding distances between nitrogen and bromide ion are 3.30, 3.31 and 3.35 Å, although the accuracies of these values are not so high. These values are comparable to those found in the other hydrobromide; 3.28, 3.41 and 3.42 Å in L-cystine dihydrobromide.[16] One O···Br$^-$ approach of 3.13 Å in the present crystal is similar to a value; 3.17 Å in L-cystine dihydrobromide.[16]

Molecular arrangement in the crystal can be well described as double-layered system parallel to the ab plane, which is characteristic for a structure

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14) G. N. Ramachandran and A. V. Lakshminarayanan, to be published in *Biopolymers*.

15) L. K. Steinrauf, J. Peterson and L. H. Jensen, *J. Am. Chem. Soc.*, **80**, 3835 (1958).

16) J. Peterson, L. K. Steinrauf and L. H. Jensen, *Acta Cryst.*, **13**, 104 (1960).

containing polar and non-polar groups together. The polar layer is held together by a network of the hydrogen bonds, as described above, between the chloride ions and amino nitrogen and between the chloride ion and carboxyl group. In the non-polar layer, the indole rings are packed mainly by van der Waals forces, in a manner similar to that found for the typical aromatic molecule. No unusually short contacts between non-bonded atoms are found in the crystal structure, and the shortest C···C and C···N distances are 3.74 and 3.42 Å respectively. The weakly basic nitrogen atom of the indole ring does not take part in the hydrogen bond. This structure well interprets the observed cleavage in the ab plane.

We wish to express our deep thanks to all our collaborators for their helpful discussions and for permission to use the computer programs. Thanks are also due to the staffs of Computing Centers of Osaka University and of the University of Tokyo for numerical computation. The computing time of IBM 7090 was made available to us through the project of 'UNICON'.