Acta Cryst. (1970). B26, 1662

Refinement of the Structure of Arginine Hydrochloride Monohydrate*

BY JEAN DOW AND L. H. JENSEN

Departments of Biochemistry and Biological Structure, University of Washington, Seattle, Washington, U.S.A.

AND S. K. MAZUMDAR, R. SRINIVASAN AND G. N. RAMACHANDRAN

Centre of Advanced Study in Physics, University of Madras, Madras-25, India†

(*Received* 17 *July* 1969)

The crystal structure of L-arginine monohydrochloride monohydrate has been refined by the method of least-squares. Counter data collected with Mo $K\alpha$ radiation were used in the refinement. The final R index is 0·033 for 2454 observed reflections. The average estimated standard deviation in the position of the Cl^- ion is 0·0006–0·0009 Å; for the C, N, and O atoms it is 0·0016–0·0030 Å and for the hydrogen atoms it is 0·020–0·040 Å. Differences in structural detail between the two molecules of the asymmetric unit are described. All 34 hydrogen atoms were located in a ΔF synthesis, and the intricate hydrogen bonding scheme has been characterized.

Introduction

The crystal structure of L-arginine monohydrochloride monohydrate was selected for X-ray crystallographic determination with a major concern for obtaining structural parameters of sufficient precision to provide meaningful structural details. L-Arginine is of interest because of its relation to the phosphorylated guanidine compounds, phosphoarginine and phosphocreatine, which are among the most energy rich of all the so-called high energy phosphate compounds. Furthermore comparative studies of the crystal structures of amino acids and simple peptides are of use in determining the effect of variation in molecular environment on the conformation of amino acid side-groups (Ramachandran, Mazumdar, Venkaresan & Lakshminarayanan, 1966).

When this work was initiated at the University of Washington, a literature search revealed no complete structure determination of a crystal containing arginine. During the course of the work, however, three separate reports of structures containing arginine appeared (Donohue & Metz, 1964; Karle & Karle, 1964; Mazumdar & Srinivasan, 1964). Although each of the reports was on a different crystal structure, that of Mazumdar & Srinivasan was identical with the one which was in the trial stage at Washington (Donohue, 1965). The work of deriving a phasing model from the Patterson synthesis was halted. Instead, it was agreed to begin refining the structure with coordinates from the initial refinement of Mazumdar & Srinivasan and to use the extensive set of diffractometer data which had already been collected at Washington.

Experimental

Crystals of L-arginine monohydrochloride monohydrate were grown from a dilute ethanolic solution of L-arginine hydrochloride (Nutritional Biochemicals Corporation, Cleveland, Ohio) by slow evaporation at room temperature. A crystal measuring approximately 0·10 × 0·13 × 0·18 mm was mounted with epoxy resin on a glass fiber. It was set to rotate about a and was used for determining the cell parameters and collecting the initial intensity data. Subsequently, a larger crystal approximately 0·27 × 0·28 × 0·30 mm, was mounted for rotation about the b axis and used to collect additional data. The final set of data consisted of 2563 reflections of which 607 of the more intense, all with a net count greater than 50 dekacounts, were from the smaller crystal and the remaining 1956 were from the larger crystal.

Cell parameters were determined on a Picker X-ray diffractometer equipped with a General Electric quarter circle goniostat. 2θ settings for 16 reflections ranging from 9·61 to 29·12 degrees were measured by determining peak positions from the half-height values for both positive and negative 2θ. Mo $K\alpha$ radiation was used ($\lambda K\alpha = 0{\cdot}71069$ Å). The following unit-cell parameters were determined by a least-squares fit to the 16 observed 2θ values:

$$a = 11{\cdot}044 \pm 0{\cdot}002, b = 8{\cdot}481 \pm 0{\cdot}001, c = 11{\cdot}214 \pm 0{\cdot}002 \text{ Å}, \beta = 91{\cdot}31 \pm 0{\cdot}01^\circ .$$

Since the only systematically absent reflections were $0k0$ for k odd, the space group was assumed to be $P2_1$. The density was observed to be 1·45 g.cm^{-3} by flotation in mixed solvents; it was calculated to be 1·446 g.cm^{-3} assuming four molecules in the unit cell or two molecules in the asymmetric unit.

Intensities were measured on a diffractometer equipped with a scintillation counter and pulse height analyzer. A Mo target tube was used at a 3° take-off angle

---

* Abstracted from a thesis submitted in partial fulfillment for the M.S. degree in the Department of Biochemistry. Presented at the Minneapolis A.C.A. meeting, August, 1967.

† Contribution No. 209 from the Centre of Advanced Study in Physics, University of Madras, Madras-25, India.

and was operated at 14 mA and 50 kV. The radiation was filtered through 0·001 inch Nb. All measurements were made using the $\omega/2\theta$ scan technique with a constant scan rate of two degrees per minute and variable scan times (Kraut, 1964) as computed from the tangent relationship of Alexander & Smith (1964). A background count was made at each end of the scan range for half the time of the total scan. All φ, χ and 2θ positions were manually set, and the measured intensities recorded in dekacounts.

All measurements were put on a common scale using four standard reflections measured at four-hour intervals. Measurements from the two crystals were scaled together using ten reflections which had net dekacounts ranging from 831 to 1361 for the smaller crystal and 7879 to 12,573 for the larger crystal.

The relative intensity was obtained by subtracting the sum of the background counts from the total scan count; if a negative value was obtained, the intensity was taken as equal to zero. Intensities were converted to $|F|^2$ in the usual way. No correction for absorption was made ($\mu=3{\cdot}60$ cm^{-1}).

Refinement

The scattering factors used for O,N,C, and Cl$^-$ were from Hanson, Herman, Lea & Skillman (1964) and those for H were from Stewart, Davidson & Simpson (1965). All calculations were carried out on an IBM 7094 computer with programs from the crystallographic computing system, *X-ray* 63 (Stewart, 1964). For refinement of the 389 parameters, it was necessary to partition the matrix into three large blocks. Thus a full refinement cycle required three passes through the computer: (1) refinement of the atomic parameters of one arginine molecule along with those of the 2 Cl$^-$ ions and 2 water oxygen atoms, all other parameters fixed; (2) refinement of the atomic parameters of the second arginine molecule along with those of the 2 Cl$^-$ ions and 2 water oxygen atoms, all other parameters fixed; (3) refinement of the parameters of the hydrogen atoms, all others fixed.

The initial refinement began with Mazumdar & Srinivasan's (1964) coordinates and a set of data collected from the smaller crystal. Refinement reduced $R(\sum|F_o|-|F_c||/\sum|F_o|)$ to 0·053, but the standard deviations in the positional parameters of the C,N and O atoms, about 0·005–0·006 Å, were greater than expected. It was at this point that additional data were collected from the larger crystal and the final set of 2563 reflections was obtained. The initial refinement cycle on the final data included *all* reflections with *unit weight*. Anisotropic thermal parameters were included but hydrogen atoms were omitted. The index R was 0·066.

All 34 hydrogen atoms were easily located from a difference synthesis and their positions were refined in a single least-squares cycle with isotropic thermal par-

Table 1. *Atomic parameters for nonhydrogen atoms*

Estimated standard deviations in parentheses.

The thermal parameters are defined by the expression:

$$T_t=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·57877 (20)	0·43397 (32)	0·42981 (19)	1·64 (8)	2·16 (10)	1·25 (8)	−0·28 (8)	0·23 (6)	−0·06 (8)
C(2)	0·52425 (20)	0·42437 (30)	0·55514 (19)	1·98 (9)	1·63 (9)	1·26 (8)	0·02 (8)	0·31 (6)	−0·24 (7)
C(3)	0·38776 (21)	0·44430 (33)	0·54862 (21)	1·56 (8)	2·50 (11)	1·71 (8)	0·27 (8)	0·44 (7)	−0·15 (8)
C(4)	0·32727 (21)	0·43032 (34)	0·67008 (21)	1·72 (8)	2·56 (11)	1·75 (8)	0·12 (8)	0·53 (7)	0·13 (8)
C(5)	0·19209 (22)	0·40616 (35)	0·65116 (22)	2·04 (9)	2·54 (11)	2·10 (9)	−0·13 (8)	0·33 (7)	−0·74 (9)
C(6)	0·11572 (19)	0·25673 (33)	0·82191 (20)	1·46 (8)	1·96 (9)	1·78 (8)	0·27 (8)	−0·07 (6)	0·23 (8)
N(1)	0·58292 (17)	0·54346 (26)	0·63526 (15)	1·67 (7)	2·18 (8)	1·38 (6)	−0·05 (7)	0·23 (6)	−0·12 (7)
N(2)	0·12711 (19)	0·38969 (26)	0·76163 (19)	2·09 (8)	1·88 (8)	2·56 (9)	−0·49 (7)	0·94 (6)	−0·17 (7)
N(3)	0·18027 (20)	0·13017 (25)	0·79442 (19)	2·74 (9)	1·60 (9)	2·43 (8)	−0·10 (7)	0·58 (6)	−0·04 (7)
N(4)	0·04036 (19)	0·24939 (32)	0·91205 (18)	2·36 (8)	2·80 (10)	2·15 (8)	−0·02 (8)	0·73 (6)	−0·22 (8)
O(1)	0·65090 (17)	0·54125 (26)	0·40903 (15)	2·67 (7)	3·32 (9)	2·08 (7)	1·12 (7)	0·86 (6)	0·18 (7)
O(2)	0·54316 (16)	0·32939 (24)	0·35765 (14)	3·11 (8)	2·57 (8)	1·50 (6)	0·54 (7)	0·39 (6)	0·33 (6)
O(3)	0·11956 (18)	0·85689 (27)	0·59570 (17)	3·59 (9)	2·97 (10)	2·86 (8)	0·47 (8)	0·42 (7)	0·08 (8)
Cl(1)	0·16061 (6)	0·75734 (0)	0·86888 (6)	3·22 (3)	2·63 (3)	2·78 (3)	0·55 (2)	0·82 (2)	0·04 (2)
C(7)	0·55854 (21)	0·33536 (32)	0·91405 (20)	1·81 (9)	1·95 (10)	1·53 (8)	−0·67 (8)	0·39 (7)	−0·11 (8)
C(8)	0·50540 (20)	0·32535 (31)	0·03959 (18)	1·98 (8)	1·54 (9)	1·33 (8)	0·13 (8)	0·23 (7)	−0·01 (8)
C(9)	0·37337 (21)	0·37687 (32)	0·03555 (21)	1·74 (8)	2·36 (11)	1·71 (9)	0·06 (8)	0·25 (7)	0·44 (8)
C(10)	0·31557 (21)	0·38601 (33)	0·15751 (22)	1·63 (8)	2·31 (11)	2·10 (9)	−0·08 (8)	0·48 (7)	−0·17 (8)
C(11)	0·18966 (23)	0·45648 (35)	0·14746 (22)	2·33 (9)	2·56 (12)	2·02 (9)	−0·22 (9)	0·12 (8)	0·36 (9)
C(12)	0·13353 (20)	0·61279 (32)	0·32316 (20)	1·77 (8)	1·85 (9)	1·78 (8)	−0·35 (8)	−0·02 (6)	−0·19 (8)
N(5)	0·57826 (18)	0·42518 (28)	0·12437 (16)	1·71 (7)	2·54 (9)	1·46 (7)	0·10 (7)	0·15 (6)	0·06 (7)
N(6)	0·13381 (19)	0·47946 (27)	0·26285 (19)	2·22 (8)	1·94 (9)	2·59 (8)	0·27 (7)	0·78 (7)	0·19 (7)
N(7)	0·20528 (21)	0·73265 (28)	0·29656 (20)	2·97 (10)	1·91 (10)	3·15 (10)	0·38 (8)	0·78 (8)	0·32 (8)
N(8)	0·05957 (19)	0·62803 (30)	0·41391 (18)	2·53 (8)	2·96 (11)	2·08 (8)	0·08 (8)	0·60 (6)	0·37 (8)
O(4)	0·61343 (18)	0·45851 (26)	0·88685 (16)	3·45 (8)	2·09 (9)	1·92 (6)	0·87 (7)	0·70 (6)	−0·21 (6)
O(5)	0·53794 (20)	0·22103 (24)	0·84668 (16)	5·10 (10)	2·04 (8)	1·82 (7)	−0·07 (8)	0·45 (7)	0·57 (6)
O(6)	0·12423 (18)	0·02641 (28)	0·09134 (16)	3·73 (9)	3·13 (10)	2·35 (7)	−0·56 (8)	0·44 (6)	−0·09 (8)
Cl(2)	0·13138 (6)	0·10463 (10)	0·36241 (5)	2·11 (2)	2·54 (3)	2·33 (2)	0·24 (2)	0·59 (2)	−0·05 (2)

ameters fixed at 2·5 Å^2. Again all data were included with unit weight: R decreased to 0.049. An additional anisotropic refinement cycle on the nonhydrogen atoms with the hydrogen atoms fixed, decreased R to 0·042. The hydrogen atoms were again refined in a single isotropic cycle in which the thermal parameters were also allowed to vary, but with the nonhydrogen atoms fixed. The resulting R was 0·040.

Thus far the refinement had included all reflections with unit weight. A weighting scheme with $w_{hkl}=1/\sigma^2_{hkl}$ was now introduced, based on the following considerations: the estimated standard deviation in a count is the square root of the number of counts, but this is a lower limit to the standard deviation of the observation. Random fluctuation in counts also arises from instability in the electronic circuitry and from other effects, and the magnitude of these can be assessed by examining the variation of the total counts for the standard reflections bracketing each four-hour interval of data collection. For the present data, this was about 1%. Therefore, the estimated standard deviation in each measurement can be taken as

$$\sigma_I=[(I_t+(0{\cdot}01I_t)^2)]^{1/2},$$

where I_t is the total count (background plus scan) for each reflection (Stewart & Jensen, 1969).

The standard deviation in each structure factor was then estimated from the relation:

$$\sigma_F=(F^2+(\sigma_I)/\mathrm{Lp})^{1/2}-F.$$

The weights, $1/\sigma^2_F$, varied from 1·3 to 67·2 with most lying in the range 20 to 40.

After one anisotropic refinement cycle on the nonhydrogen atoms, all data included and weighted as indicated above, R decreased to 0·038. This was followed by a single isotropic cycle on the hydrogen atoms and R was 0·037. The standard deviations had decreased by about 30% on introducing the weighting scheme described above.

The data were edited at this point and minor errors affecting about 30 reflections were corrected. An additional isotropic refinement cycle on the hydrogen atoms resulted in $R=0{\cdot}038$, a slight increase.

The establishment of a threshold for the minimum observed intensity had been delayed until the refinement was essentially complete in order to permit an assessment of its effects on the final results of the refinement. Therefore, at this point a reflection was coded as unobserved if the net number of counts was less than the estimated standard deviation of the measurement; 109 reflections were thus coded. The ΔF values for these reflections were included in the refinement only if $F_c>F_{\min}$ but were omitted in the calculation of R. They were weighted in the same manner as other reflections.

One anisotropic refinement cycle on the nonhydrogen atoms with the 2454 observed data yielded an R of 0·035; the following isotropic refinement cycle on the hydrogen atoms reduced R to 0·034. The estimated standard deviations decreased by about 10%. At this point, an error in position of H(21) was discovered and corrected. One isotropic refinement cycle on the hydrogen atoms followed by one anisotropic cycle on the nonhydrogen atoms and a final isotropic cycle on the hydrogen atoms yielded a final R value of 0.033.

The goodness of fit, $[\sum w(|F_o|-|F_o|)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of parameters, was 1·69 as compared with the ideal value of 1. This deviation from unity may reflect errors in the weighting scheme or systematic errors in the data, but it is more likely that it indicates, at least in part, the limitations of the model.

The final atomic parameters are listed in Tables 1 and 2. The final $|F_o|$ and $|F_c|$ values are listed in Table 3. Figs. 1 and 2 show the bond lengths and angles of primary interest.

Table 2. *Atomic parameters for hydrogen atoms*

Estimated standard deviations in parentheses.

	x	y	z	B
H(1)	0·668 (2)	0·560 (4)	0·617 (2)	2·2 (6) Å^2
H(2)	0·588 (2)	0·511 (3)	0·713 (2)	1·4 (5)
H(3)	0·536 (3)	0·638 (4)	0·633 (3)	3·3 (7)
H(4)	0·544 (2)	0·318 (4)	0·592 (2)	1·9 (6)
H(5)	0·366 (3)	0·552 (4)	0·509 (3)	2·5 (6)
H(6)	0·359 (3)	0·363 (4)	0·499 (3)	2·3 (7)
H(7)	0·341 (3)	0·515 (4)	0·717 (3)	2·9 (7)
H(8)	0·362 (2)	0·336 (4)	0·714 (2)	2·0 (5)
H(9)	0·154 (3)	0·488 (4)	0·609 (3)	3·0 (8)
H(10)	0·171 (3)	0·304 (4)	0·600 (3)	2·0 (6)
H(11)	0·095 (2)	0·445 (4)	0·783 (2)	1·8 (6)
H(12)	0·219 (2)	0·135 (4)	0·734 (2)	1·0 (4)
H(13)	0·152 (2)	0·037 (4)	0·820 (2)	1·6 (5)
H(14)	−0·005 (3)	0·332 (5)	0·921 (3)	3·3 (7)
H(15)	0·055 (3)	0·176 (5)	0·966 (3)	3·4 (7)
H(16)	0·132 (4)	0·815 (6)	0·662 (4)	6·4 (1·0)
H(17)	0·173 (4)	0·918 (6)	0·577 (4)	5·5 (1·1)
H(18)	0·659 (2)	0·410 (4)	0·111 (2)	1·5 (5)
H(19)	0·565 (3)	0·398 (4)	0·205 (3)	3·1 (7)
H(20)	0·554 (2)	0·524 (4)	0·111 (2)	1·4 (5)
H(21)	0·512 (3)	0·222 (4)	0·070 (2)	2·2 (6)
H(22)	0·371 (2)	0·480 (3)	−0·009 (2)	1·4 (5)
H(23)	0·328 (3)	0·304 (4)	−0·011 (3)	3·2 (7)
H(24)	0·365 (2)	0·452 (4)	0·218 (2)	1·9 (6)
H(25)	0·317 (2)	0·287 (4)	0·196 (2)	2·4 (6)
H(26)	0·201 (2)	0·546 (4)	0·111 (2)	2·2 (6)
H(27)	0·137 (2)	0·387 (4)	0·099 (2)	1·4 (6)
H(28)	0·091 (3)	0·399 (4)	0·284 (3)	3·0 (8)
H(29)	0·259 (3)	0·716 (4)	0·256 (3)	2·9 (8)
H(30)	0·185 (3)	0·818 (4)	0·312 (3)	2·7 (7)
H(31)	0·010 (2)	0·562 (4)	0·425 (2)	1·1 (5)
H(32)	0·068 (3)	0·699 (5)	0·464 (3)	3·0 (8)
H(33)	0·120 (3)	0·056 (4)	0·161 (3)	2·1 (6)
H(34)	0·177 (3)	0·001 (4)	0·082 (3)	4·1 (8)

Discussion

General features and comparisons

By comparing Figs. 3 and 4 it is evident that the two arginine molecules in the unit cell are related approximately by a pseudo c-glide plane at $y\simeq 0{\cdot}4$.

Bond lengths in the two molecules are closely similar with the possible exception of the C–O bonds in the two carboxyl groups. Neglecting these, since both oxy-

Table 3. *Observed and calculated structure factors*

Each group of four columns contains respectively l, $10F_o$, $10F_c$ and the phase in millicycles.

0,0,L			
2	144	155	500
3	54	8	0
4	1135	1211	500
5	<74	21	500
6	70	92	500
7	82	84	0
8	178	189	0
9	121	119	0
10	157	160	500
11	25	19	0
12	38	38	500
13	81	85	500
14	71	70	0
1,0,L			
-14	135	128	0
-13	31	25	0
-12	129	128	0
-11	<9	11	500
-10	76	71	500
-9	<7	10	0
-8	59	62	0
-7	77	77	500
-6	134	126	500
-5	82	80	500
-4	482	474	0
-3	<11	7	500
-2	474	493	500
2	545	521	500
3	114	104	0
4	447	452	500
5	62	65	0
6	127	134	500
7	145	144	500
8	54	57	0
9	104	104	500
10	281	302	0
11	23	14	0
12	25	28	0
13	33	32	0
14	107	107	500
2,0,L			
-14	18	7	0
-13	35	28	500
-12	90	94	0
-11	<11	6	0
-10	118	117	500
-9	34	39	500
-8	136	137	500
-7	39	37	500
-6	287	268	500
-5	131	132	0
-4	157	150	0
-3	93	96	0
-2	449	422	500
-1	<26	4	500
0	286	266	0
1	45	11	0
2	1340E	1460	0
3	72	74	500
4	427	421	500
5	<6	0	500
6	113	116	500
7	91	94	500
8	36	36	0
9	51	55	0
10	<7	3	0
11	161	156	0
12	51	52	500
13	<17	0	500
14	<17	0	500
3,0,L			
-14	79	77	500
-13	27	18	0
-12	198	192	0
-11	40	45	500
-10	101	100	0
-9	43	43	0
-8	309	311	500
-7	17	26	0
-6	<16	8	500
-5	85	83	500
-4	665	669	0
-3	129	130	0
-2	353	329	0
-1	<6	16	500
0	1114	1122	500
1	165	155	500
2	587	565	0
3	72	109	500
4	40	83	0
5	145	149	0
6	271	263	500
7	102	102	0
8	57	58	500
9	85	82	500
10	217	229	0
11	47	43	500
12	41	41	0
13	24	13	0
14	105	105	500
4,0,L			
-14	87	90	500
-13	28	26	500
-12	54	52	0
-11	<16	18	0
-10	151	156	0
-9	29	29	0
-8	219	217	500
-7	13	3	500
-6	96	95	0
-5	108	119	500
-4	41	59	0
-3	15	15	0
-2	233	234	0
-1	154	157	0
0	1126	1164	500
1	118	113	0
2	76	77	0
3	66	64	500
4	605	634	0
5	19	13	0
6	58	53	0
7	55	52	0
8	194	193	500
9	153	155	500
10	132	132	500
11	35	38	500
12	<17	8	500
13	123	119	0
5,0,L			
-13	<8	8	500
-12	268	270	500
-11	31	27	500
-10	202	202	0
-9	29	20	0
-8	227	225	0
-7	83	65	0
-6	164	171	500
-5	145	145	500
-4	508	496	500
-3	87	88	500
-2	85	89	0
-1	210	214	0
0	<71	28	0
1	18	26	0
2	31	30	0
3	178	174	500
4	323	331	0
5	214	230	500
6	112	117	0
7	106	108	0
8	101	97	500
9	187	194	0
10	55	55	500
11	<11	18	500
12	24	8	0
13	51	47	500
6,0,L			
-13	21	26	0
-12	108	109	500
-11	18	16	500
-10	93	92	0
-9	25	19	500
-8	226	223	0
-7	43	42	0
-6	119	132	0
-5	41	40	0
-4	170	166	500
-3	149	149	500
-2	<9	13	500
-1	22	17	0
0	321	323	0
1	211	209	0
2	195	190	500
3	103	93	0
4	<13	17	0
5	41	37	500
6	130	138	0
7	42	43	0
8	142	146	500
9	<16	0	500
10	179	185	500
11	153	163	500
12	29	31	0
13	18	16	500
7,0,L			
-12	110	111	500
-11	<17	14	0
-10	122	133	500
-9	28	32	500
-8	420	428	0
-7	<12	2	500
-6	95	96	500
-5	117	116	0
-4	628	651	500
-3	136	136	500
-2	160	159	500
-1	146	147	500
0	316	305	0
1	163	167	0
2	204	193	500
3	62	60	0
4	46	51	0
5	204	204	500
6	131	132	0
7	167	171	500
8	17	6	500
9	131	127	0
10	<11	21	500
11	142	142	0
12	65	62	0
8,0,L			
-12	27	7	500
-11	<44	51	0
-10	138	133	500
-9	39	28	500
-8	<9	21	0
-7	106	107	500
-6	181	185	0
-5	15	11	0
-4	221	226	0
-3	77	76	0
-2	270	273	500
-1	67	66	500
0	84	93	0
1	27	29	500
2	319	349	0
3	189	194	0
4	<16	1	500
5	103	97	0
6	260	265	500
7	67	71	500
8	54	57	0
9	26	28	500
10	34	36	0
11	43	44	0
9,0,L			
-11	62	63	0
-10	41	34	0
-9	24	8	500
-8	129	130	500
-7	64	61	500
-6	59	63	0
-5	35	35	0
-4	<11	6	0
-3	170	167	0
-2	238	242	500
-1	82	84	500
0	73	67	0
1	172	181	500
2	25	33	500
3	92	92	0
4	90	94	500
5	34	36	0
6	<11	10	0
7	121	121	500
8	68	66	0
9	68	71	500
10	20	21	500
11	70	75	0
10,0,L			
-10	151	146	500
-9	95	98	0
-8	171	180	500
-7	<9	1	0
-6	144	148	0
-5	139	142	500
-4	227	229	0
-3	19	28	500
-2	93	91	500
-1	101	99	0
0	99	87	500
1	62	63	500
2	74	75	0
3	21	19	500
4	<15	9	500
5	143	142	0
6	<17	20	500
7	40	36	0
8	36	31	0
10	60	63	0
11,0,L			
-9	51	52	0
-8	<17	3	500
-7	20	11	0
-6	119	118	500
-5	76	80	500
-4	93	96	0
-3	24	19	500
-2	116	117	0
-1	148	160	0
0	159	174	500
1	31	33	500
2	43	39	500
3	157	157	500
4	36	42	0
5	76	81	0
6	122	112	0
7	50	51	0
8	52	49	500
9	48	49	500
12,0,L			
-8	<18	17	500
-7	123	126	0
-6	28	32	500
-5	30	35	0
-4	53	54	0
-3	157	128	500
-2	137	136	0
-1	46	46	500
0	126	119	500
1	135	134	0
2	63	58	500
3	51	54	500
4	52	55	500
5	37	41	500
6	50	39	0
7	61	65	0
13,0,L			
-6	20	16	0
-5	<8	0	0
-4	71	68	500
-3	120	117	500
-2	72	65	0
-1	90	84	500
0	97	90	500
1	131	131	0
2	17	16	500
3	<17	0	500
4	114	112	0
5	69	67	500
14,0,L			
-3	58	59	0
-2	76	80	0
-1	67	72	500
0	<22	11	0
1	<20	13	0
2	53	53	500
0,1,L			
1	137	122	926
2	274	278	760
3	405	410	457
4	413	414	277
5	358	366	935
6	146	148	421
7	134	131	959
8	453	464	723
9	359	365	450
10	164	175	691
11	55	64	510
12	134	131	291
13	160	159	938
14	138	135	170
1,1,L			
-14	51	57	170
-13	45	48	589
-12	123	121	614
-11	163	166	409
-10	142	134	191
-9	130	130	915
-8	136	132	117
-7	202	199	919
-6	514	512	646
-5	539	553	428
-4	645	638	657
-3	67	68	748
-2	200	179	53
-1	58	66	671
1	171	163	920
2	435	435	253
3	223	218	450
4	330	336	738
5	86	85	513
6	156	155	996
7	408	414	939
8	79	73	238
9	103	104	282
10	128	137	172
11	139	133	416
12	37	48	781
13	78	79	838
14	45	43	278
2,1,L			
-14	101	93	583
-13	81	76	313
-12	33	32	801
-11	184	182	420
-10	66	66	71
-9	33	31	811
-8	117	113	660
-7	457	465	930
-6	359	356	147
-5	28	28	395
-4	332	320	120
-3	304	302	426
-2	312	309	498
-1	134	120	457
0	246	231	710
1	141	141	355
2	786	772	83
3	328	333	14
4	232	223	540
5	176	178	379
6	234	235	393
7	280	286	885
8	77	82	801
9	77	77	701
10	84	80	804
11	269	268	444
12	96	99	598
13	52	45	139
14	53	54	247
3,1,L			
-14	170	163	150
-13	80	79	867
-12	22	16	60
-11	133	134	445
-10	88	89	627
-9	120	120	417
-8	110	109	205
-7	376	378	923
-6	179	174	246
-5	190	192	965
-4	807	798	671
-3	756	750	425
-2	192	181	915
-1	181	171	524
0	576	560	213
1	49	50	184
2	324	318	214
3	403	411	916
4	523	534	724
5	128	125	625
6	160	165	714
7	90	86	492
8	154	153	202
9	173	172	43
10	76	72	133
11	115	117	311
12	89	90	851
13	77	72	557
14	27	33	422
4,1,L			
-14	51	55	361
-13	56	54	941
-12	92	97	253
-10	107	105	829
-9	125	121	420
-8	233	239	691
-7	<16	9	612
-6	93	90	205
-5	470	469	928
-4	386	370	138
-3	225	216	392
-2	79	78	233
-1	558	564	442
0	692	674	605
1	165	166	625
2	66	60	861
3	416	417	958
4	264	266	980
5	186	187	153
6	146	155	566
7	264	269	443
8	197	202	248
9	188	193	797
10	92	91	199
11	51	55	842
12	36	34	771
13	126	126	377
5,1,L			
-13	35	27	814
-12	20	13	78
-11	65	64	956
-10	70	80	746
-9	54	58	310
-8	74	75	721
-7	134	128	430
-6	121	123	329
-5	242	235	907
-4	215	220	354
-3	70	70	990
-2	112	113	994
-1	310	314	444
0	374	360	50
1	92	91	482
2	292	294	622
3	160	157	41
4	284	287	166
5	259	271	913
6	138	144	71
7	128	128	449
8	79	73	508
9	98	97	377
10	176	181	633
11	110	111	5
12	47	44	8
13	38	43	364
6,1,L			
-13	45	39	437
-12	53	53	397
-11	97	97	850
-10	45	48	76
-9	73	70	998
-8	112	121	63
-7	112	105	339
-6	60	54	479
-5	76	76	674
-4	214	216	169
-3	214	223	888
-2	140	145	845
-1	217	219	266
0	303	307	668
1	183	183	425
2	524	525	616
3	139	138	623
4	234	251	200
5	105	101	932
6	119	122	878
7	89	88	224
8	60	57	628
9	115	114	535
10	121	122	233
11	115	115	788
12	68	67	229
13	<18	1	30
7,1,L			
-12	49	52	619
-11	41	37	928
-10	111	114	392
-9	53	51	939
-8	116	117	879
-7	94	90	364
-6	292	305	735
-5	215	218	420
-4	285	280	333
-3	206	203	855
-2	163	188	402
-1	238	251	932
0	219	222	911
1	180	183	488
2	121	129	933
3	184	191	434
4	288	301	260
5	156	151	26
6	177	179	120
7	139	143	949
8	101	98	840
9	87	86	390
10	109	109	610
11	39	31	174
12	70	70	565
8,1,L			
-12	61	69	777
-11	61	82	482
-10	22	30	495
-9	38	29	837
-8	140	144	192
-7	114	115	24
-6	208	221	115
-5	37	30	153
-4	96	95	106
-3	122	122	745
-2	209	207	645
-1	135	136	937
0	52	54	309
1	205	208	227
2	100	99	64
3	242	247	417
4	261	265	652
5	126	128	644
6	95	93	463
7	141	146	883
8	47	44	31
9	66	63	141
10	24	29	913
11	100	99	506
9,1,L			
-11	85	83	382
-10	110	104	535
-9	42	44	594
-8	90	93	418
-7	66	67	771
-6	189	185	957
-5	58	64	142
-4	267	274	699
-3	87	90	346
-2	210	218	476
-1	96	96	687
0	56	58	262
1	76	78	899
2	172	169	59
3	77	83	508
4	72	68	783
5	25	25	293
6	137	139	236
7	77	79	976
8	45	43	943
9	44	38	936
10	35	37	759
11	40	39	353
10,1,L			
-10	78	79	914
-9	82	84	519
-8	90	89	362
-7	24	22	893
-6	<3	18	334
-5	119	118	39
-4	191	138	860
-3	83	76	54
-2	190	198	193
-1	111	110	627
0	165	170	391
1	38	38	943
2	47	38	183
3	70	73	262
4	171	168	833
5	105	105	407
6	63	69	565
7	32	45	313
8	86	85	431
9	73	70	937
10	45	42	979
11,1,L			
-9	98	92	373
-8	103	102	624
-7	47	48	715
-6	126	132	311
-5	115	114	839
-4	123	121	999
-3	83	81	147
-2	132	67	773
-1	121	130	437
0	117	123	559
1	64	66	669
2	55	67	275
3	119	116	1
4	52	50	915
5	56	55	312
6	96	94	799
7	27	21	607
8	44	46	317
9	47	49	794
12,1,L			
-8	104	101	625
-7	46	47	513
-6	147	149	569
-5	23	26	329
-4	35	30	688
-3	81	79	109
-2	145	147	23
-1	59	57	62
0	43	45	354
1	95	92	591
2	124	125	538
3	98	86	767
4	70	65	217
5	27	22	502
6	73	72	945
7	58	61	317
13,1,L			
-6	28	29	309
-5	57	59	666
-4	175	168	259
-3	85	80	723
-2	93	86	946
-1	81	72	32
0	61	21	977
1	41	40	467
2	32	39	420
3	31	28	136
4	20	19	387
5	79	77	127
14,1,L			
-3	<18	17	141
-2	84	77	706
0	74	81	996
1	27	20	306
2	57	65	605
0,2,L			
0	626	612	815
1	612	619	591
2	252	235	820
3	258	258	136
4	86	78	757
5	156	157	179
6	235	240	434
7	185	181	693
8	29	30	93
9	133	151	911
10	105	108	271
11	107	104	110
12	29	33	954
13	52	48	417
14	61	58	280
1,2,L			
-14	22	18	241
-13	104	102	741
-12	89	88	960
-10	110	109	596
-9	205	206	232
-8	199	202	730
-7	320	328	569
-6	136	126	232
-5	288	288	649
-4	237	231	963
-3	540	529	116
-2	566	547	870
-1	516	507	108
0	814	818	315
1	404	397	686
2	1125	1152	353
3	65	70	677
4	376	374	814
5	305	314	83
6	141	147	979
7	15	15	933
8	82	78	188
9	258	260	483
10	84	86	656
11	110	110	249
12	99	102	793
13	77	82	917
14	27	25	113
2,2,L			
-14	39	36	356
-13	86	84	275
-12	138	138	414
-11	96	98	608
-10	82	80	956
-9	95	92	958
-8	119	128	71
-7	64	63	852
-6	363	378	353
-5	98	120	556
-4	55	55	517
-3	457	460	113
-2	468	468	861
-1	499	480	121
0	221	209	645
1	809	800	583
2	469	479	432
3	541	537	614
4	300	288	909
5	54	58	225
6	185	178	927
7	265	263	124
8	53	53	441
9	108	107	866
10	<9	8	532
11	49	50	906
12	100	97	376
13	51	44	572
14	39	44	917
3,2,L			
-14	<8	6	774
-13	81	81	701
-12	52	56	217
-11	149	149	619
-10	88	87	475
-9	62	62	243
-8	56	53	518
-7	150	145	54
-6	258	257	896
-5	108	110	646
-4	154	148	791
-3	199	199	345
-2	179	180	682
-1	423	422	114
0	376	366	972
1	658	650	686
2	506	507	234
3	226	227	664
4	520	532	425
5	278	278	190
6	309	320	776
7	293	298	98
8	121	124	20
9	95	94	735
10	83	85	977
11	155	156	508
12	127	127	470
13	44	47	375
4,2,L			
-13	93	94	135
-12	<9	13	526
-11	140	135	615
-10	122	117	371
-9	220	221	623
-8	31	40	574
-7	265	262	145
-6	226	233	859
-5	301	309	99
-4	182	181	157
-3	447	446	649
-2	101	102	180
-1	135	118	383
0	526	524	499
1	322	325	195
2	150	138	647
3	213	211	667
4	233	247	243
5	232	231	715
6	220	215	883
7	206	207	237
8	31	26	460
9	169	136	147
10	58	65	112
11	129	130	705
12	62	65	320
13	60	59	639
5,2,L			
-13	34	35	210
-12	47	9	299
-11	25	23	619
-10	143	137	374
-9	143	147	607
-8	124	129	342
-7	102	105	42
-6	291	290	966
-5	333	342	80
-4	67	66	435
-3	158	158	548
-2	298	295	478
-1	230	230	536
0	115	110	926
1	251	251	33
2	546	557	920
3	98	98	613
4	339	344	308
5	72	70	290
6	112	115	531
7	45	48	503
8	195	205	813
9	78	79	922
10	30	22	647
11	68	61	788
12	40	40	431
13	61	59	414
6,2,L			
-13	75	69	47
-12	77	79	916
-11	42	48	968
-10	105	100	99
-9	125	125	634
-8	140	147	444
-7	118	121	453
-6	301	305	726
-5	196	195	194
-4	172	177	889
-3	201	197	861
-2	251	251	71
-1	430	437	625
0	147	147	497
1	278	282	264
2	316	322	568
3	82	83	992
4	137	142	70
5	189	182	857
6	112	109	229
7	64	59	696
8	96	93	548
9	156	154	287
10	92	90	271
11	60	52	154
12	145	139	995
7,2,L			
-12	84	84	686
-11	123	124	144
-10	90	84	861
-9	40	41	71
-8	58	54	322
-7	167	165	661
-6	229	236	338
-5	54	53	788
-4	136	125	186
-3	297	300	110
-2	25	19	983
-1	182	180	669
0	52	48	108
1	108	107	194
2	112	112	479
3	234	234	197
4	218	225	853
5	83	81	462
6	171	178	221
7	160	159	698
8	48	5	555
9	72	78	542
10	130	128	679
11	65	59	120
12	72	68	760
8,2,L			
-11	135	131	120
-10	82	84	880
-9	81	83	66
-8	102	103	98
-7	173	174	628
-6	232	237	407
-5	240	240	547
-4	313	325	782
-3	221	233	181
-2	158	157	857
-1	185	193	972
0	144	141	79
1	177	187	588
2	87	81	531
3	60	58	474
4	175	183	689
5	118	115	769
6	176	178	276
7	84	85	878
8	45	43	198
9	<10	18	162
10	61	62	778
11	87	79	200
9,2,L			
-11	86	84	479
-10	124	126	756
-9	54	55	207
-8	32	34	855
-7	<16	3	842
-6	189	186	347
-5	173	170	738
-4	34	32	249
-3	52	47	0
-2	44	53	166
-1	213	211	112
0	88	84	941
1	97	93	576
2	71	75	237
3	89	87	292
4	126	125	516
5	108	109	369
6	34	37	848
7	<8	24	39
8	104	102	77
9	52	54	864
10	31	24	475
10,2,L			
-10	194	200	427
-9	89	89	133
-8	79	77	853
-7	60	58	807
-6	134	131	72
-5	117	117	659
-4	149	150	404
-3	136	136	445
-2	130	138	716
-1	232	238	193
0	131	139	864
1	128	124	828
2	111	109	104
3	87	90	562
4	132	133	459
5	68	66	510
6	100	99	630
7	29	25	750
8	91	85	100
9	60	61	924
11,2,L			
-9	98	95	491
-8	111	114	655
-7	87	94	242
-6	38	40	20
-5	61	59	15
-4	150	141	222
-3	169	178	763
-2	82	80	848
-1	116	118	166
0	103	99	604
1	55	58	193
2	48	54	88
3	142	140	568
4	81	83	143
5	18	21	364
6	99	103	692
7	94	95	222
8	32	27	503
12,2,L			
-7	29	30	54
-6	118	113	832
-5	39	39	136
-4	71	73	330
-3	73	75	736
-2	35	40	289
-1	83	84	536
0	36	38	758
1	58	61	286
2	33	29	654
3	67	62	970
4	86	93	235
5	55	49	104
6	<18	10	617
7	43	52	522
13,2,L			
-5	58	54	271
-4	92	94	105
-3	30	31	943
-2	100	95	146
-1	75	63	778
0	63	57	544
1	90	86	230
2	74	76	694
3	<9	24	520
4	97	93	959
5	56	56	761
14,2,L			
-2	41	35	255
-1	174	172	745
0	69	65	182
1	<9	20	201
0,3,L			
1	334	322	329
2	80	57	388
3	310	294	293
4	142	137	449
5	201	191	928
6	188	185	460
7	108	107	262
8	106	105	488
9	28	39	453
10	269	271	42
11	65	65	189
12	76	74	482
13	24	19	900
14	103	105	513
1,3,L			
-14	<19	19	598
-13	86	83	765
-12	189	186	89
-11	57	58	785
-10	19	14	498
-9	279	290	296
-8	286	294	527
-7	157	158	772
-6	94	99	420
-5	237	242	839
-4	348	349	34
-3	141	143	787
-2	101	101	177
-1	260	250	272
0	771	772	496
1	101	93	928
2	502	497	45
3	258	249	429
4	167	164	828
5	126	127	418
6	238	240	591
7	62	67	804
8	51	44	651
9	257	267	800
10	297	303	43
11	22	13	722
12	35	37	676
13	86	83	315
2,3,L			
-13	105	105	140
-12	153	148	55
-11	68	67	315
-10	117	118	19
-9	106	105	545
-8	401	411	579
-7	128	128	704
-6	98	99	833
-5	100	101	798
-4	266	275	89
-3	274	271	924
-2	477	468	78
-1	53	46	589
0	482	481	611
1	416	410	444
2	91	90	771
3	181	174	213
4	192	199	97
5	449	447	914
6	78	75	182
7	107	112	863
8	211	221	545
9	242	241	364
10	42	45	155
11	30	28	339
12	147	150	88
13	48	52	74
3,3,L			
-13	88	83	538
-12	32	31	849
-11	58	53	581
-10	253	256	52
-9	129	131	943
-8	181	182	495
-7	186	194	79
-6	170	168	659
-5	54	47	621
-4	77	74	639
-3	200	194	525
-2	402	407	994
-1	164	160	216
0	107	99	115
1	149	150	133
2	352	352	476
3	260	260	656
4	57	58	554
5	177	173	545
6	84	83	794
7	133	145	41
8	82	83	556
9	108	105	249
10	24	19	667
11	120	116	633
12	84	81	43
13	<8	18	667
4,3,L			
-13	75	73	74
-12	196	190	494
-11	70	69	159
-10	139	134	55
-9	149	153	643
-8	125	133	918
-7	82	83	605
-6	240	240	602
-5	70	72	258
-4	162	177	529
-3	214	208	361
-2	197	199	133
-1	160	155	941
0	397	389	97
1	101	108	37
2	379	379	558
3	229	238	803
4	153	158	582
5	107	106	323
6	280	291	27
7	17	12	803
8	91	91	86
9	71	70	235
10	145	142	531
11	39	38	753
12	88	87	78
13	34	37	638
5,3,L			
-13	46	47	399
-11	64	63	684
-10	25	17	884
-9	82	79	833
-8	199	197	103
-7	126	133	182
-6	152	158	491
-5	168	177	45
-4	133	137	487
-3	149	150	396
-2	51	57	634
-1	160	155	667
0	532	540	3
1	130	130	835
2	190	192	875
3	199	204	781
4	275	287	493
5	174	168	412
6	59	56	374
7	60	60	275
8	59	60	938
9	128	130	15
10	150	151	558
11	27	30	290
12	18	8	327
6,3,L			
-12	<18	19	907
-11	44	45	78
-10	183	166	523
-9	51	52	610
-8	236	242	65
-7	164	165	645
-6	75	73	820
-5	46	42	108
-4	210	220	621
-3	293	293	328
-2	142	145	656
-1	145	148	658
0	208	208	156
1	357	362	919
2	191	199	259
3	194	192	156
4	210	218	549
5	145	154	409
6	133	131	572
7	124	126	458
8	161	161	57
9	53	55	784
10	68	87	62
11	56	53	65
12	27	35	865
7,3,L			
-12	121	115	100
-11	85	90	961
-10	88	85	534
-9	44	38	851
-8	70	70	512
-7	215	231	410
-6	51	49	458
-5	201	209	253
-4	119	120	115
-3	353	353	930
-2	98	101	409
-1	118	101	684
0	162	160	595
1	269	275	595
2	333	344	5
3	26	33	518
4	211	219	565
5	87	89	918
6	242	245	526
7	98	94	367
8	35	36	885
9	73	69	753
10	35	34	570
11	127	124	981
8,3,L			
-11	32	25	590
-10	63	59	808
-9	74	77	207
-8	142	141	500
-7	77	81	761
-6	169	173	83
-5	156	162	587
-4	142	145	863
-3	143	137	872
-2	168	175	627
-1	65	67	146
0	27	17	493
1	63	63	675
2	171	172	143
3	199	207	214
4	42	45	364
5	69	70	119
6	186	198	534
7	21	26	777
8	22	32	358
9	37	40	569
10	108	110	52
9,3,L			
-10	96	96	179
-9	79	76	57
-8	105	108	606
-7	24	30	479
-6	26	23	513
-5	185	181	437
-4	63	66	377
-3	130	124	974
-2	82	84	147
-1	179	188	119
0	94	92	617
1	160	160	455
2	117	115	546
3	159	162	642
4	148	154	60
5	115	112	801
6	124	125	970
7	29	26	191
8	129	130	581
9	30	34	349
10	30	19	52
10,3,L			
-9	55	50	265
-8	62	59	921
-7	104	105	15
-6	70	72	480
-5	95	98	606
-4	55	52	539
-3	141	155	582
-2	85	91	948
-1	174	181	991
0	18	13	99
1	84	84	58
2	<11	14	782
3	132	131	518
4	47	55	80
5	57	59	179
6	76	73	109
7	95	96	568
8	124	118	525
9	<12	25	75
11,3,L			
-8	74	73	72
-7	99	102	976
-6	43	42	621
-5	105	106	844
-4	66	60	424
-3	168	179	460
-2	45	43	64
-1	94	96	315
0	<9	12	848
1	143	155	103
2	78	74	638
3	80	83	805
4	61	56	513
5	87	89	602
6	58	64	89
7	51	52	603
8	37	43	597
12,3,L			
-7	<18	9	393
-6	39	36	746
-5	73	73	40
-4	89	87	491
-3	120	115	355
-2	45	49	503
-1	65	69	633
0	38	38	942
1	101	100	578
2	29	24	67
3	19	7	766
4	44	36	176
5	69	63	494
6	66	63	92
13,3,L			
-5	66	70	32
-4	52	47	970
-3	41	41	558
-2	41	33	576
-1	123	123	570
0	26	31	108
1	40	36	91
2	50	44	0
3	124	121	31
4	61	63	678
0,4,L			
0	46	51	590
1	454	456	973
2	118	118	291
3	542	533	383
4	184	187	676
5	371	383	437
6	57	56	570
7	367	380	875
8	90	85	155
9	141	141	718
10	93	93	123
11	56	57	250
12	<17	6	654
13	31	37	938
1,4,L			
-13	27	23	907
-12	38	40	304
-11	60	48	870
-10	29	39	615
-9	162	168	346
-8	227	230	686
-7	207	212	251
-6	81	82	255
-5	108	109	707
-4	55	92	943
-3	490	476	576
-2	85	85	820
-1	410	398	13
0	154	149	268
1	366	363	993
2	251	244	155
3	314	310	810
4	243	246	764
5	441	441	520
6	88	87	702
7	141	145	132
8	141	138	223
9	139	140	124
10	27	24	951
11	38	30	203
12	69	69	713
13	39	38	398
2,4,L			
-13	117	115	6
-12	32	31	229
-11	61	59	96
-10	51	51	676
-9	135	141	525
-8	64	65	879
-7	226	233	664
-6	231	246	152
-5	467	471	969
-4	57	55	322
-3	367	360	382
-2	113	110	644
-1	65	63	315
0	95	99	348
1	195	193	5
2	88	84	639
3	257	249	157
4	93	98	812
5	395	365	483
6	43	44	760
7	133	145	619
8	111	113	392
9	115	113	920
10	<11	2	429
11	67	67	8
12	69	69	972
13	56	53	593
3,4,L			
-13	<9	10	806
-12	62	59	304
-11	99	104	925
-10	50	50	959
-9	128	128	943
-8	96	95	717
-7	422	430	450
-6	153	154	579
-5	243	237	70
-4	156	156	278
-3	241	237	957
-2	137	131	912
-1	403	396	509
0	124	110	750
1	295	304	580
2	92	95	577
3	430	427	914
4	145	142	136
5	149	150	44
6	36	43	706
7	232	232	398
8	58	53	430
9	56	55	878
10	<10	17	120
11	84	90	572
12	44	38	44
13	71	68	297
4,4,L			
-13	53	43	798
-12	66	59	715
-11	39	45	841
-10	21	21	913
-9	125	125	179
-8	43	46	441
-7	196	205	419
-6	80	77	702
-5	179	176	836
-4	204	206	196
-3	293	295	916
-2	74	77	189
-1	406	393	440
0	111	98	872
1	139	134	200
2	95	100	554
3	215	205	36
4	128	127	324
5	91	93	17
6	115	115	992
7	93	95	576
8	63	57	883
9	68	64	497
10	70	67	552
11	52	46	556
12	<18	16	96
5,4,L			
-12	42	42	396
-11	56	55	296
-10	45	45	266
-9	234	245	925
-8	174	183	81
-7	214	213	876
-6	71	72	735
-5	373	380	460
-4	155	154	465
-3	203	198	59
-2	69	69	312
-1	81	78	788
0	271	283	867
1	244	240	519
2	185	186	752
3	42	40	696
4	212	212	368
5	246	256	968
6	66	64	213
7	59	78	325
8	100	99	775
9	158	157	469
10	62	62	551
11	41	42	571
12	60	60	323
6,4,L			
-12	45	45	890
-11	126	123	660
-10	35	33	373
-9	86	85	126
-8	39	44	251
-7	317	326	96
-6	131	139	632
-5	331	331	472
-4	112	109	667
-3	169	168	597
-2	46	49	304
-1	131	140	985
0	70	75	145
1	78	77	285
2	183	187	148
3	59	62	558
4	135	137	393
5	160	159	987
6	96	99	611
7	50	51	11
8	122	122	972
9	51	47	633
10	57	62	77
11	83	83	545
7,4,L			
-11	138	141	304
-10	68	66	482
-9	58	58	790
-8	17	21	424
-7	324	320	930
-6	165	165	91
-5	98	92	554
-4	59	64	890
-2	81	78	470
-1	153	147	867
0	108	107	288
1	148	146	4
2	176	180	934
3	136	149	235
4	193	197	768
5	74	78	865
6	157	156	442
7	96	98	613
8	49	51	153
9	97	100	313
10	36	38	845
11	54	50	321
8,4,L			
-11	97	92	812
-10	43	44	845
-9	61	55	511
-8	78	76	483
-7	70	70	64
-6	99	96	202
-5	130	126	63
-4	176	177	731
-3	277	278	412
-2	132	132	660
-1	78	83	332
0	131	135	327
1	167	177	917
2	98	97	198
3	88	88	606
4	94	91	964
5	99	96	472
6	109	105	495
7	<11	14	25
8	58	67	548
9	53	55	867
10	62	67	952
9,4,L			
-10	46	53	684
-9	103	101	472
-8	58	57	500
-7	45	46	583
-6	56	57	555
-5	206	203	996
-4	74	72	940
-3	117	119	645
-2	118	125	124
-1	169	180	615
0	113	114	379
1	80	80	41
2	73	70	503
3	126	125	92
4	138	197	915
5	29	28	339
6	74	74	838
7	56	53	856
8	128	130	480
9	27	29	327
10,4,L			
-9	23	20	31
-8	66	69	825
-7	127	125	546
-6	77	76	481
-5	151	151	950
-4	116	121	235
-3	145	153	156
-2	41	46	877
-1	180	186	339
0	97	102	735
1	91	89	674
2	44	49	454
3	109	109	853
4	53	55	210
5	125	125	393
6	75	78	20
7	<10	17	71
8	82	79	445
11,4,L			
-7	77	79	424
-6	27	33	638
-5	28	29	872
-4	79	82	455
-3	80	83	888
-2	43	46	816
-1	49	48	777
0	52	53	960
1	115	113	483
2	62	60	429
3	29	25	493
4	79	75	434
5	41	33	891
6	121	124	906
7	105	95	50
12,4,L			
-6	54	51	855
-5	33	30	386
-4	134	135	397
-3	110	107	990
-2	61	63	328
-1	33	36	224
0	78	80	949
1	119	118	474
2	58	56	895
3	53	48	865
4	57	58	385
5	81	83	988
13,4,L			
-3	69	66	866
-2	98	95	595
-1	<9	20	131
0	<8	22	829
1	39	35	389
2	49	55	992
0,5,L			
1	181	182	736
2	354	361	374
3	105	104	104
4	43	43	808
5	134	142	182
6	132	140	893
7	147	160	0
8	63	61	163
9	236	234	712
10	84	83	373
11	56	61	284
12	57	55	878
1,5,L			
-12	170	171	400
-11	84	85	602
-10	96	96	948
-9	212	218	117
-8	172	170	918
-7	145	158	911
-6	44	48	376
-5	176	179	612
-3	109	114	611
-2	56	53	179

Table 3 (*cont.*)

1,5,L			
-1	383	384	69
0	22	19	209
1	74	72	46
2	150	150	446
3	202	212	477
4	106	95	845
5	108	105	546
6	123	129	969
7	125	122	198
8	41	42	576
9	80	80	612
10	110	110	468
11	96	97	655
12	102	99	461
2,5,L			
-12	100	103	428
-11	114	113	743
-10	56	62	444
-9	144	142	284
-8	86	85	954
-7	202	205	318
-6	90	91	921
-5	117	118	829
-4	27	25	578
-3	177	173	779
-2	264	265	439
-1	215	220	410
0	105	99	719
1	160	152	277
2	133	134	921
3	194	195	662
4	141	137	342
5	117	120	706
6	104	107	829
7	47	45	358
8	105	104	859
9	139	140	45
10	68	66	340
11	87	85	743
12	91	91	401
3,5,L			
-12	32	31	733
-11	109	106	498
-10	188	187	406
-9	183	192	774
-8	128	131	870
-7	200	210	995
-6	259	261	921
-5	35	33	252
-4	83	81	183
-3	246	239	522
-2	265	271	463
-1	150	149	682
0	178	168	498
1	392	401	121
2	283	296	981
3	91	90	246
4	103	102	163
5	168	171	652
6	81	91	540
7	<16	18	730
8	17	14	14
9	218	226	158
10	42	46	120
11	106	100	623
12	96	96	395
4,5,L			
-12	26	23	953
-11	130	127	583
-10	112	110	394
-9	178	182	613
-8	61	52	65
-7	243	260	332
-6	176	175	916
-5	122	123	165
-4	19	21	351
-3	184	180	984
-2	157	157	369
-1	155	150	569
0	262	266	428
1	65	63	93
2	193	205	852
3	201	205	829
4	186	187	968
5	47	19	630
6	65	67	277
7	156	154	502
8	92	93	722
9	70	70	237
10	74	73	664
11	86	87	864
12	18	28	125
5,5,L			
-12	94	96	866
-11	105	104	365
-10	40	32	911
-9	140	141	767
-8	110	110	360
-7	156	156	883
-6	109	111	836
-5	61	60	362
-4	28	31	723
-3	151	148	144
-2	19	24	271
-1	194	210	721
0	80	79	533
1	267	271	519
2	47	47	635
3	184	178	301
4	217	224	963
5	225	227	91
6	83	85	404
7	147	151	804
8	160	161	448
9	66	66	436
10	23	28	264
11	110	110	220
6,5,L			
-11	105	101	106
-10	101	100	944
-9	36	35	33
-8	58	60	272
-7	115	115	582
-6	99	98	473
-5	143	142	407
-4	60	61	704
-3	176	181	230
-2	150	148	10
-1	73	67	967
0	101	100	135
1	202	204	776
2	259	273	447
3	172	171	960
4	108	105	850
5	107	107	212
6	98	98	68
7	50	52	462
8	48	45	267
9	80	82	627
10	113	111	826
11	64	61	291
7,5,L			
-11	32	33	111
-10	94	95	834
-9	76	77	231
-8	36	37	299
-7	120	121	811
-6	149	152	310
-5	79	78	585
-4	145	152	837
-3	56	58	282
-2	82	83	812
-1	135	135	970
0	82	82	112
1	184	192	602
2	114	110	429
3	241	260	428
4	110	108	645
5	63	57	182
6	119	114	942
7	91	94	36
8	45	44	274
9	107	107	693
10	62	64	451
8,5,L			
-10	39	48	615
-9	88	90	193
-8	30	30	876
-7	65	64	1
-6	57	61	256
-5	17	24	762
-4	58	53	708
-3	232	234	538
-2	44	45	605
-1	117	126	288
0	96	94	987
1	137	136	923
2	42	39	105
3	120	122	897
4	220	230	443
5	43	47	857
6	53	49	879
7	111	114	199
8	102	97	959
9	56	57	843
9,5,L			
-9	69	63	271
-8	67	66	671
-7	24	31	324
-6	82	81	16
-5	155	159	935
-4	95	97	143
-3	84	84	766
-2	68	87	821
-1	162	162	330
0	45	52	633
1	102	100	71
2	101	102	269
3	28	31	660
4	114	113	412
5	120	121	520
6	99	96	862
7	57	57	286
8	98	94	958
9	21	8	298
10,5,L			
-8	78	74	674
-7	78	76	212
-6	81	81	974
-5	34	38	173
-4	99	100	173
-3	97	95	749
-2	67	66	610
-1	97	102	522
0	118	118	553
1	80	79	300
2	76	76	976
3	63	68	793
4	57	55	32
5	83	85	833
6	58	64	509
7	44	47	969
11,5,L			
-6	95	96	695
-5	51	49	726
-4	50	54	21
-3	84	84	10
-2	79	82	95
-1	45	44	437
0	47	47	592
1	84	85	318
2	78	73	558
3	82	84	976
4	68	64	157
5	30	24	186
6	69	64	321
12,5,L			
-4	50	46	81
-3	145	144	80
-2	64	66	201
-1	120	118	812
0	36	41	539
1	116	117	464
2	47	50	648
3	56	57	369
4	102	96	953
0,6,L			
0	357	363	542
1	68	64	221
2	104	103	68
3	157	152	9
4	225	228	37
5	70	70	42
6	161	149	547
7	117	112	491
8	46	41	522
9	147	156	632
10	97	94	46
11	26	27	820
12	71	68	151
1,6,L			
-12	49	12	31
-11	58	59	393
-10	105	104	77
-9	77	79	150
-8	104	103	570
-7	150	148	146
-6	241	251	608
-5	70	69	833
-4	141	136	128
-3	95	89	652
-2	349	358	118
-1	29	25	423
0	190	188	616
1	187	185	451
2	190	193	572
3	179	177	519
4	150	148	106
5	127	124	815
6	91	95	861
7	168	199	931
8	51	52	623
9	109	109	249
10	70	69	399
11	<8	14	631
12	<18	24	949
2,6,L			
-12	39	40	598
-11	105	105	322
-10	<9	8	434
-9	156	157	794
-8	94	96	12
-7	122	120	642
-6	35	32	737
-5	78	75	389
-4	115	115	552
-3	115	114	874
-2	286	284	114
-1	127	123	881
0	104	108	18
1	223	218	265
2	429	434	632
3	160	164	989
4	<10	21	565
5	54	59	688
6	211	217	139
7	23	29	386
8	58	65	228
9	148	151	326
10	56	53	661
11	80	80	720
12	<18	14	435
3,6,L			
-11	26	28	706
-10	79	82	651
-9	52	49	491
-8	99	97	46
-7	78	77	163
-6	56	55	335
-5	121	121	100
-4	150	144	561
-3	112	114	378
-2	155	152	37
-1	104	106	799
0	183	177	140
1	82	80	425
2	293	302	572
3	120	108	532
4	93	95	562
5	139	147	397
6	220	214	63
7	143	152	914
8	56	58	64
9	134	138	905
10	60	60	550
11	18	21	496
4,6,L			
-11	48	43	420
-10	165	169	574
-9	107	106	278
-8	48	50	46
-7	67	64	151
-6	237	243	63
-5	138	141	822
-4	87	85	536
-3	90	93	631
-2	172	174	539
-1	93	97	743
0	191	191	73
1	67	67	109
2	175	179	853
3	117	112	75
4	218	221	620
5	31	34	791
6	121	122	219
7	113	119	543
8	119	99	81
9	45	55	16
10	<18	16	734
11	76	73	275
5,5,L			
-11	67	69	16
-10	94	91	617
-9	104	105	464
-8	72	69	503
-7	176	176	650
-6	189	189	96
-5	117	118	904
-4	82	78	81
-3	200	213	218
-2	200	199	629
-1	111	107	451
0	93	90	587
1	199	199	771
2	132	132	227
3	214	214	297
4	21	22	509
5	79	78	223
6	41	30	361
7	40	41	637
8	19	6	244
9	102	100	856
10	34	38	61
11	63	61	167
6,6,L			
-10	<18	8	347
-9	44	41	170
-8	146	146	603
-7	118	118	236
-6	53	54	109
-5	101	96	273
-4	136	138	73
-3	192	213	387
-2	177	183	614
-1	19	23	217
0	102	103	561
1	80	82	642
2	301	315	139
3	99	100	455
4	112	114	924
5	163	162	936
6	169	173	644
7	39	38	375
8	<8	14	167
9	100	96	557
10	41	36	126
7,6,L			
-10	97	99	42
-9	26	29	231
-8	122	119	548
-7	92	92	559
-6	73	75	569
-5	142	144	571
-4	184	190	35
-3	174	169	854
-2	49	52	226
-1	129	133	273
0	112	114	608
1	63	59	586
2	<17	14	643
3	26	30	649
4	33	31	346
5	85	88	177
6	72	69	628
7	31	34	72
8	<9	13	539
9	26	25	591
8,6,L			
-9	42	43	965
-8	49	44	819
-7	43	46	985
-6	153	160	592
-4	<17	12	517
-5	104	107	345
-3	74	75	28
-2	92	91	19
-1	156	163	32
0	29	24	790
1	57	57	354
2	77	77	308
3	149	148	636
4	117	120	193
5	52	52	444
6	102	103	879
7	110	114	79
8	29	33	649
9,6,L			
-8	105	107	64
-7	94	94	245
-6	162	160	632
-5	34	33	293
-4	72	73	564
-3	172	175	576
-2	204	216	121
-1	97	106	755
0	104	104	202
1	130	133	161
2	133	134	670
3	86	81	807
4	57	56	582
5	100	104	521
6	39	39	559
7	53	50	95
10,6,L			
-7	50	51	869
-6	57	54	662
-5	100	94	915
-4	62	58	627
-3	119	119	313
-2	84	78	22
-1	89	90	889
0	27	31	184
1	54	48	976
2	81	81	682
3	24	19	335
4	30	22	711
5	82	81	460
6	76	74	204
11,6,L			
-5	57	57	166
-4	86	86	579
-3	85	87	338
-2	31	32	418
-1	120	120	617
0	68	81	103
1	31	35	940
2	24	28	311
3	113	113	119
4	33	43	529
12,6,L			
-1	45	44	746
0	23	9	187
0,7,L			
1	55	57	608
2	206	213	198
3	176	180	6
4	55	53	432
5	136	135	573
6	150	149	661
7	104	107	608
8	59	56	194
9	79	80	997
10	50	47	4
11	54	55	30
1,7,L			
-11	73	73	18
-10	44	36	298
-9	160	168	539
-8	<8	11	654
-7	220	232	579
-6	68	70	376
-5	228	248	987
-4	45	42	797
-3	65	54	93
-2	121	118	955
-1	35	29	274
0	74	41	363
1	120	114	658
2	148	155	565
3	109	105	28
4	88	92	186
5	54	55	375
6	128	128	18
7	135	140	489
8	121	121	759
9	149	147	57
10	40	53	413
11	90	98	43
2,7,L			
-11	87	93	4
-10	38	44	335
-9	24	27	954
-8	29	29	921
-7	173	181	497
-6	68	63	879
-5	184	195	97
-4	29	19	895
-3	227	229	3
-2	36	40	670
-1	159	161	529
0	53	57	348
1	260	267	480
2	122	123	314
3	31	26	781
4	46	43	936
5	217	229	8
6	31	31	703
7	162	168	499
8	46	47	639
9	80	78	517
10	65	66	347
11	113	110	964
3,7,L			
-10	29	34	306
-9	37	40	965
-8	36	33	376
-7	159	171	530
-6	74	73	665
-5	141	142	573
-4	47	52	325
-3	120	115	15
-2	119	119	232
-1	56	53	353
0	113	111	863
1	118	119	18
2	83	85	692
3	78	81	655
4	57	54	608
5	119	115	96
6	98	99	177
7	50	59	857
8	97	97	905
9	69	70	662
10	<18	8	897
4,7,L			
-10	<18	11	430
-9	97	97	77
-8	61	59	980
-7	107	108	10
-6	96	97	910
-4	30	27	629
-3	83	85	65
-2	109	112	358
-1	178	192	942
0	68	70	929
1	45	47	69
2	<8	16	463
3	291	305	512
4	67	68	509
5	34	28	761
6	46	41	77
7	121	125	71
8	35	35	179
9	138	137	441
10	64	63	596
5,7,L			
-10	67	61	664
-9	56	53	942
-8	43	26	408
-7	91	93	37
-6	82	81	255
-5	242	248	536
-4	62	61	515
-3	110	105	588
-2	103	103	473
-1	101	100	56
0	61	62	39
1	165	165	159
2	183	189	924
3	62	59	339
4	49	49	574
5	55	61	683
6	110	111	513
7	74	79	957
8	89	91	230
9	70	66	792
6,7,L			
-9	<9	19	235
-8	92	83	599
-7	107	105	64
-6	<12	13	323
-5	<8	12	752
-4	131	132	93
-3	122	123	510
-2	73	70	858
-1	55	56	16
0	89	83	483
1	179	188	930
2	45	49	855
3	27	36	929
4	34	32	263
5	191	206	546
6	61	62	435
7	17	12	567
8	33	29	253
9	95	93	113
7,7,L			
-8	75	71	433
-7	99	93	572
-6	101	101	274
-5	76	82	965
-4	29	23	58
-3	56	57	589
-2	129	132	730
-1	62	61	471
0	69	73	375
1	61	63	233
2	58	52	985
3	169	179	123
4	69	68	914
5	88	90	495
6	21	28	406
7	86	84	584
8	42	42	452
8,7,L			
-7	34	35	669
-6	134	140	590
-5	126	130	92
-4	75	79	175
-3	54	57	384
-2	153	169	52
-1	58	58	514
0	95	90	670
1	49	50	681
3	102	102	915
4	79	74	172
5	41	43	527
6	<18	9	51
7	26	36	593
9,7,L			
-6	74	71	487
-5	31	40	726
-4	52	58	544
-3	69	68	903
-2	73	72	993
-1	26	23	959
0	60	67	885
1	59	59	499
2	74	71	402
3	79	82	7
4	46	41	675
5	92	95	131
6	86	79	968
10,7,L			
-5	33	36	667
-4	60	63	551
-3	61	63	289
-2	67	68	254
-1	43	42	50
0	57	66	976
1	61	57	552
2	30	26	457
3	101	100	495
4	72	65	434
11,7,L			
-1	37	33	894
0	97	100	68
0,8,L			
0	174	174	933
1	106	104	35
2	130	127	471
3	109	107	678
4	62	53	404
5	34	26	235
6	44	41	944
7	32	23	248
8	64	60	947
9	66	71	375
10	37	42	116
1,8,L			
-9	67	65	893
-8	<8	22	975
-7	69	71	31
-6	35	30	431
-5	38	38	101
-4	66	59	583
-3	86	86	753
-2	171	165	468
-1	60	60	528
0	319	326	4
1	302	307	265
2	170	182	997
3	80	80	729
4	205	206	473
5	127	127	706
6	79	65	547
7	59	57	565
8	37	26	826
9	95	90	97
2,8,L			
-9	135	132	688
-8	83	76	454
-7	53	53	552
-6	68	91	823
-5	80	77	233
-4	140	136	29
-3	87	89	319
-2	133	139	406
-1	206	203	658
0	135	136	571
1	107	105	105
2	185	193	895
3	109	103	894
4	113	107	356
5	93	91	737
6	72	73	419
7	70	75	254
8	51	43	879
9	127	125	244
3,8,L			
-9	108	105	711
-8	57	56	459
-7	30	29	209
-6	63	66	300
-5	88	85	171
-4	82	79	903
-3	125	122	138
-2	113	113	618
-1	117	116	603
0	179	179	427
1	<17	7	814
2	197	191	42
3	106	104	277
4	99	98	915
5	17	14	123
6	42	46	417
7	41	32	659
8	67	67	489
9	81	83	665
4,8,L			
-9	47	50	81
-8	40	43	325
-7	47	47	781
-6	80	81	633
-5	96	97	561
-4	37	32	542
-3	93	88	257
-2	151	151	123
-1	23	25	862
0	156	152	502
1	204	220	676
2	120	117	665
3	67	72	362
4	74	73	963
5	64	66	139
6	63	60	296
7	35	28	683
8	40	41	525
9	<19	6	415
5,8,L			
-8	46	34	84
-7	137	137	648
-6	95	96	321
-5	73	75	495
-4	47	44	617
-3	104	104	194
-2	157	170	877
-1	105	104	62
0	64	60	418
1	157	156	783
2	136	137	361
3	96	92	195
4	159	155	948
5	103	105	236
6	52	54	981
7	49	48	843
8	91	93	364
6,8,L			
-8	137	133	969
-7	54	50	28
-6	23	14	430
-5	79	76	968
-4	154	155	516
-3	96	98	622
-2	28	32	496
-1	50	48	213
0	101	102	30
1	72	69	913
2	34	33	439
3	76	77	525
4	25	20	636
5	114	113	489
6	59	56	865
7	25	21	214
7,8,L			
-7	57	51	198
-6	91	94	45
-5	45	52	612
-4	36	42	361
-3	125	126	638
-2	97	101	545
-1	86	84	271
0	81	78	965
1	86	90	175
2	38	37	150
3	70	70	879
4	41	39	448
5	43	36	846
6	<11	18	640
8,8,L			
-6	39	42	930
-5	69	73	923
-4	81	74	397
-3	120	115	843
-2	103	105	523
-1	83	79	386
0	65	66	832
1	83	84	231
2	45	45	134
3	92	90	887
4	45	49	197
5	56	57	597
9,8,L			
-3	29	18	626
-2	81	82	401
-1	37	37	597
0	19	32	609
1	69	69	322
2	51	51	964
3	52	48	824
0,9,L			
1	39	40	663
2	122	121	714
3	34	26	465
4	<9	18	495
5	<15	28	977
6	148	161	168
7	50	47	797
8	26	24	657
1,9,L			
-8	96	101	114
-7	56	46	599
-6	27	24	439
-5	72	76	401
-4	72	69	541
-3	64	68	903
-2	68	69	20
-1	56	55	753
0	53	48	825
1	53	46	369
2	73	75	450
3	<8	9	293
4	98	102	589
5	51	47	623
6	108	106	82
7	87	89	933
8	<8	14	918
2,9,L			
-8	80	87	144
-7	98	93	917
-6	48	39	89
-5	78	77	46
-4	229	246	651
-3	35	32	424
-2	49	52	291
-1	94	96	458
0	152	152	148
1	60	60	256
2	111	115	49
3	86	85	933
4	139	140	660
5	42	43	317
6	40	40	290
7	18	31	66
8	105	110	140
3,9,L			
-7	93	90	0
-6	173	175	135
-5	56	57	689
-4	46	44	192
-3	116	117	413
-2	84	86	632
-1	73	73	497
0	100	100	660
1	71	70	815
2	83	81	119
3	96	97	966
4	25	33	534
5	21	18	113
6	121	118	587
7	87	89	551
4,9,L			
-7	86	64	785
-6	40	43	215
-5	79	76	838
-4	65	65	712
-3	54	56	230
-2	76	82	652
-1	82	81	504
0	48	44	271
1	63	60	650
2	80	80	155
3	67	83	203
4	86	87	50
5	98	86	977
6	45	51	679
7	45	44	444
5,9,L			
-6	36	34	154
-5	44	34	292
-4	178	191	155
-3	17	20	50
-2	41	41	673
-1	55	55	299
0	132	130	653
1	<8	7	735
2	<18	13	413
3	17	15	831
4	102	105	97
5	108	103	959
6	114	108	640
6,9,L			
-5	84	84	557
-4	22	22	138
-3	110	107	808
-2	53	54	58
-1	64	68	98
0	36	24	139
1	69	68	479
2	102	103	612
3	80	82	599
4	81	74	193
5	25	24	81
7,9,L			
-4	57	56	280
-3	21	8	775
-2	36	47	268
-1	61	62	51
0	34	24	858
1	55	50	229
2	112	109	677
3	26	17	756
4	<19	17	390
8,9,L			
-2	18	26	127
-1	45	49	825
0	75	71	163
1	57	56	192
0,10,L			
0	167	163	350
1	94	94	632
2	53	47	419
3	126	125	78
4	91	87	891
5	36	33	16
6	49	43	22
1,10,L			
-6	29	20	589
-5	42	41	579
-4	55	58	358
-3	158	154	53
-2	<9	16	698
-1	<18	14	508
0	103	106	804
1	151	151	508
2	<18	5	762
3	25	32	84
4	33	27	25
5	71	67	51
6	25	30	230
2,10,L			
-5	123	118	535
-4	53	49	908
-3	63	53	171
-2	54	47	228
-1	144	146	116
0	75	77	260
1	77	79	610
2	69	73	340
3	154	153	635
4	65	70	677
5	105	95	78
3,10,L			
-5	63	56	629
-4	37	38	607
-3	62	69	528
-2	53	55	538
-1	131	132	12
0	75	70	745
1	58	59	875
2	54	53	888
3	139	136	552
4	<10	26	256
5	<10	10	189
4,10,L			
-4	20	4	95
-3	99	102	543
-2	<8	17	898
-1	55	53	113
0	69	71	223
1	60	62	198
2	61	59	41
3	91	88	526
4	85	80	368
5,10,L			
-3	69	61	636
-2	76	74	830
-1	79	79	539
0	101	101	488
1	69	72	950
2	64	59	709
3	67	66	962
6,10,L			
0	<8	5	480

gen atoms are involved in different hydrogen bonding and packing (see below), one calculates a root-mean-square difference for the remaining nine bonds between nonhydrogen atoms of 0·0052 Å. Since the bonds in the two molecules are independently determined, division by $\sqrt{2}$ leads to an estimate of the standard deviation of 0·0037 Å, just a little greater than the 0·0033 Å as determined from the refinement.

A similar comparison of the bond angles in the two molecules, but neglecting the angles about the carboxyl carbon atoms, gives an estimate of the standard deviation in the angles of 0·57°. This value exceeds the mean of the standard deviation estimated from the refinement 0·21°, by a factor approaching 3. The greater variability of bond angles as compared with bond lengths probably stems from the relatively smaller energies necessary to deform them. Presumably packing energies are sufficient to produce changes in angles appreciably larger than the standard deviations of the present refinement.

The guanidyl groups

The average value for the three guanidyl C–N bond lengths in molecule I is 1·324 Å, in molecule II it is 1·325Å. These agree well with the value of 1·323 ± 0·006 Å reported by Haas, Harris & Mills (1965) for C–N bonds of guanidinium chloride.

In the present investigation, the terminal C–N bonds of the guanidyl groups average 1·327 Å while the N(2)–C(6) and N(6)–C(12) bonds average 1·320 Å. The difference, however, is only marginally significant.

Both guanidyl groups in arginine hydrochloride are planar. The standard deviation of the four nonhydrogen atoms from the least-squares plane in molecule I is 0·003 Å; in molecule II it is 0·001 Å. The deviations of the hydrogen atoms from the guanidyl planes are listed in Table 4, and it is evident that corresponding atoms in the two groups tend to have similar deviations. Since the standard deviations for the hydrogen atoms are in the range 0·02–0·04 Å, any deviation in Table 4 exceeding about 0·1 Å indicates that the cor-

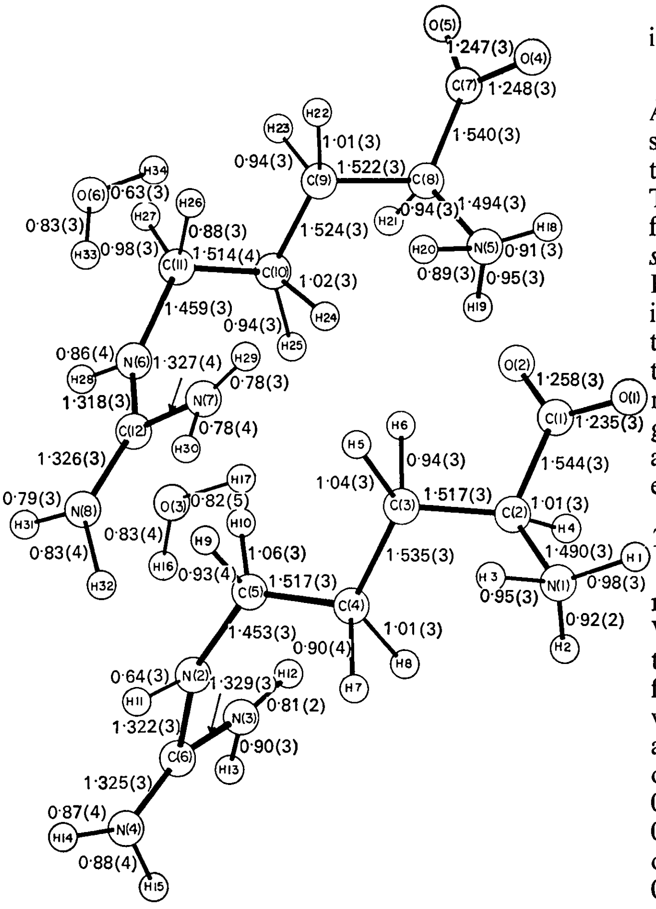

Fig. 1. Bond lengths of L-arginine hydrochloride monohydrate.

responding atom is probably significantly out of the plane. Thus H(13) and H(15) in molecule I and H(29), H(30) and H(32) in molecule II are probably out of the guanidyl planes. It is likely that the displacements of the hydrogen atoms result in additional linearity and increased stability of the hydrogen bonds.

Table 4. *Deviations of the hydrogen atoms from guanidyl planes*

Molecule I		Molecule II	
H(11)	0·03 Å	H(28)	0·06 Å
H(12)	0·10	H(29)	0·19
H(13)	0·28	H(30)	0·31
H(14)	0·09	H(31)	0·10
H(15)	0·30	H(32)	0·19

The angles about C(6) and C(12) in the guanidyl groups differ significantly from 120°. The deviations are in the same sense for corresponding angles in the two molecules although they are appreciably larger for molecule II than for molecule I.

The average value for the two C–NH_3^+ bond lengths is 1·492 Å while for the two $\mathrm{C{-}N}{<}^{\mathrm{C}}_{\mathrm{H}}$ bonds it is 1·456 Å. These values probably differ significantly from those suggested by Sutton (1965), 1·479 and 1·472 Å respectively, and they differ significantly from each other. The latter difference is probably due in part to the fact that in the first case the nitrogen atom is in the sp^3 valence state and in the second it is in the sp^2 state. Hahn (1957) in his review of the structural characteristics of amino acids noted an apparent lengthening of the C–NH_3^+ bond. Although at the time of his review the number of determinations of high precision were not sufficient to permit convincing conclusions, he suggested that this trend could result from an increase in atomic radius upon tetrahedral hybridization and from electrostatic effects.

The carboxyl groups

The average value for the two C–O bond lengths in molecule I is 1·246 Å and in molecule II it is 1·248 Å. While the two bonds in molecule II are virtually identical, in molecule I they are significantly different. The four atoms C(1), C(2), O(1) and O(2) are coplanar within experimental error while atoms C(7), C(8), O(4) and O(5) are not. In the first case the average deviation of the four atoms from the best least-squares plane is 0·002 Å and the deviation of N(1) from this plane is 0·15 Å, while in the second case the average deviation of the four atoms from the least-squares plane is 0·092 Å and N(5) deviates from this plane by 0·36 Å.

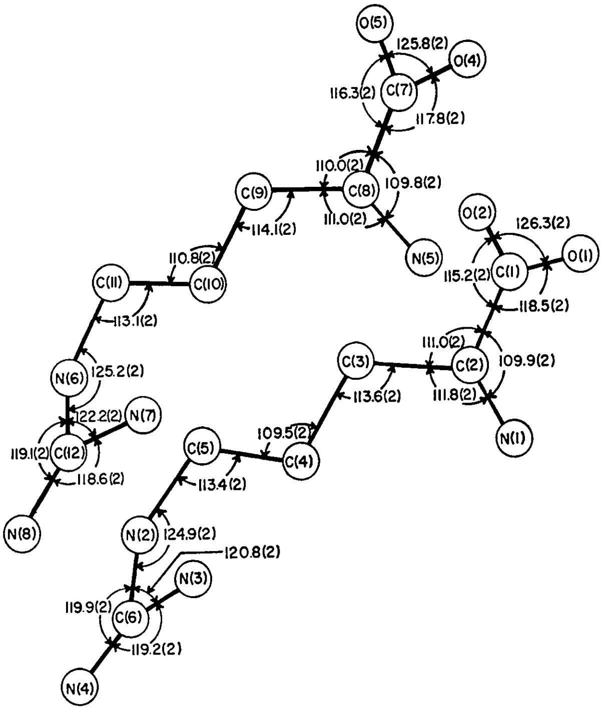

Fig. 2. Bond angles of L-arginine hydrochloride monohydrate.

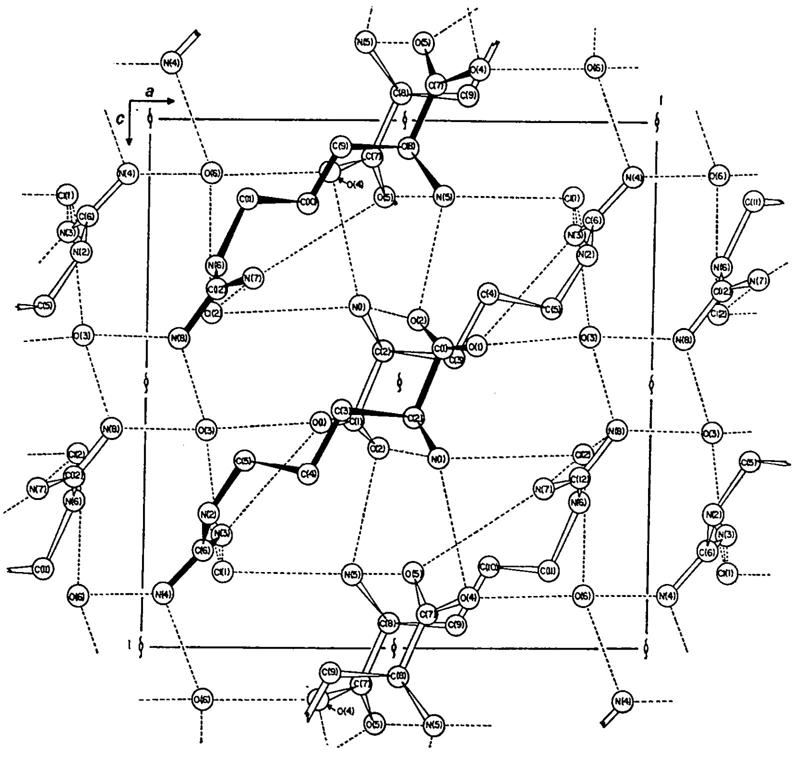

Fig. 3. A drawing of the structure viewed along **b**.

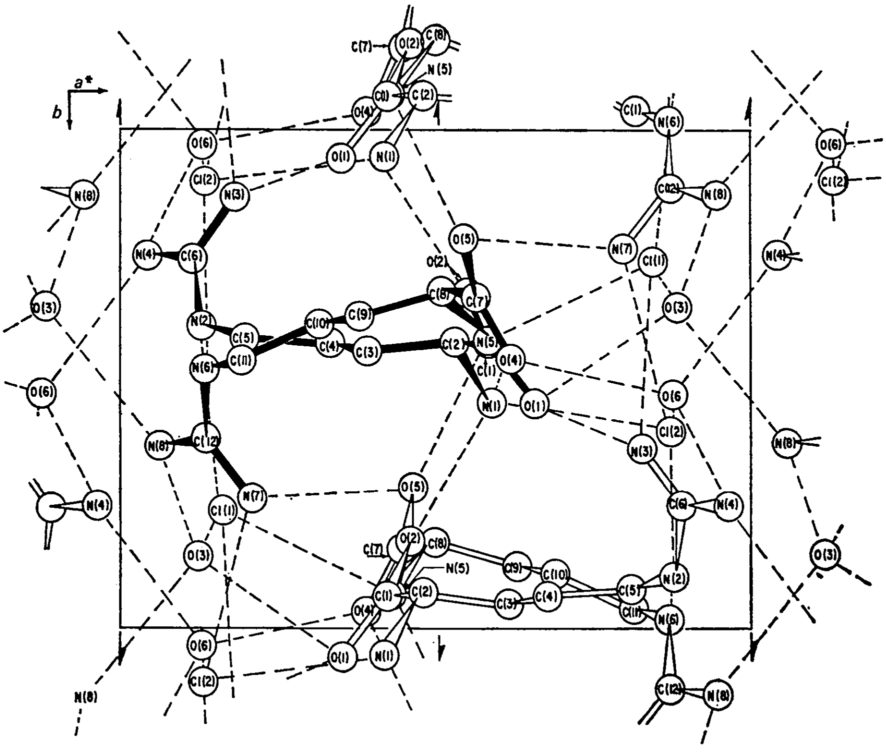

Fig. 4. A drawing of the structure viewed along **c**.

Thus, although the carboxyl groups appear similar in the structures when viewed along [001] (Fig. 4) it is evident that there are appreciable differences in the packing forces about these groups in the two molecules.

The N(1)···O(1) contact distance in molecule I is 2·66 Å; the corresponding distance N(5)···O(4) in molecule II is 2·72 Å. These are in agreement with the value 2·70 Å which Ramachandran, Ramakrishnan & Sasirekharan (1963) have proposed as the 'fully allowed distance' and 2·60 Å for the outer limit in their definition of the parameters of the polypeptide backbone.

Covalent bonds involving hydrogen

The hydrogen atoms, as located from a final difference synthesis, are shown in Fig. 5. As has been frequently observed, the C–H, N–H and O–H bond length are appreciably less than the internuclear distances. The average value for 14 C–H distances is 0·97 Å, about 0·1 Å shorter than the observed spectroscopic value of 1·09 Å. It has been suggested (Stewart *et al.*, 1965) that this difference is the result of assuming a spherical electron density distribution for the hydrogen atom and that the X-ray crystallographically derived values for these distances would be lengthened by the introduction of the appropriate complex scattering factors.

The average value found for 6 N(sp^3)–H distances in this study is 0·93 ± 0·014 Å, while that found for 10 N(sp^2)–H distances is 0·81 ± 0·024 Å, where the errors indicated are estimates of the standard deviation in the mean values. One of the N(sp^2)–H bonds, N(2)–H(11), is inordinately short and inconsistent with the other nine values. Neglect of this bond gives for the average of the other 9 N(sp^2)–H distances a value of 0·83 ± 0·011 Å. Either of the average N(sp^2)–H distances is apparently significantly less than the average N(sp^3)–H distance. However one may feel about the certainty of the observed difference, it is not surprising that the length of bonds involving hydrogen would be sensitive to the valence state of the atom to which they are bonded and the charge it might carry. In the present instance, both the valence state of the amino nitrogen atoms and their charge should tend to make N(sp^3)–H bonds longer than N(sp^2)–H bonds.

The average length of the four O–H bonds is 0·78 Å. Again, there is one inordinately short bond, and it is inconsistent with the other three. Neglecting it, the average of the three consistent O–H bonds is 0·83 Å, probably a more realistic value.

Hydrogen bonds

The structure is held together by an extensive system of hydrogen bonds, and it is remarkable that all twenty

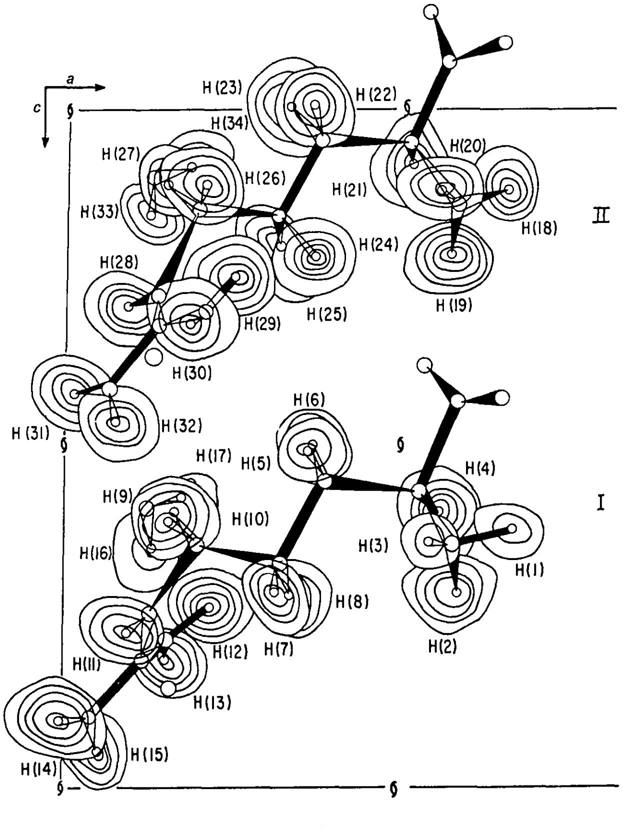

Fig. 5. A composite of sections from the final difference map, viewed along **b**. The contributions of the hydrogen atoms were omitted from the F_c calculations. Contours are at intervals of 0·1 e.Å^{-3}, beginning with 0·2 e.Å^{-3}.

of the hydrogen atoms in the asymmetric unit bonded to nitrogen and oxygen are involved in such bonds. The hydrogen bonds as viewed along [010] and [001] are shown in Figs. 3 and 4 respectively.

Data for the hydrogen bonds are summarized in Table 5. Inspection of the Table will indicate that eight of the hydrogen bonds of each molecule are the same, but the other two are different.

One of the latter, N(7)–H(29)···O(5), is unusually long. Indeed, the H(29)···O(5) distance is 2·54 Å, almost equal to the sum of the van der Waals radii, 2·60 Å. However, the N(7)–H(29) bond length equal to 0·78 Å is appreciably shorter than the internuclear distance of about 1·0 Å. Thus the internuclear H(29)···O(5) distance is presumably 0·2–0·3 Å less than the sum of the van der Waals radii. Furthermore, the hydrogen bond angle N–H···O differs by less than 16° from a straight angle. We conclude, therefore, that there is interaction between H(29) and O(5) corresponding to a weak hydrogen bond.

Similar arguments apply to the N(2)–H(11)···Cl(1) bond. The H(11)···Cl(1) distance of 2·91 Å is only slightly less than the sum of the van der Waals radii, 3·0 Å. However, the N(2)–H(11) bond is inordinately short and the internuclear distance must exceed the observed length by at least 0·35 Å. Thus the H(11)···Cl(1) internuclear distance is 0·3–0·4 Å less than the sum of the van der Waals radii, and this can be taken as evidence for a hydrogen bond.

There are no really short hydrogen bonds in the structure. Indeed, the lengths tend to be average or greater indicating rather weak bonds. Evidently minimum energy is attained in the crystal by maximizing the number of bonds at the expence of bond strength.

Conformation

The conformation of the arginine side group in various crystals, including the present compound (preliminary data), was discussed in a paper by Ramachandran, *et al.* (1966). A summary of the various angles φ, ψ and ψ_l in these compounds has been reported by Lakshminarayanan, Sasisekharan & Ramachandran (1967). In view of this, the discussion of the conformational aspects will be brief. The angles φ, ψ and ψ_l (as defined by Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga 1966) have been recalculated with the coordinates reported in this paper and these are listed in Table 6. They are all within 2 or 3° of the values for the preliminary structure.

The carboxyl oxygen atoms are appreciably tilted away from the plane N–C^{α}–C′ (by about 30°) in molecule II, while they are only about 6° out of plane in molecule I. On the other hand, the dihedral angle χ_1, which defines the location of the atom C^{γ}, is practically the same in both molecules, and is close to the value of 300°, corresponding to a *trans* conformation with respect to C′. This angle is near 180° in arginine HCl and near 60° in arginine $2H_2O$ and arginine 2HI (Lakshminarayanan *et al.*, 1967). The atoms C^{δ} and C^{ε} are both *trans* to C^{α} and C^{γ} respectively in both the molecules, a fact found to be universally true in all the arginine structures studied so far.

On the other hand, the angle χ_4 is *different* in the two molecules, being close to −90° and +90° respectively, so that the guanidyl group is rotated in opposite directions at C^{δ} in the two cases. The guanidyl groups themselves, however, are practically planar in both molecules, as noted above, and both have a closely similar conformation.

Table 5. *Hydrogen bonds in arginine hydrochloride*

Molecule I					Molecule II				
X–H···*Y*	H···*Y*	*X*···*Y*	Angle *X*–H–*Y*	SymOp† *X*→*Y*	*X*–H···*Y*	H···*Y*	*X*···*Y*	Angle *X*–H–*Y*	SymOp† *X*→*Y*
N(1)–H(1)····Cl(2)	2·25 Å	3·20 Å	162·1°	2	N(5)–H(18)···Cl(1)	2·38 Å	3·22 Å	151·4°	3
* –H(2)····O(4)	2·01	2·92	173·4	5	* –H(19)···O(2)	1·83	2·78	175·1	1
–H(3)····O(2)	1·85	2·80	173·7	2	–H(20)···O(5)	2·02	2·84	153·1	2
N(2)–H(11)···Cl(1)	2·91	3·36	130·7	1	N(6)–H(28)···Cl(2)	2·68	3·37	137·6	1
*N(3)–H(12)···O(1)	2·32	3·07	155·2	3	*N(7)–H(29)···O(5)	2·54	3·29	164·5	2
–H(13)···Cl(1)	2·44	3·28	156·8	4	–H(30)···Cl(2)	2·56	3·34	176·6	6
N(4)–H(14)···O(6)	2·11	2·97	168·9	2	N(8)–H(31)···O(3)	2·26	3·03	164·0	7
–H(15)···O(6)	2·03	2·90	167·6	5	–H(32)···O(3)	2·06	2·88	169·6	1
O(3)–H(16)···Cl(1)	2·39	3·20	165·9	1	O(6)–H(33)···Cl(2)	2·29	3·11	169·8	1
–H(17)···O(1)	2·21	2·98	157·2	2	–H(34)···O(4)	2·36	2·96	159·0	8

* Bonds which are different for the two molecules in the asymmetric unit.

† The following transformations define symmetry operations relating asymmetric unit containing donor atom *X* to asymmetric unit containing acceptor atom *Y*. (1) x, y, z; (2) $\bar{x}+1, y-\frac{1}{2}, \bar{z}+1$; (3) $\bar{x}+1, y+\frac{1}{2}, \bar{z}+1$; (4) $x, y+1, z$; (5) $x, y, z+1$; (6) $x, y-1, z$; (7) $\bar{x}, y+\frac{1}{2}, \bar{z}+1$; (8) $\bar{x}+1, y+\frac{1}{2}, \bar{z}$.

Table 6. *The various conformational angles in the two molecules of the structure*

(Notation as in Edsall *et al.*, 1966)

	ψ_1	ψ_2	χ_1	χ_2	χ_3	χ_4	χ_{51}	χ_{52}
Molecule I	154·9	332·0	306·1	173·9	185·2	96·7	346·0	166·3
Molecule II	174·1	353·6	301·1	195·6	179·3	276·0	10·6	189·7

Support under grant GM-10828 from the National Institutes of Health is gratefully acknowledged.

References

ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195.

DONOHUE, J. (1965). Private communication.

DONOHUE, J. & METZ, H. C. (1964). *Amer. Cryst. Assoc. Abstracts*, p. 47.

EDSALL, J. T., FLORY, P. J., KENDREW, J. C., LIQUORI, A. M., NEMETHY, G., RAMACHANDRAN, G. N. & SCHERAGA, H. A. (1966). *J. Mol. Biol.* **15**, 339; see also *Biopolymers*, **4**, 121.

HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* **19**, 676.

HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

KRAUT, J. (1964). Private communication.

KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 835.

LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). In *Conformation of Biopolymers*, Ed. G. N. RAMACHANDRAN. London: Academic Press.

MAZUMDAR, S. K. & SRINIVASAN, R. (1964). *Curr. Sci.* **33**, 573.

RAMACHANDRAN, G. N., MAZUMDAR, S. K., VENKATESAN, K. & LAKSHMINARAYANAN, A. V. (1966). *J. Mol. Biol.* **15**, 232.

RAMACHANDRAN, G. N., RAMAKRISHNAN, C. & SASISEKHARAN, V. (1963). In *Aspects of Protein Structure*, Ed. G. N. RAMACHANDRAN, p. 121. London: Academic Press.

STEWART, J. M. (1964). Technical Report Tr64-6. (NSG-398). Computer Science Center, Univ. of Maryland and Research Computing Center, Univ. of Washington.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

STEWART, R. F. & JENSEN, L. H. (1969). *Z. Kristallogr.* **128**, 133.

SUTTON, L. E. (1965). *Interatomic Distances and Molecular Configurations in Molecules and Ions, Supplement*. Special Publication No. 18, S19s. London: The Chemical Society.

Acta Cryst. (1970). B**26**, 1671

Die Kristallstruktur von Triazidocarbonium-hexachloroantimonat, $[C(N_3)_3]SbCl_6$

VON ULRICH MÜLLER* UND HARTMUT BÄRNIGHAUSEN

Institut für Anorganische Chemie der Universität, 75 *Karlsruhe*, *Englerstrasse* 11, *Deutschland*

(*Eingegangen am* 7. *Juli* 1969)

$[C(N_3)_3]SbCl_6$ crystallizes in space group $P2_1/c$ with 4 formula units per unit cell; the lattice parameters are $a = 9{\cdot}27$, $b = 10{\cdot}96$, $c = 15{\cdot}30$ Å and $\beta = 113{\cdot}4°$. The crystal structure was solved by means of three-dimensional Patterson and Fourier syntheses and refined by the method of least-squares to a reliability index of $R = 6{\cdot}8\%$ for the 1070 observed reflexions. The structure is built up from not quite planar, propeller-like $C(N_3)_3^+$ ions (idealized point symmetry 3) and practically octahedral $SbCl_6^-$ ions in an arrangement that has some resemblance to the structure type of CsCl. The bond lengths between the nitrogen atoms of the three very similar, non-linear azido groups of the $C(N_3)_3^+$ ion differ widely, the mean values of 1·39 Å for α-N-β-N and 1·05 Å for β-N-γ-N leading to the conclusion that these correspond to single and triple bonds respectively. The three C-α-N distances (mean value 1·34 Å) show partial π-bonding.

Einleitung

Triazidocarbonium-hexachloroantimonat $[C(N_3)_3]SbCl_6$ wurde erstmals von Müller & Dehnicke (1966) dargestellt und charakterisiert. Der aus der Bandenzahl des Infrarot-Spektrums abgeleitete Strukturvorschlag, der für das $C(N_3)_3^+$-Ion die Punktsymmetrie $3m$ (C_{3v}) postulierte, blieb jedoch nicht unwidersprochen. So nahm Schmidt (1967) im Rahmen einer Arbeit über strukturell verwandte Verbindungen auch das IR-Spektrum von $[C(N_3)_3]SbCl_6$ erneut auf und deutete es an Hand eines Modells der Punktsymmetrie $\bar{6}$ (C_{3h}). Um zu einer zuverlässigen und insbesondere weiterreichenden Information über die Geometrie des $C(N_3)_3^+$-Ions zu gelangen, haben wir die vorliegende röntgenographische Kristallstrukturbestimmung unternommen. Sie zeigt, dass das $C(N_3)_3^+$-Ion im Kristallverband zwar streng genommen symmetrielos ist, dass aber die Punktsymmetrie 3 (C_3) eine sehr gute Näherung darstellt und dass sogar die Abweichung von $\bar{6}$ noch relativ klein ist.

Experimentelles und Kristalldaten

Zu röntgenographischen Untersuchungen geeignete Einkristalle von $[C(N_3)_3]SbCl_6$ erhielten wir aus einer Lösung des Präparats in 1,2-Dichloräthan durch partielles Verdunsten des Lösungsmittels unter verminder-

---

* Gegenwärtige Anschrift: Institut für Anorganische Chemie der Universität, 355 Marburg, Gutenbergstr. 18, Deutschland.