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The Crystal Structures of L-Citrulline Hydrochloride and L-Homocitrulline Hydrochloride

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The crystal structures of L-citrulline hydrochloride and its homologue L-homocitrulline hydrochloride have been determined using diffractometer data. L-Citrulline hydrochloride: $NH_2CONH(CH_2)_3CH(NH_3^+)COOH.Cl^-$, monoclinic, $C2$, $a=18{\cdot}089$, $b=5{\cdot}150$, $c=11{\cdot}918$ Å, $\beta=106{\cdot}9°$, $R=0{\cdot}040$, the average e.s.d. of the bond distances 0·005 Å. L-Homocitrulline hydrochloride: $NH_2CONH(CH_2)_4CH(NH_3^+)COOH.Cl^-$, orthorhombic, $P2_12_12_1$, $a=10{\cdot}518$, $b=21{\cdot}627$, $c=4{\cdot}916$ Å, $R=0{\cdot}069$, the average e.s.d. of the bond distances 0·008 Å. There is a close similarity between the dimensions of the citrulline and homocitrulline molecules in the two crystals. Also there are several common features in the two hydrogen bond schemes. The present L-citrulline HCl structure is compared with that reported previously (Naganathan & Venkatesan, *Acta Cryst.* (1971), B**26**, 790), and some significant differences between the two results are pointed out.

Introduction

Citrulline is an intermediate in the ornithine cycle in mammals. In nature it is found in the water melon. Although this is not a constituent amino acid of proteins, the conformation and the size of this acid are of importance in connexion with the basic amino acids such as lysine, arginine and ornithine. The present paper deals with the crystal structures of L-citrulline hydrochloride,

$NH_2CONH(CH_2)_3CH(NH_3^+)COOH.Cl^-$,

and its homologue L-homocitrulline hydrochloride, $NH_2CONH(CH_2)_4CH(NH_3^+)COOH.Cl^-$.

When the present paper was under preparation, the crystal structure of L-citrulline hydrochloride was presented by Naganathan & Venkatesan (1971). There are, however, small but significant discrepancies in the two structures obtained independently. The unit cell dimensions and some of the bond distances in their results are a little smaller than those in ours. For a few atoms, their y parameters deviate significantly from ours. Thus our structure of L-citrulline hydrochloride is also reported here, although the primary purpose of the present paper lies in the critical comparison of the structures of citrulline and homocitrulline.

Experimental

Each crystal was obtained by recrystallization from a solution of the amino acid in a dilute hydrochloride containing a small amount of acetone. Preliminary X-ray work on the crystals was done using the photographic method. The determination of the cell size and the intensity measurements were performed on the Rigaku Denki Computer-controlled four-circle diffractometer (AFC-II and IV). Zr-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å) was used with a pulse height analyser, and integrated intensities were measured by the $\omega/2\theta$-scan method, in which the background intensity was estimated from the intensity measurements at the starting and the end points of every scan. Two or three standard reflexions were monitored after the measurement of every 50 reflexions. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was made in view of the small linear absorption coefficient for Mo $K\alpha$ radiation. The crystallographic data and some details of the intensity measurement are listed in Table 1.

Structure determination

The procedures for the structure determination and the refinement were almost the same for both crystals. Most of the non-hydrogen atoms could be located from the heavy atom Fourier synthesis based on the chloride ion. The hydrogen atoms were found on the difference electron density map, and were included in the refinement. The computation was done on the NEAC 2200-500 computer in the Computing Centre of this University. The block-diagonal least-squares program *HBLS* IV (Ashida, 1967) was used, which minimizes $\sum w(|F_o|-|F_c|)^2$. The weighting scheme was: $w=1{\cdot}0$ when $F_o\neq 0$ and $w=0{\cdot}5$ when $F_o=0$. The scattering factors for all the atoms were taken from *International Tables for X-ray Crystallography* (1962).

The structure of L-citrulline hydrochloride

The final R value is 0·042 for all reflexions. The final atomic parameters are listed in Tables 2 and 3, and the observed and calculated structure factors in Table 4.

Table 1. *The crystallographic data and experimental conditions*

	Citrulline hydrochloride	Homocitrulline hydrochloride
Crystallographic data		
Shape of crystals	plate	needle
Crystal system	monoclinic	orthorhombic
Space group	$C2$	$P2_12_12_1$
a	18·089	10·518 Å (±0·1 %)
b	5·150	21·627
c	11·918	4·916
β	106·9°	
Z	4	4
ϱ_{obs}*	1·32	1·32 g.cm^{-3}
ϱ_{calc}	1·32	1·34
Experimental		
Scan speed (2θ/min)	2	4°
Background counting time	15	7·5 sec
Scan range (2θ)	$1{\cdot}4+0{\cdot}76 \tan \theta_B$	$2{\cdot}0+0{\cdot}7 \tan \theta_B$†
μ (Mo $K\alpha$)	3·62	3·45 cm^{-1}
Crystal size	0·20 × 0·15 × 0·35	0·05 × 0·33 × 0·30 mm
Maximum $2\theta_B$	55	55°
No. of reflexions	1363	1691

* by the flotation method
† θ_B: Bragg angle

Table 2. *Citrulline hydrochloride: the final atomic coordinates (fractional) and thermal parameters* (× 10^4) *with standard deviations in parentheses*

Standard deviations are in units of the last digits. The anisotropic coefficients have the form: $\exp \{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0·1568 (1)	0·2500 (3)	0·1479 (1)	40 (0)	296 (3)	56 (1)	6 (2)	47 (1)	41 (3)
C(1)	0·1504 (2)	0·6016 (8)	0·4831 (3)	19 (1)	274 (15)	43 (2)	−1 (7)	7 (2)	9 (10)
C(2)	0·1353 (2)	0·8132 (7)	0·3917 (3)	20 (1)	216 (14)	49 (2)	−5 (6)	9 (2)	−1 (9)
C(3)	0·0495 (2)	0·8454 (8)	0·3247 (3)	19 (1)	221 (12)	58 (2)	8 (6)	11 (3)	22 (10)
C(4)	0·0092 (2)	0·6004 (8)	0·2659 (3)	18 (1)	247 (15)	68 (3)	−6 (7)	13 (3)	−17 (11)
C(5)	−0·0716 (2)	0·6725 (8)	0·1895 (3)	19 (1)	333 (17)	62 (3)	−26 (7)	8 (3)	31 (11)
C(6)	−0·1620 (2)	0·3078 (8)	0·1709 (3)	16 (1)	343 (18)	49 (2)	4 (7)	12 (2)	−39 (10)
N(1)	0·1821 (1)	0·7586 (8)	0·3105 (2)	20 (1)	263 (11)	57 (2)	−16 (7)	21 (2)	41 (11)
N(2)	−0·1155 (2)	0·4522 (9)	0·1275 (3)	24 (1)	518 (18)	45 (2)	−70 (8)	20 (2)	−47 (11)
N(3)	−0·2075 (2)	0·1385 (8)	0·0964 (3)	27 (1)	395 (15)	50 (2)	−43 (7)	20 (2)	−65 (10)
O(1)	0·1921 (1)	0·4191 (6)	0·4823 (2)	27 (1)	268 (10)	57 (2)	29 (5)	20 (2)	47 (8)
O(2)	0·1148 (2)	0·6443 (8)	0·5614 (2)	47 (1)	577 (18)	64 (2)	150 (8)	58 (3)	139 (11)
O(3)	−0·1646 (1)	0·3252 (7)	0·2735 (2)	31 (1)	480 (16)	49 (2)	−65 (7)	33 (2)	−85 (9)

The bond distances and angles are shown in Fig. 1. The averages of the standard deviations for the bond distances and angles among the C, N and O atoms are 0·005 Å and 0·3° respectively.

The lengths of the seven C–H bonds are in the range 0·96 to 1·11 Å with an average of 1·02 Å, and the lengths of the six N–H bonds range from 0·90 to 0·99 Å with an average of 0·95 Å. One O–H bond is 1·05 Å long.

As expected, the crystal structure obtained agrees essentially with that reported by Naganathan & Venkatesan (1971). The citrulline molecule consists of three planar groups, the carboxyl group (I), the aliphatic *trans* zigzag chain (II) and the carbamylamino group (III). The equations of the best planes are listed in Table 5, and the relative orientations of these planar

Table 3. *The final parameters of the hydrogen atoms*

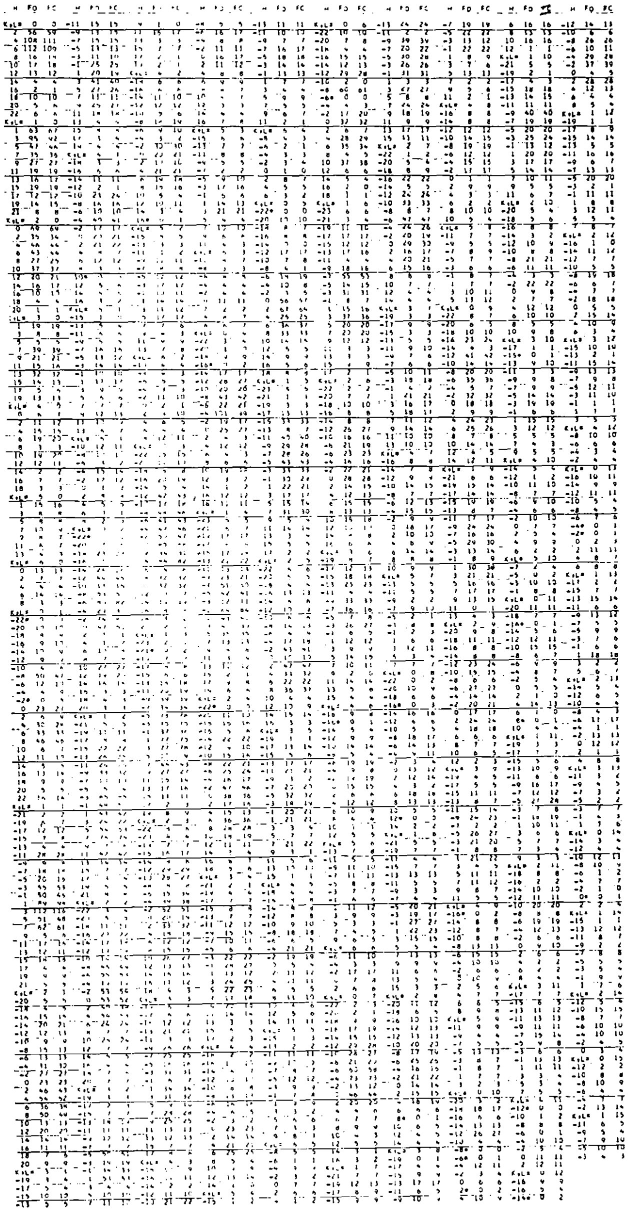
	x	y	z	B(Å^2)	Bonded to
H(1)	0·173	0·606	0·268	2·7	N(1)
H(2)	0·176	0·892	0·255	1·8	N(1)
H(3)	0·237	0·775	0·346	2·4	N(1)
H(4)	−0·117	0·456	0·052	1·2	N(2)
H(5)	−0·202	0·112	0·020	2·7	N(3)
H(6)	−0·234	−0·003	0·125	1·8	N(3)
H(7)	0·130	0·518	0·633	5·0	O(2)
H(21)	0·155	0·974	0·431	1·5	C(2)
H(31)	0·041	0·995	0·262	1·0	C(3)
H(32)	0·023	0·918	0·376	0·5	C(3)
H(41)	0·005	0·483	0·326	2·5	C(4)
H(42)	0·043	0·524	0·212	1·0	C(4)
H(51)	−0·101	0·785	0·243	1·6	C(5)
H(52)	−0·068	0·801	0·131	1·2	C(5)

$\langle\sigma(x)\rangle=0{\cdot}04$ $\langle\sigma(y)\rangle=0{\cdot}05$ $\langle\sigma(z)\rangle=0{\cdot}04$ Å
$\langle\sigma(B)\rangle=0{\cdot}9$ Å^2

groups are shown in Fig. 5. These three planes are found to intersect roughly perpendicularly to each other; the dihedral angles are 88° for I and II, 77° for I and III, and 90° for II and III.

Since the hydrogen bond scheme is the same as that given in Fig. 2 of Naganathan & Venkatesan (1971), the packing diagram is omitted here. The H(3) atom of the α-amino group participates in the bifurcated hydrogen bond, in which the two acceptor atoms are located fairly symmetrically with respect to the N^{α}–H(3) bond. Some of the details around the hydrogen bonds are shown in Fig. 2.

Table 4. *Citrulline hydrochloride: observed and calculated structure factors*



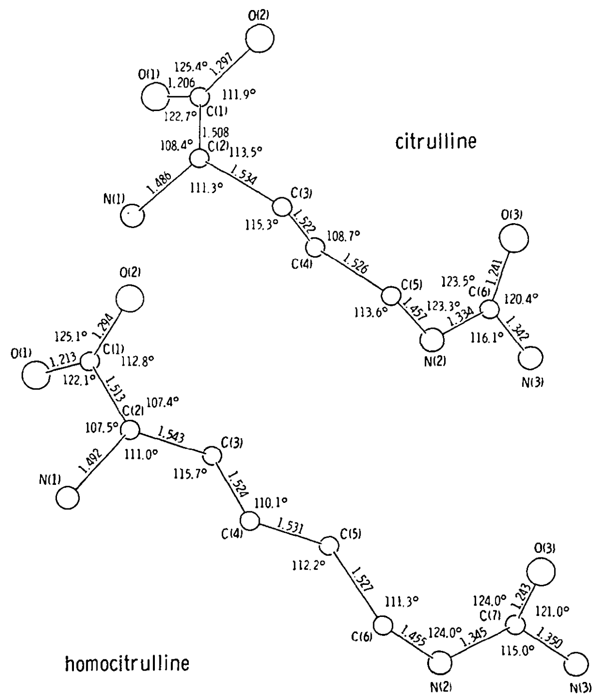


Fig. 1. Bond distances and angles. The averages of the standard deviations are 0·005 Å and 0·3° for citrulline, and 0·008 Å and 0·5° for homocitrulline.

The structure of L-homocitrulline hydrochloride

The final R value is 0·069 for all non-zero reflexions, and it is 0·086 if all the reflexions are included. The parameters are listed in Tables 6 and 7, and the observed and calculated structure factors in Table 8. The bond distances and angles are shown in Fig. 1. The averages of the standard deviations for the bond distances and angles are 0·008 Å and 0·5° respectively.

The nine C–H bond distances range from 0·96 to 1·07 Å with an average of 1·02 Å, and the six N–H bonds from 0·85 to 1·02 Å with an average of 0·91 Å. One O–H distance is 0·92 Å.

The homocitrulline molecule also consists of three planar groups, the carboxyl group (I), the *trans* zigzag aliphatic chain (II), and the carbamylamino group (III). The equations of the planes are listed in Table 9. The dihedral angles among the planes are 100° for I and II, 88° for I and III, and 96° for II and III.

The homocitrulline molecule and the chloride ion are held together in the crystal by seven hydrogen bonds. The hydrogen bond scheme is shown in Figs. 3 and 4.

Discussion

Conformation

The conformations of the citrulline and homocitrulline molecules in their hydrochloride crystals are compared in Fig. 5. As mentioned previously, each molecule consists of the three planar groups, the car-

Table 5. *Citrulline hydrochloride*: *best planes and displacements from the planes*

(*a*) Equations of the best planes
$X=ax+cz\cos\beta,\ Y=by,\ Z=cz\sin\beta$

		Atoms
I†	$0\cdot6553X+0\cdot5124Y+0\cdot5550Z=5\cdot3359$	O(1) O(2) C(1) C(2)
II†	$0\cdot5641X+0\cdot2160Y-0\cdot7970Z=-2\cdot1024$	N(2) C(2) C(3) C(4) C(5)
III	$0\cdot6604X-0\cdot6971Y+0\cdot2791Z=-2\cdot7712$	O(3) N(2) N(3) C(6)

boxyl group, the carbamylamino group and the aliphatic side chain. A fully extended planar conformation of the aliphatic side chain is a common characteristic of the related basic amino acids so far reported. The conformations of the two molecules are, however, different from each other owing to the internal rotation of the C^{α}–C^{β} bonds. The conformation of the carboxyl group and the aliphatic chain in citrulline is the same as that of arginine found in its dihydrate (Karle & Karle, 1964), while the conformation of the lysine part of homocitrulline is the one which is found in L-lysine.HCl.$2H_2O$ (Wright & Marsh, 1962). The difference in the conformations may be due to the necessity of making up the effective hydrogen bond

Table 5 (*cont.*)

(*b*) Displacements (Å) of atoms from the planes

I		II		III	
O(1)	0·002	N(2)	0·019	O(3)	−0·001
O(2)	0·002	C(2)	0·061	N(2)	−0·001
C(1)	−0·006	C(3)	−0·039	N(3)	−0·001
C(2)	0·002	C(4)	−0·072	C(6)	0·002
N(1)*	0·083	C(5)	0·027	C(5)*	−0·211
C(3)*	−1·202	N(1)*	1·375	H(4)*	−0·102
H(7)*	0·139	C(1)*	−1·029	H(5)*	0·095
		C(6)*	−1·095	H(6)*	0·210

* Atoms with asterisks are not included in the calculation of the best planes.

† In the report of Naganathan & Venkatesan (1971) there seem to be misprints in the signs of coefficients of the equations of the planes II and III.

Table 6. *Homocitrulline hydrochloride*: *the final atomic coordinates and thermal parameters with standard deviations*

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0·0695 (1)	0·8285 (1)	0·0238 (2)	81 (1)	16 (0)	356 (5)	2 (1)	−56 (5)	1 (2)
C(1)	1·0819 (5)	1·0182 (2)	0·3161 (11)	65 (5)	17 (1)	321 (21)	25 (4)	−39 (19)	−18 (8)
C(2)	1·0286 (4)	0·9707 (2)	0·5109 (11)	62 (4)	14 (1)	267 (19)	9 (3)	24 (18)	−1 (8)
C(3)	0·8987 (5)	0·9497 (2)	0·3976 (10)	51 (4)	20 (1)	388 (25)	10 (4)	−36 (18)	−44 (9)
C(4)	0·8316 (5)	0·8992 (2)	0·5588 (12)	57 (4)	22 (1)	368 (25)	17 (4)	−57 (20)	−32 (10)
C(5)	0·7169 (5)	0·8750 (3)	0·3993 (13)	56 (4)	23 (1)	456 (29)	20 (4)	−61 (21)	−8 (11)
C(6)	0·6486 (5)	0·8227 (2)	0·5485 (13)	68 (5)	18 (1)	484 (29)	16 (4)	−94 (22)	−28 (11)
C(7)	0·4358 (5)	0·8172 (2)	0·3359 (12)	57 (4)	16 (1)	432 (24)	16 (4)	−26 (21)	7 (9)
N(1)	1·1201 (4)	0·9180 (2)	0·5210 (10)	56 (3)	17 (1)	332 (19)	6 (3)	−11 (17)	−18 (8)
N(2)	0·5528 (4)	0·7939 (2)	0·3767 (12)	64 (4)	15 (1)	607 (28)	4 (3)	−89 (21)	33 (9)
N(3)	0·3669 (4)	0·7883 (2)	0·1422 (12)	72 (4)	22 (1)	541 (28)	−8 (4)	−93 (21)	98 (10)
O(1)	1·1652 (4)	1·0057 (2)	0·1547 (9)	77 (4)	23 (1)	422 (19)	3 (3)	97 (16)	−46 (8)
O(2)	1·0257 (4)	1·0713 (2)	0·3348 (10)	131 (5)	18 (1)	605 (26)	−11 (4)	224 (22)	−57 (8)
O(3)	0·3909 (3)	0·8613 (2)	0·4663 (10)	76 (3)	22 (1)	587 (24)	−13 (3)	−87 (18)	102 (9)

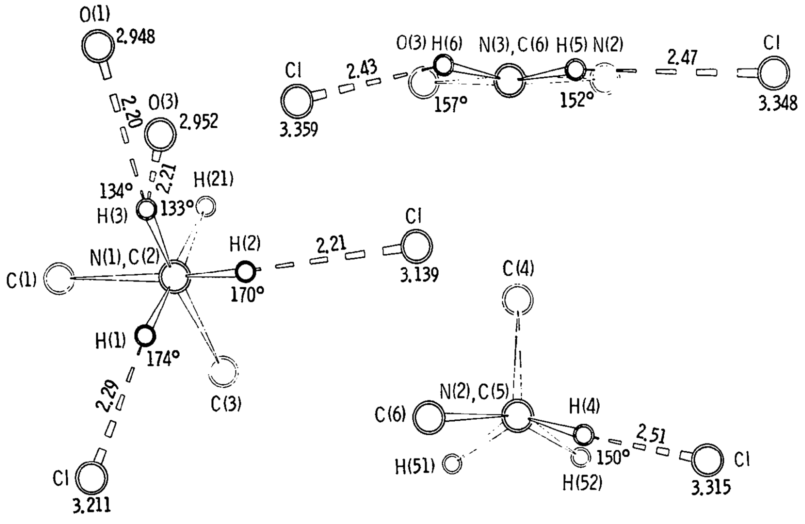


Fig. 2. Citrulline hydrochloride: The environments of the hydrogen bonds viewed down the N–C bonds. The donor–acceptor distances are shown near by the acceptor atoms. The H–acceptor distances and the donor–H–acceptor angles are also shown. The H(3) atom participates in a bifurated hydrogen bond. One more hydrogen bond in the crystal is O(2)–H(7)···O(3); O(2)···O(3)=2·520 Å, H(7)···O(3)=1·49 Å, ∠O(2)–H(7)···O(3)=169°.

Table 7. *Homocitrulline hydrochloride: the final parameters of the hydrogen atoms*

	x	y	z	B(Å^2)	Bonded to
H(1)	1·108	0·897	0·668	1·9	N(1)
H(2)	1·124	0·893	0·346	3·1	N(1)
H(3)	1·205	0·935	0·518	3·6	N(1)
H(4)	0·571	0·759	0·292	1·7	N(2)
H(5)	0·396	0·761	0·034	2·6	N(3)
H(6)	0·291	0·807	0·135	5·1	N(3)
H(7)	1·057	1·096	0·199	6·0	O(2)
H(21)	1·021	0·989	0·711	1·8	C(2)
H(31)	0·846	0·988	0·397	0·9	C(3)
H(32)	0·916	0·937	0·196	1·1	C(3)
H(41)	0·808	0·912	0·760	3·9	C(4)
H(42)	0·888	0·865	0·590	0·9	C(4)
H(51)	0·657	0·908	0·370	2·0	C(5)
H(52)	0·742	0·864	0·212	3·5	C(5)
H(61)	0·611	0·837	0·732	1·8	C(6)
H(62)	0·714	0·789	0·600	1·2	C(6)

$\langle\sigma(x)\rangle=0·06$ $\langle\sigma(y)\rangle=0·06$ $\langle\sigma(z)\rangle=0·07$ Å
$\langle\sigma(B)\rangle=1·4$ Å^2

Table 8. *Homocitrulline hydrochloride: observed and calculated structure factors* (×5)

K	FO	FC
H,L=	0	0
2	80	81
4	128	132
6	330	344
8	225	227
10	155	155
12	141	142
14•	0	7
16	34	34
18	30	33
20	102	105
22	22	14
24	50	51
26	72	71
28	31	34
30	19	10
H,L=	0	1
1	175	171
2	94	98
3	364	378
4	340	357
5	93	101
6	55	55
7	150	160
8	61	56
9	98	94
10	49	49
11	172	175
12	23	28
13	104	101
14	120	129
15	33	32
16	57	56
17	60	62
18	40	48
19	112	114
20	21	21
21	10	1
22	20	28
23	39	30
24	17	17
25	20	27
26•	0	9
27	22	15
28	17	9
29•	0	8
H,L=	0	2
0	347	351
1	52	54
2	105	107
3	9	4
4	234	233
5	108	111
6	120	131
7	60	67
8	97	98
9	52	52
10	72	66
11	118	112
12	80	75
13	63	62
14	112	112
15	75	70
16	40	47
17	11	14
18	14	11
19	45	45
20	63	61
21	10	1
22	29	30
23	34	27
24	48	45
25	14	1
26	31	33
27•	0	6
28	14	18
H,L=	0	3
1	39	41
2	80	84
3	129	129
4	72	71
5	153	151
6	35	37
7	101	97
8	54	59
9	30	35
10	32	30
11	37	30
12	[illegible]	14
13	67	72
14	[illegible]	47
15	[illegible]	[illegible]
16	[illegible]	2
17	47	44
18•	[illegible]	11
19	53	51
20	21	26
21•	[illegible]	2
22	14	14
23•	0	7
24	[illegible]	18
25	51	47
26	[illegible]	24
27•	0	3
H,L=	0	4
0	37	29
1	52	58
2	22	21
3	55	59
4	64	59
5	24	25
6	[illegible]	56
7	[illegible]	29
8	34	34
9	71	74
10	53	54
11	94	96
12	77	78
13•	0	0
14	66	68
15	54	53
16	38	36
17	21	20
18	5	0
19	25	26
20	46	48
21	34	26
22	12	6
23	21	6
24•	0	1
H,L=	0	5
1	37	40
2•	0	3
3•	0	0
4	16	13
5	19	26
6	15	12
7	21	27
8	54	51
9	13	1
10	17	9
11	22	17
12	12	6
13•	0	6
14	22	17
15	34	26
16•	0	7
17	20	18
18	19	23
19	41	38
20	15	8
H,L=	0	6
0	47	53
1	31	28
2	23	5
3	36	36
4•	0	14
5	7	1
6	35	34
7•	0	10
8	20	15
9	37	32
10	8	5
11	25	22
12	38	29
13•	0	4
14	4	5
H,L=	1	0
1	178	176
2	27	17
3	78	70
4	200	197
5	270	276
6	90	91
7	79	75
8	191	191
9	8	5
10	150	157
11	100	104
12	71	74
13	137	138
14	116	108
15	28	23
16	204	200
17•	0	4
18	19	23
19	15	22
20	7	8
21	29	25
22	61	60
23	20	22
24	13	14
25•	0	1
26	23	17
27	8	4
28	28	22
29	8	11
30	11	4
H,L=	1	1
0	62	63
1	101	104
2	412	408
3	557	563
4	196	202
5	287	293
6	94	97
7	231	229
8	20	13
9	163	164
10	90	90
11	104	105
12	140	138
13•	0	2
14	24	23
15	40	35
16	102	101
17	119	120
18	33	32
19	19	17
20	50	50
21	24	30
22	33	31
23	62	65
24	22	26
25	22	21
26	17	7
27	35	31
28	23	24
29	28	34
H,L=	1	2
0	146	144
1	164	163
2	221	221
3	134	129
4	99	99
5	60	58
6	166	163
7	29	28
8	87	87
9	124	120
10	127	126
11•	0	11
12	96	95
13	56	57
14	114	116
15	22	18
16	62	60
17	59	56
18	57	57
19	28	31
20	33	33
21	23	23
22	58	57
23	27	25
24	36	36
25	14	13
26•	0	4
27	24	19
28	17	21
H,L=	1	3
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1	61	61
2•	0	8
3	122	120
4	72	68
5	60	55
6	61	62
7	38	36
8	69	73
9	103	106
10	74	78
11	17	9
12	88	90
13	66	63
14	54	55
15	32	25
16	68	71
17	51	56
18	58	54
19•	0	10
20	18	18
21	49	43
22	15	21
23	18	23
24	20	17
25	31	25
26	6	2
27	22	25
H,L=	1	4
0•	0	0
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2	93	90
3	42	42
4	52	52
5	54	60
6	59	59
7	22	15
8	22	32
9	46	41
10	56	51
11	18	13
12	46	52
13	9	14
14	41	41
15	11	20
16•	0	6
17	25	26
18	23	18
19•	2	14
20	18	20
21	12	19
22	49	49
23•	0	15
24•	0	7
H,L=	1	5
0	13	12
1	21	23
2	69	72
3	65	63
4	28	30
5	20	20
6	45	50
7	15	15
8	49	40
9	51	49
10•	0	15
11	13	17
12	11	15
13	8	23
14	39	36
15	19	17
16	20	17
17	29	31
18	27	27
19	24	17
20	8	12
H,L=	1	6
0	9	10
1	46	45
2	14	13
3	21	17
4•	0	13
5•	0	11
6	18	3
7	17	24
8	23	18
9	10	2
10	18	14
11•	0	14
12	17	15
13	23	18
14	20	11
H,L=	2	0
0	422	432
1	88	73
2	32	35
3	109	106
4	94	92
5	204	206
6	120	124
7	100	100
8	297	299
9	202	197
10	78	76
11	146	144
12	65	66
13	162	161
14	47	43
15	69	66
16	17	19
17	53	55
18•	0	8
19	54	50
20	71	72
21	78	74
22	35	35
23	74	77
24•	0	8
25	25	26
26	21	28
27	6	13
28	18	17
29	13	11
H,L=	2	1
0	118	114
1	178	179
2	28	26
3	198	195
4	240	239
5	156	149
6	277	283
7	126	119
8	77	71
9	124	121
10	123	120
11	144	138
12	92	87
13	109	105
14	76	72
15	38	40
16	49	49
17	8	12
18	88	88
19	86	85
20	13	15
21	26	23
22	51	49
23	21	18
24	22	20
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26	31	31
27	13	12
28	9	8
29	14	4
H,L=	2	2
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1	189	185
2	78	75
3	37	36
4	60	53
5	79	81
6	138	138
7	216	214
8	155	151
9	117	112
10	115	113
11	65	64
12	35	32
13	147	148
14	45	51
15	51	52
16	59	61
17	22	20
18	65	66
19	63	64
20	44	45
21	57	51
22	23	12
23	29	27
24	37	34
25	32	33
26	18	18
27	8	14
28•	0	7
H,L=	2	3
0	93	93
1	92	85
2	120	123
3	96	98
4	79	79
5	119	115
6	77	72
7	52	51
8	7	15
9	75	75
10	48	48
11	57	55
12	14	18
13	34	38
14	25	14
15	58	65
16	40	42
17	48	46
18	29	33
19	26	23
20	21	24
21	11	16
22	29	25
23•	0	8
24	14	17
25	28	29
26	34	35
H,L=	2	4
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1	85	89
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3	27	24
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5	38	44
6	61	63
7	78	80
8	38	35
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10	36	32
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14	27	31
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16	19	18
17	20	24
18	20	17
19	41	36
20	23	25
21	35	33
22	28	29
23	14	9
24	17	19
H,L=	2	5
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2	63	65
3	50	47
4	36	30
5	24	10
6	45	46
7	21	29
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9	23	26
10	19	24
11	16	24
12	22	14
13•	0	15
14	22	19
15	30	29
16	6	15
17	7	15
18	23	17
19	31	24
20	16	10
H,L=	2	6
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3	21	18
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8•	0	18
9	28	21
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11	20	16
12	19	10
13	23	10
14	11	19
H,L=	3	0
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2	5	3
3	322	324
4	316	318
5	54	55
6	23	24
7	167	163
8	239	235
9	78	77
10	142	138
11	141	135
12	55	48
13	60	60
14	27	25
15	65	66
16	19	27
17	49	42
18	27	33
19	97	103
20	23	11
21	71	72
22	31	31
23	49	50
24	28	30
25	31	28
26	16	0
27•	0	9
28	17	10
29	18	20
H,L=	3	1
0	36	37
1	85	81
2	85	85
3	150	146
4	267	264
5	231	224
6	309	297
7	185	177
8	108	103
9	17	15
10	161	155
11	48	45
12	52	50
13	14	13
14	49	46
15	65	66
16	113	117
17	13	23
18	10	17
19	44	49
20	85	89
21	40	46
22	42	43
23	15	11
24	37	31
25•	0	5
26	23	22
27	14	21
28	26	33
29•	0	4
H,L=	3	2
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2	100	98
3	210	205
4	120	115
5	70	71
6	47	41
7	152	148
8	154	143
9	125	123
10	35	33
11	48	47
12	17	19
13	40	39
14	19	19
15	60	59
16	56	55
17	28	24
18	54	52
19	30	35
20	40	42
21	36	33
22	20	25
23	47	45
24	34	31
25	12	11
26	20	22
27	17	18
28•	2	19
H,L=	3	3
0	33	31
1	85	87
2	26	25
3	62	60
4	166	164
5	119	119
6	41	43
7	18	13
8	65	66
9	28	28
10	113	115
11	64	69
12	52	51
13	72	71
14•	0	12
15	20	25
16	112	118
17	37	38
18	43	41
19	29	34
20•	0	8
21	18	19
22	29	30
23	19	6
24	34	26
25	16	20
26	22	4
H,L=	3	4
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1	51	54
2	20	24
3	66	65
4	27	27
5	40	44
6	49	50
7	49	48
8	75	73
9	70	69
10	18	8
11	23	27
12	46	49
13	13	19
14	35	34
15	46	46
16	18	10
17	22	18
18	10	14
19	3	4
20	21	21
21	17	14
22•	0	5
23	28	21
H,L=	3	5
0	26	25
1	32	34
2	24	19
3	27	22
4	38	42
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18	27	29
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H,L=	3	6
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1	32	32
2•	0	12
3	11	14
4	25	16
5	29	26
6	23	15
7	25	19
8	26	19
9	25	27
10	19	16
11	25	16
12	22	25
13•	0	11
H,L=	4	0
0	373	374
1	129	130
2	40	36
3	136	137
4	35	40
5	71	75
6	85	85
7	99	95
8	17	8
9	66	67
10	43	42
11	13	12
12	66	64
13	128	124
14	16	16
15	26	29
16	12	14
17	104	103
18	29	30
19	34	27
20	16	16
21	8	5
22	46	50
23	42	44
24	8	10
25	47	47
26	24	26
27	29	27
28•	0	7
29	18	14
H,L=	4	1
0	125	124
1	84	80
2	232	229
3	212	205
4	209	202
5	57	52
6	224	217
7	104	104
8	150	142
9	45	41
10	118	113
11	109	100
12	108	100
13	19	14
14	110	110
15•	0	11
16	42	49
17	50	49
18	71	73
19	11	19
20	71	71
21	51	46
22	46	45
23	28	35
24	15	29
25	14	1
26	32	37
27	22	19
28	20	0
H,L=	4	2
0	144	138
1	131	128
2	155	152
3	73	69
4	151	147
5	57	57
6	30	29
7	146	141
8	90	85
9	64	61
10	34	36
11	56	60
12	73	70
13	132	126
14	32	32
15	35	36
16	37	32
17	38	38
18	54	57
19	57	55
20	11	3
21	38	35
22	26	24
23	12	20
24	30	23
25	24	19
26	14	6
27	30	30
H,L=	4	3
0	141	138
1	47	48
2	13	14
3	63	64
4•	0	12
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6	118	120
7	46	51
8	38	36
9	61	60
10	27	29
11	45	44
12	95	89
13	29	31
14•	0	16
15	36	35
16	21	14
17	12	10
18	45	43
19	26	20
20	11	27
21	30	28
22	21	11
23	20	16
24	22	25
25	17	9
H,L=	4	4
0	15	11
1	61	58
2	54	52
3	42	39
4	67	67
5	33	27
6	36	38
7	55	58
8	10	8
9•	0	3
10	27	24
11	50	51
12	31	34
13	53	51
14•	0	4
15	38	33
16	41	38
17	12	12
18	18	20
19	24	35
20	13	14
21	27	28
22	22	15
23•	0	10
H,L=	4	5
0	14	13
1	11	7
2	52	55
3	30	34
4	31	26
5	46	44
6	34	26
7	42	38
8	45	45
9	43	43
10	17	24
11	41	35
12	42	36
13	22	20
14•	0	14
15•	0	18
16•	0	4
17	42	41
18•	2	19
19	21	10
H,L=	4	6
0•	0	7
1	20	13
2	31	25
3•	0	4
4	22	20
5•	0	16
6	10	7
7	9	22
8	19	16
9	21	17
10•	0	11
11	4	10
12	23	19
H,L=	5	0
1	112	115
2	101	98
3	111	111
4	78	74
5•	0	14
6	28	26
7	49	43
8	18	16
9	253	253
10	171	165
11	151	141
12	35	32
13	48	51
14	17	18
15	170	168
16	71	69
17	95	92
18	44	40
19	68	69
20	15	20
21	44	41
22	43	41
23	8	10
24	14	3
25	45	43
26	29	27
27	15	2
28•	0	7
H,L=	5	1
0•	0	9
1	90	86
2	118	115
3	148	146
4	67	63
5	76	75
6	26	24
7	102	97
8	43	42
9	96	96
10	87	87
11	48	47
12	45	46
13	65	65
14	57	60
15	70	70
16	14	16
17	12	15
18	39	33
19	16	21
20	20	33
21	18	25
22	45	39
23	22	27
24	8	13
25	24	28
26	35	34
27•	0	12
28	19	23
H,L=	5	2
0	27	29
1	68	64
2	109	103
3	95	94
4	118	112
5	117	113
6	40	39
7	55	52
8	21	15
9	64	60
10	83	83
11	58	55
12	47	49
13	42	52
14	63	64
15	69	80
16	44	49
17	57	59
18	26	28
19	16	13
20	18	14
21	39	33
22	33	34
23	30	30
24	24	25
25	4	11
26	28	30
27	6	11
H,L=	5	3
0	34	31
1	68	71
2	47	47
3	24	23
4	106	106
5	77	78
6	13	16
7	94	95
8	24	26
9•	3	13
10	85	85
11	47	46
12	18	14
13	35	31
14	37	42
15	29	31
16	46	47
17	19	15
18	30	29
19	26	23
20•	0	4
21	8	15
22	25	28
23•	0	8
24	35	26
25	22	18
H,L=	5	4
0	109	109
1	40	39
2	20	19
3	38	37
4	46	49
5	76	70
6	53	57
7	24	25
8	25	25
9	19	20
10	57	57
11	50	43
12	41	35
13	15	23
14	40	41
15	14	19
16	9	14
17	13	16
18	21	24
19•	2	18
20	25	28
21	29	28
22	13	21
H,L=	5	5
0	28	21
1	27	29

Table 8 (*cont.*)

K	FO	FC
2	17	22
3	29	31
4•	[illegible]	12
5	14	14
6	[illegible]	17
7	15	17
8	15	17
9	37	37
10	[illegible]	31
11	[illegible]	25
12	19	13
13	19	14
14	31	24
15	6	12
16	[illegible]	6
17	[illegible]	14
18	[illegible]	17
H,L=	5	6
0	34	31
1	22	16
2	17	12
3•	[illegible]	11
4•	[illegible]	12
5	[illegible]	15
6	22	23
7	[illegible]	11
8•	[illegible]	15
9	[illegible]	19
10	31	26
H,L=	6	0
0	120	123
1	151	147
2	[illegible]	136
3	82	79
4	93	90
5	60	70
6	121	110
7	83	76
8	87	93
9	134	129
10	105	103
11	90	96
12	22	3
13	69	72
14	56	54
15•	[illegible]	3
16	[illegible]	10
17	42	42
18	10	15
19•	[illegible]	7
20	[illegible]	49
21	15	15
22	[illegible]	9
23	[illegible]	21
24	[illegible]	24
25	[illegible]	36
26	36	38
27•	[illegible]	18
H,L=	6	1
0	[illegible]	19
1	121	117
2	[illegible]	129
3	52	53
4	24	19
5	[illegible]	66
6	20	24
7	121	118
8	105	100
9	24	27
10	[illegible]	70
11	[illegible]	32
12	129	132
13	[illegible]	164
14	55	56
15	31	30
16	24	20
17	35	36
18	[illegible]	42
19	[illegible]	62
20	29	27
21	27	32
22	[illegible]	19
23	10	11
24	24	21
25	23	19
26	16	11
27	20	26
H,L=	6	2
0	71	71
1	120	123
2	46	44
3	32	33
4	41	44
5	90	85
6	73	72
7	79	83
8	47	45
9	85	85
10	65	63
11	9	9
12	54	54
13	19	20
14	32	37
15	37	34
16	22	12
17•	0	9
18	35	[illegible]
19	17	15
20	29	26
21	16	21
22	15	11
23	14	8
24	32	34
25•	0	13
26	24	23
H,L=	6	3
0	34	34
1	121	122
2	57	70
3	[illegible]	69
4	48	39
5	52	51
6	18	21
7	46	68
8	51	56
9	64	65
10•	0	8
11	37	41
12	58	61
13	35	38
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16	33	32
17	36	36
18	22	15
19	27	28
20	20	17
21	30	33
22	20	9
23	24	28
24	36	[illegible]
H,L=	6	4
0	26	28
1	14	11
2	38	31
3•	0	6
4	28	24
5	64	71
6	40	45
7	39	42
8	21	21
9	21	25
10	14	10
11	40	36
12	58	57
13	43	38
14	14	15
15	14	11
16•	0	14
17•	0	11
18	28	23
19•	0	8
20•	0	11
21	24	19
H,L=	6	5
0	18	26
1	26	28
2	26	20
3	25	29
4	14	21
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6•	[illegible]	4
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8	15	15
9	23	28
10	13	11
11	28	22
12	21	18
13	27	24
14	19	14
15	20	14
16	13	20
H,L=	6	6
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1	17	5
2	18	10
3	4	15
4	14	10
5	22	10
6	8	14
7•	[illegible]	10
8	15	19
H,L=	7	0
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2	44	44
3	149	145
4	114	117
5	63	63
6	50	49
7	34	29
8	82	70
9	81	77
10	139	136
11	10	12
12	32	33
13	4	5
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15	10	9
16	85	84
17	51	51
18	17	15
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22	38	35
23	22	1
24	33	31
H,L=	7	1
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1	82	83
2	96	97
3	160	159
4	28	30
5	27	31
6	85	70
7	26	24
8	71	72
9	30	39
10	55	54
11	50	47
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14	10	14
15	54	52
16	49	52
17	20	27
18•	0	5
19•	0	7
20	15	7
21	46	47
22•	0	12
23	37	39
H,L=	7	2
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3	65	67
4	141	140
5	63	63
6	87	89
7	66	65
8	115	117
9	21	15
10	80	80
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12	42	45
13	38	39
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15	34	33
16	67	63
17	22	13
18	32	34
19	32	31
20	7	11
21	18	19
22	26	23
H,L=	7	3
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7	55	55
8	42	41
9	38	39
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11	46	53
12	26	23
13	26	32
14	19	15
15	52	56
16	17	16
17	30	29
18	23	12
19•	0	4
20•	0	1
H,L=	7	4
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1	31	32
2	59	55
3•	0	2
4	63	64
5	40	46
6	18	10
7	20	18
8	39	37
9	5	18
10	38	42
11	39	37
12	22	18
13	24	25
14•	0	2
15	33	28
16	33	32
H,L=	7	5
0	28	29
1	23	20
2•	0	10
3	24	22
4	12	14
5	8	12
6	23	20
7	12	7
8	8	14
9	45	42
H,L=	8	0
0	80	75
1•	0	17
2	56	55
3	24	21
4	16	14
5	26	28
6	125	124
7	78	77
8	50	49
9	61	59
10	41	42
11	21	24
12	55	61
13	11	12
14	87	89
15	9	2
16	13	13
17	10	5
18	44	46
19	25	30
20	23	24
21•	0	1
22	4	3
H,L=	8	1
0	75	74
1	76	75
2	47	45
3	64	63
4	40	46
5	69	69
6	54	52
7	78	78
8	87	87
9	24	26
10	77	81
11	84	88
12	7	11
13	70	71
14	30	29
15•	0	17
16	22	19
17	17	9
18	21	16
19	40	40
20	26	25
21	43	42
H,L=	8	2
0	19	11
1•	0	5
2	55	53
3	32	29
4	25	23
5	48	50
6	47	53
7	51	51
8	36	39
9	39	37
10	27	27
11	9	11
12	30	33
13	34	34
14	44	43
15	19	20
16•	0	5
17	26	27
18	63	60
19	24	20
20	16	23
21	25	17
H,L=	8	3
0	53	53
1	100	103
2	18	24
3	23	22
4	44	44
5	45	43
6	89	87
7	56	56
8	36	34
9	50	47
10	21	25
11	32	29
12	23	22
13	26	28
14	35	31
15	11	9
16•	0	13
17	17	9
18	27	17
H,L=	8	4
0	10	5
1	20	17
2	30	28
3	34	36
4	29	16
5	22	26
6	31	34
7	19	13
8	18	25
9	23	29
10	24	21
11	26	23
12	28	21
13	19	15
14	23	29
H,L=	8	5
0	22	15
1	30	25
2	20	18
3	10	8
4	14	17
5	21	21
6	11	16
H,L=	9	0
1	15	14
2	49	50
3	92	85
4	50	55
5	70	60
6	91	99
7	77	78
8	37	40
9	51	54
10	14	9
11	60	67
12•	0	14
13•	0	5
14	16	17
15	40	39
16	34	38
17	55	54
18	7	6
19	19	12
20•	0	14
21	21	10
H,L=	9	1
0	19	6
1	41	43
2	45	50
3	31	30
4	16	14
5	96	101
6	28	29
7	47	47
8	74	76
9	64	66
10	17	10
11	81	78
12	33	31
13	11	14
14	43	40
15	25	20
16	21	24
17	22	30
18	11	8
19	19	7
20	17	18
H,L=	9	2
0•	0	10
1	48	45
2	54	52
3	89	86
4	67	64
5	30	29
6	18	26
7	44	48
8	42	47
9	70	65
10	26	30
11	22	24
12	24	25
13	10	15
14	14	17
15	21	18
16	34	31
17	50	53
18	24	17
19	22	16
H,L=	9	3
0	34	32
1	14	9
2	52	53
3	17	23
4	35	36
5	7	13
6	42	39
7	11	5
8•	0	10
9	33	41
10	38	37
11•	0	15
12	26	23
13	12	10
14	19	17
15	40	38
16	29	27
H,L=	9	4
0	24	22
1	6	12
2	16	22
3	29	33
4	21	21
5	20	14
6	34	34
7•	0	12
8	24	25
9	12	17
10•	0	13
11	12	14
H,L=	10	0
0	42	40
1	36	35
2	60	62
3	66	60
4	20	26
5	51	54
6	51	51
7	48	44
8	42	44
9	27	20
10	59	54
11	62	62
12	29	25
13	24	24
14	27	27
15	29	19
16	10	10
17	37	33
18	7	10
19•	0	10
H,L=	10	1
0	137	140
1	29	28
2	10	9
3	46	43
4	45	46
5	34	42
6	38	39
7	12	11
8	44	46
9	40	39
10	26	25
11	38	34
12	51	54
13	28	24
14	42	38
15	18	11
16	11	10
17	19	16
18	18	19
H,L=	10	2
0•	0	10
1	47	51
2	13	13
3	33	34
4	40	40
5	62	65
6	26	22
7	68	69
8	24	26
9	16	11
10•	0	14
11	28	26
12	24	28
13	35	29
14	21	25
15	28	25
16•	0	6
17	31	28
H,L=	10	3
0	35	33
1	15	23
2	15	18
3	21	17
4	29	27
5	10	16
6	18	15
7	23	15
8	22	24
9	9	12
10	14	14
11	19	20
12	24	25
13	12	9
H,L=	10	4
0	15	5
1	31	28
2	6	3
3	33	31
4	20	22
5	48	46
6	16	2
7	14	22
H,L=	11	0
1	7	6
2	43	44
3	23	23
4	37	38
5	65	65
6	21	23
7	42	46
8	28	28
9	46	43
10•	0	10
11	32	30
12	10	5
13	11	10
14	26	32
15	25	28
16•	0	14
H,L=	11	1
0	46	45
1	25	20
2	74	73
3	19	19
4	45	45
5	20	10
6•	0	11
7•	0	7
8	32	31
9	19	21
10	44	40
11	19	21
12	31	33
13	16	15
14	52	50
15	29	28
16	11	14
H,L=	11	2
0•	0	8
1	23	21
2	11	8
3	27	34
4•	0	11
5	25	19
6	11	15
7	6	9
8	9	13
9	35	35
10	9	4
11•	0	9
12	26	21
13	20	20
14	15	27
H,L=	11	3
0•	0	3
1	27	30
2	71	66
3	6	21
4	19	21
5•	0	6
6	11	13
7	18	15
8	23	26
9	8	11
10	44	41
H,L=	12	0
0•	0	8
1	50	53
2	21	20
3	11	14
4	15	13
5	38	40
6	40	42
7	22	23
8	7	6
9•	0	1
10	11	5
11	31	34
12	38	43
13	19	6
H,L=	12	1
0•	0	10
1	25	26
2	9	11
3	24	11
4•	0	6
5	11	14
6	31	27
7	23	22
8	24	21
9	8	8
10	30	26
11•	0	22
12	40	47
H,L=	12	2
0•	0	10
1	39	43
2	32	32
3	11	12
4	31	31
5	45	45
6•	0	11
7	38	32
8	11	21
9	21	17
10	32	31
H,L=	12	3
0	24	29
1	38	31
2•	0	9
H,L=	13	0
1•	0	0
2	13	4
3	26	27
4	41	40
5•	0	4
6	16	19
7	33	31
8	5	2
H,L=	13	1
0•	2	10
1	42	35
2	18	19
3	24	19
4	37	41
5	19	22
6•	0	10
7	30	28

networks rather than to the intramolecular steric hindrance.

Bond distances and angles

All the bond distances and angles found in the present study agree well with those which have been found most commonly in many amino acids and related compounds. Furthermore, the similarity between the dimensions of the citrulline and homocitrulline molecules in the two crystals is striking. The only exception is the C^{β}–C^{α}–C′ (carboxyl) angle: 113·5° in citrulline and 107·4° in homocitrulline. The difference in the angles is significant. It cannot, however, be elucidated simply from the difference in the conformations of the two molecules alone. The angles in other related compounds are 108·4° in L-arginine.$2H_2O$ (Karle & Karle, 1964), 109·8° in L-lysine.HCl.$2H_2O$ (Wright & Marsh, 1962), 110·2° in L-ornithine.HCl (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967), 110·0 and 111·0° in L-arginine.HCl.H_2O (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970).

The C^{α}–C′ bond distances in both crystals seem to be somewhat shorter than the C^{α}–C^{β} distances. However, on the basis of available data for accurately determined structures of the amino acids with an unionized carboxyl group, Sundaralingam & Putkey (1970) have concluded that the C^{α}–C′ (sp^3–sp^2) distance is comparable with the C^{α}–C^{β} (sp^3–sp^3) distance, and as weighted averages, they proposed the values of 1·524

Table 9. *Homocitrulline hydrochloride: best planes and displacements from the planes*

(*a*) Equations of the best planes

The coordinates (X, Y, Z) are in Å.

		Atoms
I	$-0{\cdot}6790X-0{\cdot}2794Y-0{\cdot}6789Z=-8{\cdot}8774$	O(1) O(2) C(1) C(2)
II	$-0{\cdot}5334X+0{\cdot}6811Y+0{\cdot}5016Z=-4{\cdot}8597$	C(2) C(3) C(4) C(5) C(6)
III	$0{\cdot}3641X+0{\cdot}6317Y-0{\cdot}6844Z=-1{\cdot}9639$	O(3) N(2) N(3) C(7)

Table 9 (*cont.*)

(*b*) Displacements (Å) of atoms from the planes

I		II		III	
O(1)	0·005	C(2)	−0·083	O(3)	−0·002
O(2)	0·005	C(3)	0·058	N(2)	−0·002
C(1)	−0·014	C(4)	0·087	N(3)	−0·002
C(2)	0·004	C(5)	−0·019	C(7)	0·006
N(1)*	−0·365	C(6)	−0·039	C(6)*	0·180
H(7)*	0·085	N(2)*	−0·349	H(4)*	−0·123
		C(1)*	−0·163	H(5)*	0·109
				H(6)*	−0·019

* Atoms with asterisks are not included in the calculation of the best planes.

and 1·523 Å, for the C^{α}–C' and C^{α}–C^{β} distances respectively. The average bond distances of the C–C single bonds in the side chains are 1·527 Å for citrulline and 1·531 Å for homocitrulline. These values are in close agreement with those found in the related compounds mentioned above. The shape and the size of the carbamylamino group in both crystals coincide well with those reported for urea (Vaughan & Donohue, 1952) and those for the peptide linkage given by Corey & Pauling (1952). The bond distances of the C(2)–N(2) bonds, 1·455 and 1·457 Å, are in close agreement with an average value of 1·455 Å for the N–C^{α} bonds in the peptide linkages (Marsh & Donohue, 1967).

Hydrogen bonds

The overall hydrogen bond schemes in the two crystals are very different, resulting in a difference in the packing in the crystals. The 'local' hydrogen bond schemes are, however, essentially the same for both crystals, although there is not a bifurcated hydrogen bond in the homocitrulline crystal (Figs. 3 and 5). All the hydrogen atoms of the carbamylamino nitrogen atoms form hydrogen bonds to the chloride ions, the mean distance of the six hydrogen bonds in both crystals being 3·338 Å. Each α-amino group forms two hydrogen bonds to the chloride ions, the mean distance of the four bonds being 3·175 Å. Thus the hydrogen bond between the α-amino group and the chloride ion is significantly stronger than the one between the carbamylamino group and the chloride ion. It is interesting to remember that the hydrogen bonds in urea are 'weak', the distances of the two N–H···O bonds being 2·99 and 3·04 Å (Vaughan & Donohue, 1952). The lengthening of these hydrogen bonds is due to the smaller formal positive charge on the nitrogen atoms in the carbamylamino group and in urea.

The other hydrogen atom of the α-amino group forms a bond of 2·873 Å to the oxygen atom of the carboxyl group in homocitrulline, while in citrulline it forms a bifurcated bond to an oxygen atom of the carboxyl group (2·948 Å) and to the oxygen atom of the carbamylamino group (2·952 Å). The donor–acceptor distance in a simple hydrogen bond is shorter than that in a bifurcated one.

In the crystal there is one more hydrogen bond of the type O–H···O, which connects the carboxyl group with the carbamylamino group of the neighbouring molecules, the distance being 2·520 Å in citrulline and 2·485 Å in homocitrulline. Both the hydrogen bonds are fairly strong.

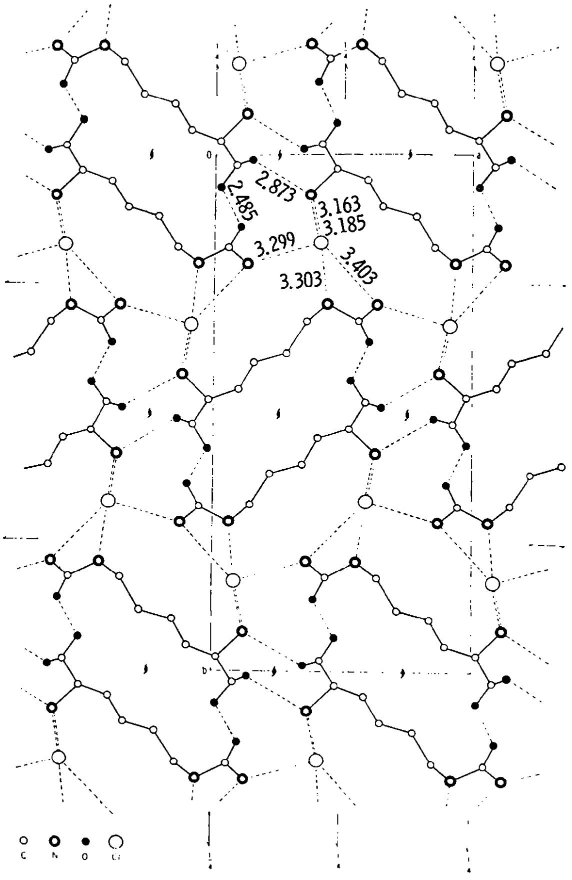

Fig. 3. Homocitrulline hydrochloride: the structure seen along the *c* axis, the *c* axis downwards. Hydrogen bonds are shown by broken lines.

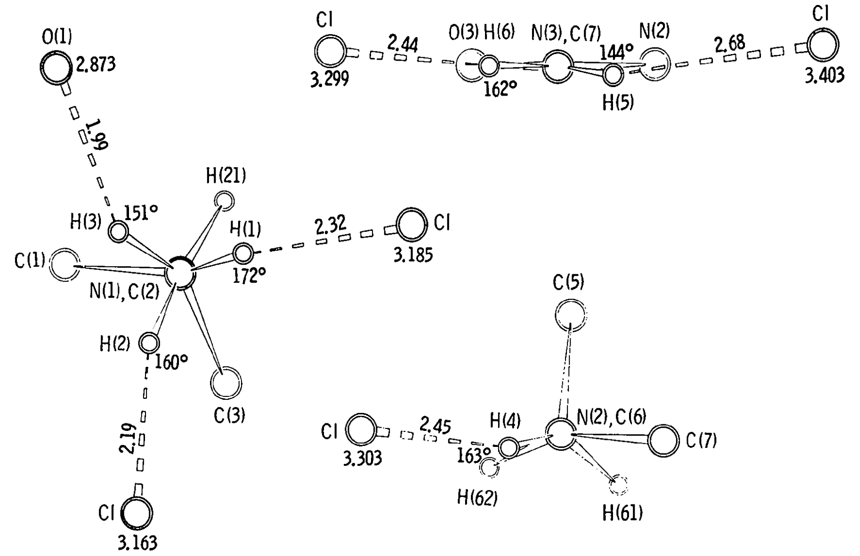

Fig. 4. Homocitrulline hydrochloride: The environments of the hydrogen bonds. One more hydrogen bond is O(2)–H(7)···O(3); O(2)···O(3)=2·485 Å, H(7)···O(3)=1·57 Å, ∠O(2)–H(7)···O(3)=180°.

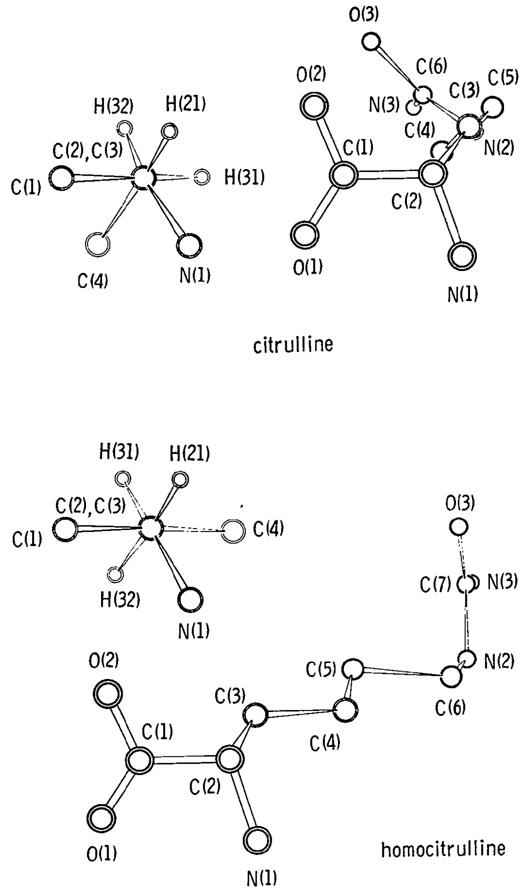

Fig. 5. A comparison of the conformations of citrulline and homocitrulline molecules in their hydrochlorides. One is a view of the molecule projected onto the plane of C′–C$_\alpha$–N$_\alpha$, while the another shows the internal rotation of the C$_\alpha$–C$_\beta$ bond.

Comments on the two citrulline hydrochloride structures

The crystal structure of L-citrulline hydrochloride reported by Naganathan & Venkatesan (1971) shows systematic variations from the present result. Their a, b and c are all about 1·2% smaller than ours. They found some of the bond distances to be shorter than usual: for example, C(1)–O(2), 1·251 Å (1·297 Å); C(2)–N(1), 1·460 (1·486); C(3)–C(4), 1·491 (1·522); C(5)–N(2), 1·414 (1·457); N(1)–H(2)···Cl, 3·074 (3·139), where the values in the parentheses are the present ones. These distances in our result agree well with those usually found in the related compounds. The shorter bond distances obtained by N & V seem to be mainly attributable to their small unit cell dimensions.

The x and z parameters in both the results show a satisfactory agreement, while the parameters such as y, β_{22}, β_{12} and β_{23} show fairly large discrepancies. The largest deviation is found with respect to N(2), for which y differs by 9σ, β_{22} by 6σ and β_{12} by 16σ (σ being those in our result). The systematic discrepancies are mostly found in the y parameters, so that all the C, N and O atoms are unidirectionally displaced with a mean displacement $\langle \Delta y \rangle = 0{\cdot}0052$ (ranging from 0·0014 to 0·0084 with the same sign, 0·0052 corresponding to 6σ).

At the refinement stage, N & V used the full-matrix least-squares procedure. In order to make an comparison appropriate, therefore, a full-matrix least-squares refinement procedure was also applied to our final result. However, shifts exceeding $\sigma/4$ did not occur. In view of this fact, it is likely that the discrepancies in parameters found between the two results are mainly due to the differences in the intensity measurement and data processing. Incidentally, N & V's work was done using Weissenberg photographs around one axis, with scaling by layerwise Wilson plots.

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The Crystal and Molecular Structures of the 1:1 Addition Compounds of Piperidine with *p*-Bromobenzoic Acid and *p*-Chlorobenzoic Acid

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The structures of the two 1:1 addition compounds of piperidine with *p*-bromobenzoic acid, $BrC_6H_4CO_2H.C_5H_{11}N$, and with *p*-chlorobenzoic acid, $ClC_6H_4CO_2H.C_5H_{11}N$, have been determined from three-dimensional X-ray diffraction data. Both compounds crystallize in the orthorhombic space group *Pbca* with eight formula units in the unit cell. The cell dimensions are: $a=10{\cdot}70$, $b=27{\cdot}30$, $c=9{\cdot}04$ Å for the *p*-bromo compound, and $a=10{\cdot}68$, $b=26{\cdot}37$, $c=9{\cdot}01$ Å for the *p*-chloro compound. The structures were refined by the block-diagonal least-squares method, with anisotropic temperature factors. The final *R* values for observed reflexions are 0·086 and 0·123 for the *p*-bromo and *p*-chloro compounds respectively. Both structures are isotypic. The structure is composed of an alternate sequence of acid and base moieties held together by $N^+–H\cdots O^-$ hydrogen bonds. The $N^+–H\cdots O^-$ distance ranges from 2·67 to 2·76 Å. The hydrogen bonds form an infinite chain around the twofold screw axis parallel to the *c* axis. These molecular chains are packed intimately by van der Waals forces to make up a whole crystal. In either compound, the piperidine ring takes a normal chair form, and the carboxyl group is twisted out of the plane of the benzene ring at an angle of about 8°.

Introduction

The formation of the solid 1:1 and 2:1 addition compounds of benzoic acid and piperidine and those of some *p*-substituted benzoic acids and piperidine have previously been reported (Kashino, 1967; Kashino, Kanei & Hasegawa, 1971). The infrared spectra of the 1:1 compounds were very similar to those of the corresponding sodium benzoates. Thus, it was concluded that the acid moiety in the 1:1 compounds is almost fully ionized. However, the symmetric carboxylate stretching of the adducts showed significantly lower values of 1385–1375 cm^{-1} compared with the values of 1427–1406 cm^{-1} for the corresponding sodium benzoates.

It may be desirable to obtain information about the spatial configuration of individual molecules in these crystals and more information about the nature of the bond between the acid and the base components. As a first step, the crystal structure determinations of the present compounds were undertaken.

Experimental

The 1:1 addition compound of *p*-bromobenzoic acid and piperidine was prepared by dissolving equimolar quantities of *p*-bromobenzoic acid and piperidine in dry benzene. The compound crystallized as transparent tabular plates having well developed {010}. As the compound was hygroscopic and gradually decomposed to its acid and base components, the specimens cut from larger crystals were sealed in glass capillaries. Two different crystals with approximate cross-sections of 0·12 × 0·18 mm and 0·10 × 0·15 mm were used for the X-ray analysis, the former for *a* axis photographs and the latter for *c* axis photographs. Using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å), multiple-film equi-inclination Weissenberg photographs were taken for the layers from