Acta Cryst. (1972). B28, 2510

The Crystal and Molecular Structure of Tris-(4,4′-diaminodiphenylmethane)–Sodium Chloride

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(*Received* 18 *June* 1971 *and in revised form* 27 *March* 1972)

The crystal structure of tris-(4,4′-diaminodiphenylmethane)–sodium chloride, $(C_{13}H_{14}N_2)_3.NaCl$ or $(MDA)_3.NaCl$, has been determined by X-ray diffraction. The space group is rhombohedral, $R\bar{3}c$, with $a=12{\cdot}101$ (14) Å, $\alpha=99{\cdot}06$ (3)° and $Z=2$. The hexagonal cell has $a=18{\cdot}396$ (15) Å, $c=17{\cdot}400$ (15) Å and $Z=6$. Intensity data were collected on an automatic three-circle diffractometer using θ–2θ scans. The structure was solved by direct methods using the Sayre equation and E maps to locate the non-hydrogen atoms. Structural parameters and isotropic thermal motions were refined by the method of least squares to a final R value of 0·069. Approximate positions of the hydrogen atoms were determined from Fourier difference maps. The structure consists of rows of alternating Na and Cl atoms lying along threefold axes and separated by the organic molecules which lie on twofold axes. The amine-ion distances, Na–N, H(2)–Na and H(2)–Cl, are all smaller than the sum of the van der Waals radii and, for H(2)–Cl, meet the criterion for hydrogen bonding. The N–Na–N angle is 87·06°; the octahedron centered on Na is thus slightly stretched along the threefold axis.

Introduction

The crystal and molecular structure of tris-(4,4′-diaminodiphenylmethane)–sodium chloride, $(MDA)_3.NaCl$, was undertaken as part of the investigation of a recently discovered class of organic adducts. Marullo & Lloyd (1966) discovered the first example of the precipitation of simple sodium salts such as sodium chloride from aqueous solution by compound formation with a nonionic organic substance. The compound precipitating these salts was *p,p′*-diamino-2,3-diphenylbutane (DPB). Shields (1968) reported the precipitation of sodium chloride with a similar organic compound, 4,4′-diaminodiphenylmethane (MDA), to form crystals of $(MDA)_3.NaCl$. Chemical and infrared studies indicated that the diamine was hexacoordinated with the cation *via* a nitrogen donor ligand. This was further confirmed by Cochran, Allen & Marullo (1967). Of the alkali metals only the lithium salts were known to form isolable coordination compounds with nitrogen donor ligands.

This paper presents the detailed structure of the linkage of the MDA molecules with the sodium and chloride ions. The relationship of the six nearest neighbor nitrogen atoms with the sodium ion is established.

Experimental

Crystals of $(MDA)_3.NaCl$ were precipitated from solution by the method given by Shields (1968). Data and experimental conditions are given in Table 1.

For the collection of the X-ray intensity data, a crystal ground into a sphere 0·46mm diameter and mounted with the c axis nearly parallel to the spindle was used. Intensity data were collected on a three-circle automatic diffractometer using a θ–2θ step scan. The detector was a NaI(Tl) scintillation counter operated at 985 V, with a pulse height analyzer adjusted to accept 90% of the K radiation.

Table 1. *Crystal data*

Chemical formula		$(C_{13}H_{14}N_2)_3$ NaCl
Habit		Nearly clear hexagonal prisms
Density		
Measured by gradient column		1·28 g.cm^{-3}
Calculated		1·27 g.cm^{-3}
Space group		$R\bar{3}c$
Cell constants		
R cell	a	12·101 ± 0·014 Å
	α	99·063 ± 0·031°
	V	1700·1 Å^3
	Z	2
H cell	a	18·396 ± 0·015 Å
	c	17·400 ± 0·015
	V	5100·2 Å^3
	Z	6
Radiation		Cu $K\alpha_1$, 1·5412 Å with Ni filters
Measurement temperature		~22·5°C
Conditions limiting reflections (hexagonal indexing)		hkl: $-h+k+l=3n$ $h\bar{h}l$:$(h+l=3n)$; $l=2n$
μ(Cu $K\alpha$)		14·14 cm^{-1}

The diffractometer program was a modified version of that by Busing, Ellison, Levy, King & Roseberry (1968). The background was taken as the average of stationary counts collected at each end of the scan. Data were collected to a maximum $\sin\theta/\lambda$ of 0·53. Of 1636 independent reflections, 1116 had counts of significant intensity (≥approximately 1/1000 of the strongest) for measuring. The intensities of equivalent reflections were equal within their statistical error, *i.e.* $\sigma(I)/I \le N^{-1/2}$. Absorption corrections appropriate to a spherical crystal, and Lorentz and polarization factors were applied to the intensity data. The data were placed on an approximate absolute scale by generating normalized structure factor magnitudes $|E|$ such that 5%

of the values were greater than 2, the statistical expectation for a centrosymmetric structure. Structure factor magnitudes, $|F|$, were then derived.

Anomalous scattering (a maximum $\Delta f''$ for Cl of about 10% at the limit of the data shere and therefore affecting only the weak intensities) was not corrected. Extinction did not appear to strongly affect any reflections.

Structure determination and refinement

The Na and Cl atoms must be in special positions along the threefold axis. As multiple adducts of DPB had already been prepared, a logical position for the Na atoms was 0, 0, 0 and 0,0,1/2 with the Cl atoms positioned midway between.* The organic molecule must lie on the twofold axis. The structure factor contribution from the Na and Cl atoms in these positions in $R\bar{3}c$ is given by

$$\begin{aligned} F_{(\mathrm{Na}+\mathrm{Cl})} &= 2(f_{\mathrm{Na}}+f_{\mathrm{Cl}}), && \text{for } l=4n, \\ &= 2(f_{\mathrm{Na}}-f_{\mathrm{Cl}}), && \text{for } l=4n+2 \text{ and} \\ &= 0, && \text{for } l=\text{odd}. \end{aligned}$$

The intensity data displayed a definite trend affecting the stronger reflections having $l=4n$, and a centrosymmetric structure with the Na and Cl atoms in the positions assumed was evident. Consequently, there should be a definite tendency for the $l=4n$ reflections to have positive phases.

A computer program, written by Long (1965) and revised by Streib & Tsai (1968), was used to generate phase relations among the 165 reflections with $|E|$ greater than 1·5. One origin determining reflection plus four more reflections having a large number of interactions were used as a starting set, with all possible combinations of signs, to generate additional signs for the remaining reflections. Only one of the 16 different listings of reflections with generated phases contained a high probabilty for $l=4n$ reflections to be positive. This list was used to calculate E map sections from which approximate locations of all the nonhydrogen atoms were determined.

Positional, anisotropic temperature factor and scale factor parameters were refined using the least-squares program *ORFLS* written by Busing, Martin & Levy (1962). The quantity minimized was $\sum w(|F_o|-K|F_c|)^2$. The weights w were obtained from the estimated errors by the method given by Stout & Jensen (1968). The standard deviation is $\sigma_F=[\sigma_{pk}^2+(0{\cdot}02\,N_{pk})^2]^{1/2}/2(\mathrm{Lp}I)^{1/2}$, where $\sigma_{pk}=(N_T+N_{b1}+N_{b2})^{1/2}$, $N_{pk}=N_T-N_{b1}-N_{b2}$, Lp is the Lorentz–polarization factor, I is the scaled observed intensity, N_T is the integrated count through the diffraction peak, N_{b1} and N_{b2} are the background counts. The relevant scattering factors listed in *International Tables for X-ray Crystallography* (1962) were used.

The R index, $\sum||F_o|-|F_c||/\sum|F_o|$, converged to 0·079. The approximate positions of the hydrogen atoms were then located on difference maps. Two final cycles of refinement, including but not varying the hydrogen atom parameters, resulted in a final R of 0·069. The scattering factor tables for fully ionized sodium and chlorine atoms were used in the refinement and calculation of the structure factors.

Structural results

The final fractional coordinates and thermal parameters of the asymmetric unit are given in Table 2. The greatest shift in any position on the last refinement cycle was 0·00004 and the largest standard deviation was 0·00053. All fractional coordinates refer to the hexagonal unit cell. Interatomic distances and angles were computed using the program *ORFFE*, written by Busing, Martin & Levy (1964). Fig. 1 shows the interatomic distances and interbond angles. Distances of N, Na and Cl to pertinent MDA atoms are given in Table 3. The van der Waals radii are taken from Bondi 1964). The approximate fractional positions of the hydrogen atoms, as determined from the difference maps, are given in Table 4. The structure is illustrated in Fig. 1 and 2, which were drawn with the aid of the plot program *ORTEP* (Johnson, 1965).

Fig. 1 shows the basic MDA molecule in this structure. The dihedral angle is 90°, with C(2) above the figure plane. Atoms N, C(1), C(4), C(7), C′(4), C′(1)

Table 2. *Parameters of non-hydrogen atoms and their estimated standard errors*

The estimated standard errors in the last significant figure are in parentheses. The expression for the anisotropic temperature factor is in the form $T=\exp(-\Sigma\beta_{ij}h_ih_j)$.

	Positional parameters × 10^4			Thermal parameters × 10^4					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1149 (3)	156 (3)	895 (3)	22 (2)	25 (2)	32 (2)	9 (2)	−8 (2)	−1 (2)
C(1)	1914 (3)	951 (3)	870 (3)	28 (3)	28 (3)	20 (2)	18 (2)	−7 (2)	0 (2)
C(2)	2037 (3)	1594 (3)	1384 (3)	29 (3)	28 (3)	20 (2)	16 (2)	0 (2)	−1 (2)
C(3)	2769 (3)	2356 (3)	1350 (3)	29 (3)	26 (3)	23 (2)	14 (2)	0 (2)	−1 (2)
C(4)	3387 (3)	2513 (3)	817 (3)	21 (3)	25 (3)	26 (2)	14 (2)	0 (2)	4 (2)
C(5)	3252 (4)	1887 (4)	309 (3)	28 (3)	38 (3)	26 (2)	20 (3)	4 (2)	−1 (2)
C(6)	2529 (3)	1104 (4)	324 (3)	26 (3)	40 (3)	25 (2)	20 (3)	2 (2)	0 (2)
C(7)	4224 (4)	3333	833	29 (3)	35 (3)	44 (3)	17 (2)	3 (2)	6 (2)
Na	0	0	0	23 (2)	23 (2)	20 (2)	12 (2)	0	0
Cl	0	0	2500	38 (2)	38 (2)	18 (1)	19 (2)	0	0

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* In the remainder of the paper, we refer the hexagonal cell exclusively.

Table 3. *Interatomic distances*

The values in parentheses are the standard deviations in the last significant figures and include standard errors in the cell parameters of ±0·015 Å in *a* and *c*.

Atom pairs	Distance	Sum of van der Waals radii
N°–Na^{+}	2·524 (5) Å	3·07 Å
N°–Cl^{-}	3·426 (5)	3·30
$H^{\circ}(1)$–Na^{+}	3·00 (8)	2·75
$H^{\circ}(2)$–Na^{+}	2·60 (8)	2·75
$H^{\circ}(1)$–Cl^{-}	3·97 (8)	2·95
$H^{\circ}(2)$–Cl^{-}	2·45 (8)	2·95
N–N(120° rot)	3·44 (1)	3·10
N–N(inv + rot)	3·70 (1)	3.10

Table 4. *Approximate hydrogen atom positions* ($\times 10^2$)*

	x	*y*	*z*
H(C2)	15	15	18
H(C3)	29	29	17
H(C5)	37	19	−1
H(C6)	24	5	0
H(C7)	45	33	3
H(1)N	12	−4	8
H(2)N	7	0	13

* Taken from difference maps which had a grid of approximately 0·01 Å. Positions are estimated to within the difference peak, ±0·04 Å for ring hydrogen and ±0·08 Å for amine hydrogen atoms.

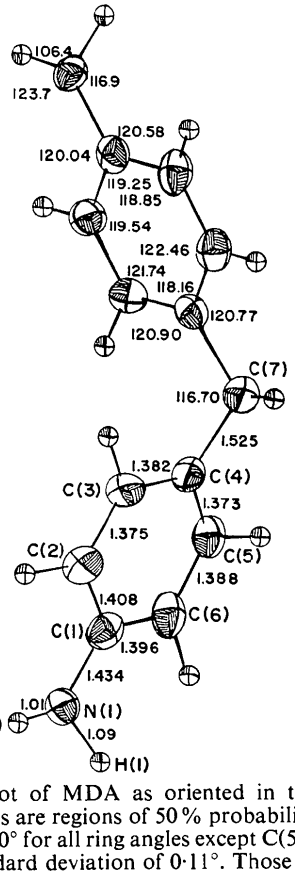

Fig. 1. *ORTEP* plot of MDA as oriented in the unit cell. Thermal ellipsoids are regions of 50% probability. Standard deviations are 0·10° for all ring angles except C(5)–C(4)–C(7), which has a standard deviation of 0·11°. Those for N–C(1)–C(2) and N–C(1)–C(6) are 0·19 and 0·16° respectively. Standard deviations are 0·004 Å for all ring bond lengths except C(5)–C(6), which has a standard deviation of 0·01 Å. N–C(1) has a standard deviation of 0·009 Å.

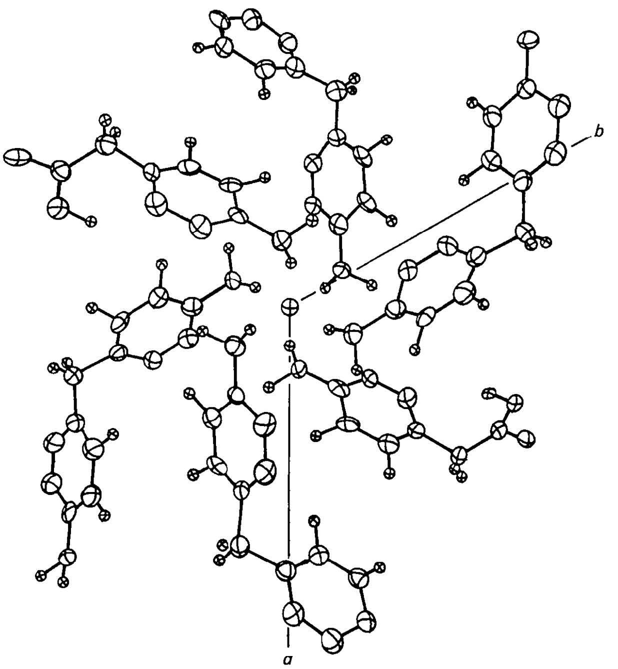

Fig. 2. Projection of $-0{\cdot}15 \le z \le 0{\cdot}15$ onto the (001) plane

and N′ all lie at approximately the same *z* coordinate and are almost planar in this figure.

Fig. 2 shows a section of the cell with $-0{\cdot}15 \le z \le 0{\cdot}15$. The Na atom is at the origin. The Cl atom lies above the Na at $0,0,\frac{1}{2}$. The hexacoordination of the nitrogen atoms about the sodium atom is apparent. The long axes of the MDA molecules lie nearly parallel to the (001) plane.

Fig. 3 shows the positions of the amino groups of the MDA molecules relative to the sodium and chlorine ions. The six nitrogen atoms are coordinated to the sodium ion. The observed distance, 2·524 A°, is less than the sum of the van der Waals radii, 3·07 A°. The nitrogen atoms do not quite form an octahedron. The two N–N nearest-neighbor distances are 3·445 and 3·704 A°. The N–Na–N angle is 87·06° and the triangles of nitrogen atoms perpendicular to the threefold axis are closer to Cl^{-} than in an ideal octahedron. The nitrogen–chlorine distance, 3·426 A°, is too large for any interaction. One of the amine hydrogens, H(1), lies almost in the (001) plane, 3·00 A° from Na and 3·97 A° from Cl. The other amine hydrogen, H(2), is positioned upward, 2·60 A° from Na and 2·45 A° from Cl, closer than the sum of the van der Waals radii. The H(2)–Cl distance satisfies the Hamilton–Ibers (1968) criterion for hydrogen bonding. Such bonding could explain the distortion of the nitrogen atoms from ideal octahedral array. Aniline and analogous compounds have a high dipole moment of 1·5 to $6{\cdot}8 \times 10^{-18}$ e.s.u. MDA would be expected to have a high dipole moment.

Table 5. *Observed and calculated structure factors*

H	K	L	FO	FC
14	-1	-6	86	85
12	0	-6	121	-124
13	1	-6	86	88
16	-3	-5	17	-18
14	-2	-5	44	44
12	-1	-5	33	-31
15	-1	-5	26	23
11	1	-5	32	33
14	1	-5	26	-23
12	2	-5	44	-41
13	3	-5	17	19
18	-5	-4	24	27
16	-4	-4	69	67
14	-3	-4	129	132
12	-2	-4	13	-16
15	-2	-4	31	-27
10	-1	-4	62	59
13	-1	-4	87	86
16	-1	-4	44	47
8	0	-4	166	159
11	0	-4	28	-34
9	1	-4	57	54
12	1	-4	87	86
15	1	-4	45	45
10	2	-4	13	-14
13	2	-4	31	-30
11	3	-4	130	129
12	4	-4	68	68
13	5	-4	24	27
14	-4	-3	35	34
17	-4	-3	65	-67
12	-3	-3	48	48
10	-2	-3	11	14
13	-2	-3	102	-103
8	-1	-3	35	-30
14	-1	-3	54	47
7	1	-3	36	35
13	1	-3	54	-48
8	2	-3	11	-13
11	2	-3	102	106
9	3	-3	48	-47
10	4	-3	35	-32
13	4	-3	65	67
19	-7	-2	34	-36
16	-6	-2	22	22
14	-5	-2	15	14
17	-5	-2	15	13
12	-4	-2	39	-38
15	-4	-2	34	35
18	-4	-2	33	31
10	-3	-2	3	-3
13	-3	-2	17	13
16	-3	-2	35	-35
8	-2	-2	18	-21
11	-2	-2	21	22
6	-1	-2	89	-72
9	-1	-2	6	-6
12	-1	-2	42	45
15	-1	-2	74	-72
4	0	-2	381	-444
7	0	-2	58	60
13	0	-2	124	-118
16	0	-2	28	30
5	1	-2	90	-85
8	1	-2	6	-8
11	1	-2	41	43
14	1	-2	74	-73
6	2	-2	18	-12
9	2	-2	21	24
10	3	-2	17	14
13	3	-2	35	-37
8	4	-2	40	-39
11	4	-2	34	31
14	4	-2	33	32
9	5	-2	15	16
12	5	-2	15	14
10	6	-2	21	23
13	6	-2	13	12
11	7	-2	34	-36
19	-7	-1	25	29
17	-6	-1	26	27
12	-5	-1	15	15
10	-4	-1	70	-68
16	-4	-1	23	-23
8	-3	-1	48	-51
11	-3	-1	25	-21
14	-3	-1	79	75
17	-3	-1	17	18
6	-2	-1	115	-106
9	-2	-1	5	-2
12	-2	-1	36	-37
15	-2	-1	73	-71
18	-2	-1	15	-18
4	-1	-1	157	155
7	-1	-1	58	-52
10	-1	-1	12	-12
13	-1	-1	69	-69
16	-1	-1	28	27
3	1	-1	158	-161
6	1	-1	58	50
9	1	-1	12	14
12	1	-1	67	70
15	1	-1	28	-26
4	2	-1	118	90
10	2	-1	37	37
13	2	-1	72	74
16	2	-1	14	21
5	3	-1	49	39
8	3	-1	25	22
11	3	-1	77	-71
14	3	-1	17	-14
6	4	-1	66	63
12	4	-1	23	26
7	5	-1	15	-16
11	6	-1	26	-26
12	7	-1	25	-27
10	-9	0	25	20
16	-8	0	72	78
19	-8	0	24	26
14	-7	0	59	54
17	-7	0	59	63
12	-6	0	57	55
15	-6	0	66	64
10	-5	0	75	76
13	-5	0	11	8
19	-5	0	69	69
8	-4	0	169	173
11	-4	0	59	61
17	-4	0	89	88
6	-3	0	66	80
9	-3	0	22	-9
12	-3	0	101	102
15	-3	0	17	13
18	-3	0	30	29
4	-2	0	179	187
7	-2	0	146	144
10	-2	0	135	137
13	-2	0	69	63
16	-2	0	58	57
2	-1	0	78	69
5	-1	0	74	80
8	-1	0	114	110
11	-1	0	80	83
14	-1	0	27	-28
3	0	0	16	37
6	0	0	43	43
9	0	0	205	213
12	0	0	118	115
15	0	0	27	25
1	1	0	79	69
4	1	0	74	69
7	1	0	114	114
10	1	0	80	81
13	1	0	27	-27
2	2	0	186	187
5	2	0	146	148
8	2	0	135	136
11	2	0	67	64
14	2	0	58	57
3	3	0	67	80
6	3	0	19	-8
9	3	0	100	104
12	3	0	19	11
15	3	0	31	31
4	4	0	174	173
7	4	0	59	61
13	4	0	89	86
5	5	0	71	76
8	5	0	12	10
14	5	0	70	71
6	6	0	57	55
9	6	0	65	65
7	7	0	59	54
10	7	0	58	61
8	8	0	70	78
11	8	0	24	28
9	9	0	25	20
17	-8	1	37	44
12	-7	1	15	-16
15	-7	1	37	-39
10	-6	1	69	63
13	-6	1	32	30
19	-6	1	40	37
8	-5	1	48	39
11	-5	1	34	-34
17	-5	1	49	51
6	-4	1	115	90
9	-4	1	32	-33
12	-4	1	49	-38
15	-4	1	29	25
4	-3	1	154	-161
7	-3	1	82	63
10	-3	1	190	-190
5	-2	1	110	85
8	-2	1	121	103
14	-2	1	28	-24
3	-1	1	43	32
6	-1	1	13	-16
9	-1	1	40	35
12	-1	1	19	17
15	-1	1	40	37
2	1	1	43	-38
5	1	1	12	3
8	1	1	40	-39
11	1	1	18	-17
14	1	1	40	-35
3	2	1	111	-120
6	2	1	122	-112
9	2	1	6	0
12	2	1	28	27
1	3	1	160	155
4	3	1	83	-69
7	3	1	193	191
2	4	1	119	-106
5	4	1	30	28
8	4	1	49	42
11	4	1	25	-22
3	5	1	49	-51
6	5	1	34	36
12	5	1	49	-49
4	6	1	65	-68
7	6	1	32	-28
13	6	1	40	-36
5	7	1	15	15
8	7	1	36	38
9	8	1	37	-42
18	-11	2	34	-36
14	-9	2	15	16
17	-9	2	13	-15
12	-8	2	39	-39
15	-8	2	16	15
10	-7	2	4	-1
19	-7	2	27	29
8	-6	2	17	-12
11	-6	2	38	-32
14	-6	2	20	-19
6	-5	2	86	-85
9	-5	2	49	-37
15	-5	2	33	-30
18	-5	2	20	20
4	-4	2	373	-444
7	-4	2	24	35
10	-4	2	56	55
13	-4	2	59	-56
16	-4	2	79	-84
5	-3	2	150	151
8	-3	2	55	-47
11	-3	2	63	-61
14	-3	2	15	-16
17	-3	2	43	43
3	-2	2	213	-201
6	-2	2	69	-50
9	-2	2	19	8
12	-2	2	9	-6
15	-2	2	18	14
1	-1	2	70	71
4	-1	2	51	56
7	-1	2	43	-31
10	-1	2	59	60
2	0	2	249	264
5	0	2	38	-42
8	0	2	43	43
11	0	2	13	-8
14	0	2	70	69
17	0	2	47	-46
0	1	2	73	71
3	1	2	51	35
6	1	2	43	-34
9	1	2	59	59
1	2	2	219	-202
4	2	2	70	-69
7	2	2	19	7
10	2	2	9	-7
13	2	2	18	14
2	3	2	155	143
5	3	2	55	-51
8	3	2	63	-62
11	3	2	16	-15
14	3	2	43	44
0	4	2	397	-444
3	4	2	24	27
6	4	2	57	54
9	4	2	59	-55
12	4	2	80	-85
1	5	2	89	-72
4	5	2	46	-41
10	5	2	33	-32
13	5	2	20	18
2	6	2	17	-21
5	6	2	39	-39
8	6	2	19	-18
6	7	2	9	1
12	7	2	28	28
4	8	2	39	-38
7	8	2	15	14
5	9	2	15	14
8	9	2	14	-13
6	10	2	22	22
7	11	2	34	-36
14	-10	3	35	-32
12	-9	3	49	-47
15	-9	3	17	19
18	-9	3	24	28
10	-8	3	13	-13
13	-8	3	17	-21
8	-7	3	34	35
11	-7	3	24	-24
9	-6	3	59	-53
12	-6	3	15	-13
18	-6	3	26	26
7	-5	3	47	37
10	-5	3	95	-89
16	-5	3	13	-12
5	-4	3	278	263
8	-4	3	188	189
11	-4	3	51	-48
17	-4	3	15	12
6	-3	3	115	92
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8	1	13	72	67
11	1	13	17	-17
1	3	13	13	-14
7	3	13	27	-27
10	3	13	19	20
8	4	13	38	38
3	5	13	36	-38
6	5	13	14	19
9	5	13	13	-14
4	6	13	17	-16
7	6	13	27	27
6	8	13	21	22
1	9	13	26	-30
11	-9	14	19	19
9	-8	14	20	-26
10	-7	14	16	-19
11	-6	14	76	-73
9	-5	14	31	-32
7	-4	14	20	-13
5	-3	14	64	-63
11	-3	14	23	19
3	-2	14	45	-47
6	-2	14	34	36
9	-2	14	19	18
1	-1	14	7	-16
7	-1	14	38	-35
10	-1	14	22	-23
2	0	14	42	41
5	0	14	33	31
8	0	14	63	-61
11	0	14	17	13
0	1	14	8	-14
6	1	14	37	-36
9	1	14	23	-23
1	2	14	46	-48
4	2	14	34	35
7	2	14	19	18
2	3	14	64	-60
8	3	14	23	23
0	4	14	9	-7
3	4	14	20	-14
4	5	14	31	-32
5	6	14	26	-23
3	7	14	16	-21
1	8	14	20	-24
2	9	14	19	17
10	-8	15	13	13
11	-7	15	17	-19
10	-5	15	20	-22
8	-4	15	35	37
9	-3	15	23	-24
4	-2	15	15	13
7	-2	15	22	16
2	-1	15	37	-38
5	-1	15	64	62
8	-1	15	24	20
1	1	15	36	36
4	1	15	64	-62
7	1	15	23	-21
2	2	15	14	-12
5	2	15	21	-18
6	3	15	22	25
4	4	15	34	-37
5	5	15	20	22
4	7	15	17	19
2	8	15	13	-12
9	-7	16	31	31
7	-6	16	46	50
10	-6	16	18	18
5	-5	15	44	46
8	-5	16	50	54
6	-4	16	56	59
9	-4	16	24	29
4	-3	16	42	44
7	-3	16	14	15
10	-3	16	32	33
8	-2	16	39	40
3	-1	16	64	62
6	-1	16	56	53
9	-1	16	29	31
1	0	16	6	4
4	0	16	133	138
2	1	16	63	69
5	1	16	55	53
8	1	16	28	29
6	2	16	39	42
1	3	16	41	43
4	3	16	14	14
7	3	16	32	33
2	4	16	56	60
5	4	16	24	25
0	5	16	44	46
3	5	16	50	52
1	6	16	46	51
4	6	16	18	20
2	7	16	31	30
8	-6	17	11	11
3	-2	17	15	-15
4	-1	17	29	-29
3	1	17	28	29
1	2	17	16	15
3	-3	18	28	30
4	-2	18	15	-17
0	0	18	183	-189
2	2	18	15	-17
0	3	18	28	30

All the interatomic distances less than 4·0 A° were calculated. There is no indication of hydrogen bonding between MDA molecules and there are no abnormally short intermolecular contacts.

Table 5 contains a listing of the observed and calculated structure factors for each reflection measured.

We wish to thank Dr W. R. Busing for helpful suggestions and the use of his programs, Dr N. P. Marullo for consultations relating to the chemistry, Dr T. C. Shields for his encouragement, Dr K. F. Streib for the Sayre equation program and Dr H. E. Vogel, who secured the support for this work.

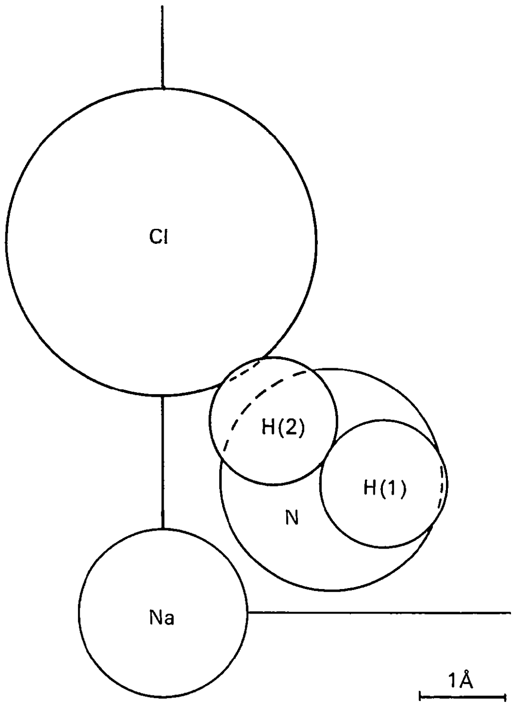

Fig. 3. Amine location relative to the sodium and chlorine ions. Ionic radii are used for Na and Cl; neutral radii are used for N and H.

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Acta Cryst. (1972). B**28**, 2514

A Neutron Diffraction Study of the Structure of L-Glutamic Acid.HCl

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(*Received* 6 *December* 1971)

A neutron diffraction study of L-glutamic acid hydrochloride, $C_5H_{10}O_4N.Cl$, has been carried out. The structure is orthorhombic, space group $P2_12_12_1$, with four molecules per unit cell. The cell parameters are: $a=5{\cdot}151$ (6), $b=11{\cdot}79$ (2) and $c=13{\cdot}35$ (2) Å. Intensities of 639 (606 non-zero) independent reflexions have been measured at a wavelength of 1·406 Å, using the diffractometer in symmetrical setting. The positions of the ten hydrogen atoms in the asymmetric unit have been determined from a Fourier map of the nuclear scattering density computed using the phases from the X-ray heavy-atom positions. The structure has been refined to a final conventional R value of 4·3% by the method of least-squares. It consists of molecules hydrogen-bonded in zigzag chains along the **c** direction. Details of hydrogen bonding and molecular conformation are discussed. The average C–H bond length is 1·090 (11) Å. The average values of the C–C–H and H–C–H angles are 109·4 (7) and 106·0 (12)°, while those of the C–N$^+$–H and H–N$^+$–H angles are 109·9 (7) and 109·0 (9)°.

Introduction

A detailed knowledge of the hydrogen atom positions and the side group conformations in amino acids is of considerable interest in the calculation of the configuration of the side groups associated with polypeptide chains. This paper reports a precision neutron diffraction study of the structure of L-glutamic acid.HCl as part of the program of studies currently in progress in our laboratory on the structure and hydrogen-bonding properties of amino-acids. A two-dimensional X-ray study of this structure was carried out by Dawson (1953) but the hydrogen atom positions were not determined.

Experimental

Large, clear and well formed crystals of L-glutamic acid.HCl, $C_5H_9O_4N.HCl$, were easily obtained by slow evaporation from a saturated aqueous solution with excess 20% hydrochloric acid. The crystals were