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The Crystal Structure of *cyclo*Hexylamine Hydrochloride

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The crystal structure of *cyclo*hexylamine hydrochloride has been determined, making use of the isomorphism of the hydrochloride with the corresponding hydrobromide and the Okaya–Nitta inequality method. Both compounds crystallize with the symmetry of C_{2v}^5–$Pca2_1$. The dimensions of the unit cell, containing four chemical units, are $a = 9{\cdot}36$, $b = 11{\cdot}47$, $c = 7{\cdot}41$ Å for the hydrochloride and $a = 9{\cdot}56$, $b = 11{\cdot}29$, $c = 7{\cdot}83$ Å for the hydrobromide. The *cyclo*hexyl ring has the puckered form, while the crystal structure may be described as having a layer structure made by nitrogen and chlorine atoms, to which the *cyclo*hexyl rings are anchored by the equatorial C–N bonds.

A discussion on the relation between the present structure, alkylamine hydrohalides and aniline hydrochloride is given.

Introduction

Since the crystal structures of aniline hydrochloride (Brown, 1949) and of many aliphatic amine hydrohalides (Wyckoff, 1931, p. 362; Hughes & Lipscomb, 1946; King & Lipscomb, 1950) are known, it seems of interest to investigate a closely related compound, *cyclo*hexylamine hydrochloride. It is also of interest to obtain information about the configuration of the six-membered aliphatic ring, though compounds with such a ring have already been studied: α-phloroglucitol dihydrate (Andersen & Hassel, 1948); 1,2,4,5-tetrachloro*cyclo*hexane (m.p. 174° C.) (Hassel & Lund, 1949); 1,2,3,4-tetrabromo*cyclo*hexane (m.p. 142° C.) (Lund, 1950); 1,2-dichloro-4,5-dibromo*cyclo*hexane (Hassel & Lund, 1952); gammexane (Vloten, Kruissink, Strijk & Bijvoet, 1950); δ-benzene hexachloride (Bommel, Strijk & Bijvoet, 1950); ε-1,2,3,4,5,6-hexachloro*cyclo*hexane (Norman, 1950); pentachloro*cyclo*hexene (Pasternak, 1951); β-1,2,4,5-tetrabromo*cyclo*hexane (Haak, Vries & MacGillavry, 1952); 1-chloromercuri-2-methoxy*cyclo*hexane (Brook & Wright, 1951); adamantane (Nowacki, 1945; Giacomello & Illuminati, 1945); *cyclo*hexane (Oda, 1948); *cyclo*hexanol (Oda, 1949); and *cyclo*hexanoxime (Shimada, Okaya & Nakamura, to be published later).

Crystal data

The needle- and plate-shaped crystals of *cyclo*hexylamine hydrochloride were crystallized from ethyl alcohol and also from a dioxane–ethyl alcohol mixture by slow evaporation; m.p. 205–207° C. Perfect cleavage is shown parallel to (010).

In order to minimize absorption, crystals of cross-section less than 0·3 mm. and of a shape as regular as possible were used. Using Cu $K\alpha$ radiation, Laue photographs and oscillation and Weissenberg photographs around each principal axis were taken; from those the following crystallographic constants were obtained. The unit cell with Laue symmetry D_{2h} is of the dimensions

$$a = 9{\cdot}36 \pm 0{\cdot}03,\quad b = 11{\cdot}47 \pm 0{\cdot}03,\quad c = 7{\cdot}41 \pm 0{\cdot}03 \text{ Å}\,.$$

Assuming four chemical units in a cell with the above dimensions, the density is calculated to be 1·13±0·02 g.cm.$^{-3}$, which is in good agreement with the observed value (1·13±0·01 g.cm.$^{-3}$) determined by flotation in a toluene–chloroform mixture. Using the multiple-film technique, intensities were estimated visually with a calibrated scale. The corrections for polarization and Lorentz factors were made in the usual way and that for absorption was neglected.

The systematic absences, $(0kl)$ when l is odd, $(h0l)$ when h is odd, lead to either C_{2v}^5–$Pca2_1$ or D_{2h}^{11}–$Pcam$, of which the latter was found to be excluded in the course of the structure determination.

We have also prepared *cyclo*hexylamine hydrobromide and found it to be isomorphous with the hydrochloride. The dimensions of the unit cell, containing four chemical units and of the space group C_{2v}^5–$Pca2_1$, are

$$a = 9{\cdot}56 \pm 0{\cdot}04,\quad b = 11{\cdot}29 \pm 0{\cdot}05,\quad c = 7{\cdot}83 \pm 0{\cdot}04 \text{ Å}\,.$$

Structure determination

As the projection of the structure on to (001) is the same for the two space groups mentioned above, we

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first prepared two Patterson syntheses using the data of the hydrochloride and hydrobromide. The projection for the latter gave clearly the approximate positions of the halogen atoms. The structure factors ($hk0$) for the hydrochloride were calculated using the coordinates of the chlorine atoms only, and it was found that the signs of the large structure factors were, in most cases, the same as those given by the Okaya–Nitta inequality methods (Okaya & Nitta, 1952). The first electron-density projection for the hydrochloride was synthesized using the observed $|F(hk0)|$ values with the signs determined as above. It gave the approximate positions for the five carbon atoms within the ring, besides the chlorine atoms, from which, by repeated structure-factor calculations and Fourier syntheses, the map shown in Fig. 1(a) was obtained. Although the five atomic peaks of the *cyclo*hexyl ring are seen to be very well resolved the positions of C_1 and N are badly masked by the overlapping of the chlorine atom. We have prepared difference Fourier syntheses, first using $F_o - F_c'$ as the coefficients, where F_c' stands for the calculated structure factors with the chlorine atoms alone. This gave us the resolved peaks for C_1 and N, and there was observed a slight shift of the atomic parameters of the other five carbon atoms. The final adjustment of x and y parameters was made by the difference syntheses, where calculated structure factors including all the atoms except hydrogen were used.

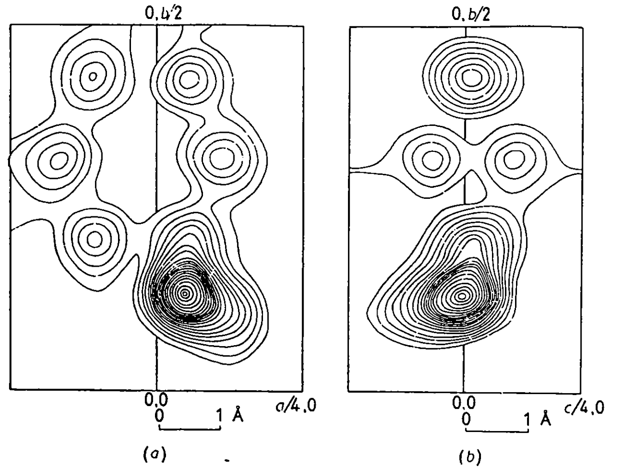

Fig. 1. (a) Projection of electron density on (001). Contours are drawn at intervals of 1 e.Å^{-2}, beginning with the 2 e.Å^{-2} line. (b) Projection of electron density on (100). Contours are drawn at intervals of 1 e.Å^{-2}, beginning with the 3 e.Å^{-2} line.

Now the question has to be solved whether the space group is D_{2h}^{11} or C_{2v}^{5}. If we take D_{2h}^{11}, all the six carbon and one nitrogen atoms within the cyclohexylamine group, together with one chlorine atom, should lie on the mirror plane at $z = \frac{1}{4}$ or $\frac{3}{4}$. In this case, the reflexions ($00l$) should be in phase with all atoms, so that these reflexions should always be stronger than other reflexions with the same l. However, this is not the case, and hence the space group is uniquely determined to be C_{2v}^{5}. The possibility of a planar configuration of the ring is thus ruled out.

Since the space group is proved to be C_{2v}^{5}–$Pca2_1$, the two projections (100) and (010) possess no centres of symmetry, so that the usual inequality relations of Harker–Kasper, Okaya–Nitta, etc. cannot be applied. Therefore, we set up inequality relations which hold in the case of non-centrosymmetric structures (to be published). These new inequality relations proved useful in arriving at a crude (100) projection, from which the result shown in Fig. 1(b) was obtained by successive approximation. The refinement of y and z parameters was made using the same difference syntheses as for the (001) projection.

The final atomic coordinates are listed in Table 1. The discrepancy factor R was 0·178 for ($hk0$) and

Table 1. *Atomic parameters*

	x/a	y/b	z/c
Cl	0·048	0·130	0·500
N	0·118	0·113	−0·087
C_1	0·059	0·203	0·028
C_2	0·113	0·316	−0·063
C_3	0·052	0·428	0·024
C_4	−0·112	0·425	0·005
C_5	−0·171	0·314	0·097
C_6	−0·105	0·204	0·009

Table 2. *Intermolecular and intramolecular distances*

(±0·05 Å)

$C_1(A)$–$C_2(A)$	1·55 Å	Cl(A)–Cl(B)	5·29 Å
$C_2(A)$–$C_3(A)$	1·55	Cl(A)–Cl(C)	4·77
$C_3(A)$–$C_4(A)$	1·54	Cl(A)–Cl(D)	5·55
$C_4(A)$–$C_5(A)$	1·55		
$C_5(A)$–$C_6(A)$	1·56	$C_1(A)$–$C_1(B)$	5·15
$C_6(A)$–$C_1(A)$	1·54	$C_1(A)$–$C_2(B)$	4·51
$C_1(A)$–N(A)	1·45	$C_2(A)$–$C_2(B)$	4·45
		$C_2(A)$–$C_3(B)$	4·57
N(A)–Cl(A)	3·14	$C_3(A)$–$C_3(B)$	5·14
N(A)–Cl(B)	3·20	$C_3(A)$–$C_4(F)$	3·58
N(A)–Cl(C)	3·25	$C_3(A)$–$C_4(E)$	3·95
		$C_3(A)$–$C_3(E)$	4·17
Cl(A)–$C_1(A)$	3·60	$C_4(A)$–$C_4(E)$	4·46
Cl(A)–$C_1(B)$	3·78	$C_5(C)$–$C_4(D)$	3·86
Cl(A)–$C_1(C)$	3·96	$C_5(C)$–$C_5(D)$	3·99
Cl(A)–$C_2(A)$	3·92	$C_5(C)$–$C_6(D)$	3·82
Cl(A)–$C_6(A)$	4·00		
Cl(A)–$C_2(B)$	3·85		
Cl(A)–$C_6(C)$	3·87		

Table 3. *Bond angles*

(±5°)

$C_1(A)$–$C_2(A)$–$C_3(A)$	113°	$C_6(A)$–$C_1(A)$–N(A)	109°
$C_2(A)$–$C_3(A)$–$C_4(A)$	108	$C_2(A)$–$C_1(A)$–N(A)	112
$C_3(A)$–$C_4(A)$–$C_5(A)$	109		
$C_4(A)$–$C_5(A)$–$C_6(A)$	108	Cl(A)–N(A)–Cl(B)	113
$C_5(A)$–$C_6(A)$–$C_1(A)$	112	Cl(B)–N(A)–Cl(C)	119
$C_6(A)$–$C_1(A)$–$C_2(A)$	107	Cl(C)–N(A)–Cl(A)	99
$C_1(A)$–N(A)–Cl(A)	116	N(A)–Cl(A)–N(C)	104
$C_1(A)$–N(A)–Cl(B)	102	N(A)–Cl(A)–N(B)	88
$C_1(A)$–N(A)–Cl(C)	118	N(B)–Cl(A)–N(C)	112

0·167 for (0*kl*), including all the observed terms up to $\sin\theta = 0{\cdot}894$ for (*hk*0) and $\sin\theta = 0{\cdot}902$ for (0*kl*) with a temperature factor $B = 5{\cdot}0$ Å^2. These parameters led to the distances and bond angles listed in Tables 2 and 3.

Discussion of the structure

Fig. 2(*a*, *b*) illustrates the projected structure of the molecules. It is revealed that the *cyclo*hexylamine (or rather the *cyclo*hexylammonium) ion has the well known chair configuration with the C–N bond in the direction corresponding to the so-called ϰ-configuration. Almost all the bond distances and bond angles within the ion show but small deviations from the normal values, as is seen in Tables 2 and 3. The crystal structure of *cyclo*hexane derivatives so far reported failed to give very accurate coordinates of the atoms within the ring, chiefly because they are masked

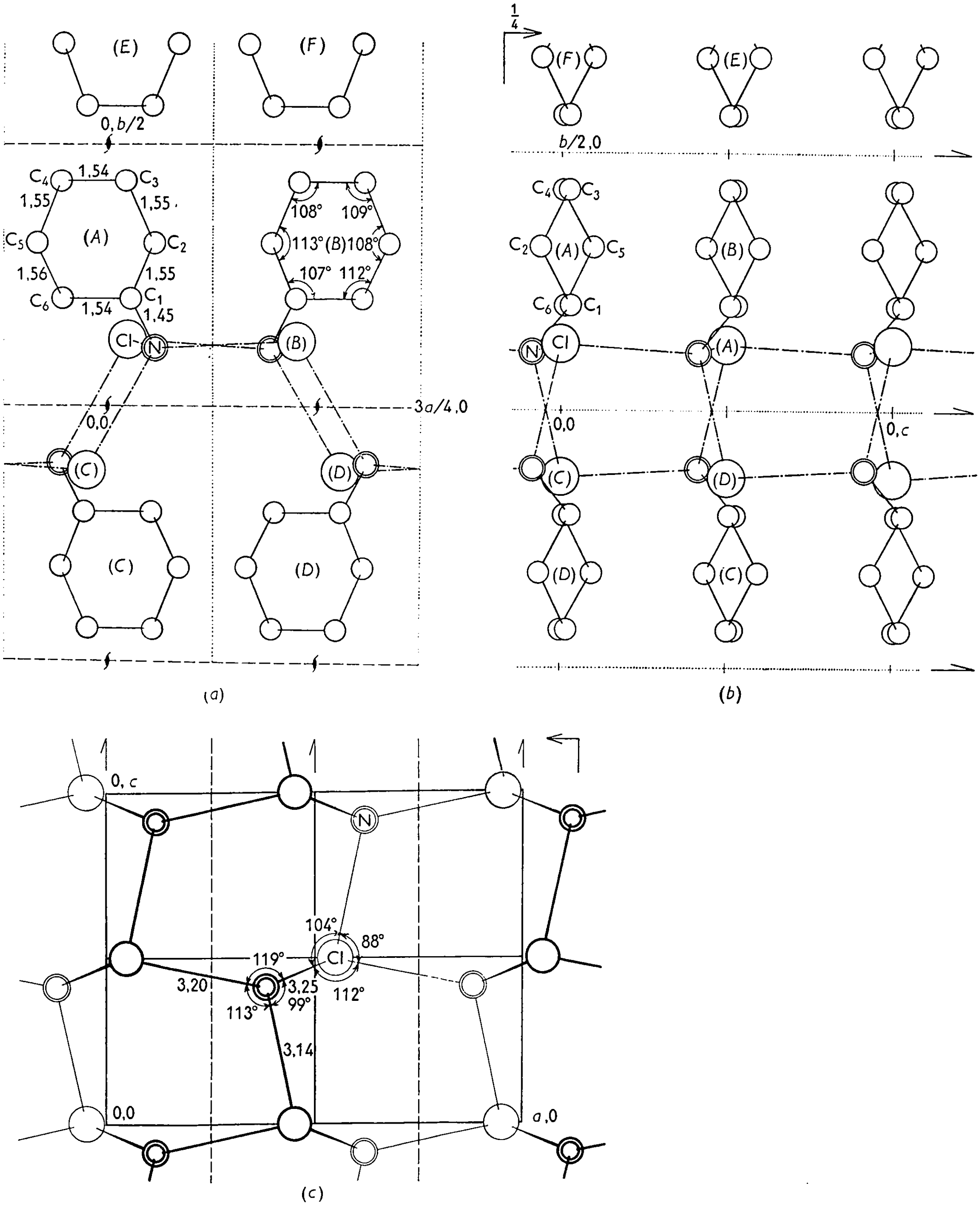

Fig. 2. Illustrative projection of the structure (*a*) on (001), (*b*) on (100). (*c*) Partial illustrative projection of the structure on (010). The lines between N and Cl atoms show their threefold coordination, *cyclo*hexyl rings being omitted.

by heavy atoms. The present investigation seems to give the most reliable figure for the structure of the cyclohexyl ring.

Fig. 2(*c*) shows only the chlorine and nitrogen atoms to reveal their mutual linking in the (010) projection. Besides the directly bonded carbon atom at 1·45 Å, the nitrogen atom is surrounded by three chlorine atoms at distances 3·14, 3·20 and 3·25 Å.* There are found six chlorine atoms in pairs at 4·77, 5·29 and 5·55 Å around a chlorine atom, and three nitrogen atoms at 3·14, 3·20 and 3·25 Å form a deformed triangular pyramid. The closer intermolecular approaches are 3·58, 3·82 and 3·86 Å between carbon atoms of neighbouring rings, and the shortest distance between carbon and chlorine atoms is found to be 3·60 Å between C_1 and Cl, the others being all larger than 3·80 Å.

As is seen from Fig. 2, there are layers consisting of nitrogen and chlorine atoms parallel to (010), and the *cyclo*hexyl rings are, as it were, anchored to such layers by the C–N bonds. Such a layer structure explains the perfect cleavage parallel to (010), because only weak van der Waals forces are exerted on the neighbouring *cyclo*hexyl rings of the adjacent layers.

It is well known that the lower-membered alkylamine hydrohalides form the crystal structure of a distorted caesium chloride arrangement, whereas the higher-membered alkylamine hydrohalides crystallize in a layer-lattice structure derivable from the sodium chloride arrangement. It can be said that the structure of aniline hydrochloride has a close relationship to the structure of the lower-membered alkylamine hydrohalide, while the structure of *cyclo*hexylamine hydrochloride is analogous to the structure of the higher-membered alkylamine hydrohalides. It is interesting to see that the length of the two groups (phenyl and *cyclo*hexyl) are in the region where the structure-type transition occurs. Moreover, it may be added that the difference of the structure type for these two salts will be partly due to the difference of the distribution of the positive charge within the derived ammonium ions.

The crystal structure of geranylamine hydrochloride determined by Jeffrey (1945) can also be compared to that of *cyclo*hexylamine hydrochloride.

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* The nitrogen and chlorine atoms are likely to be linked by the hydrogen bond NH · · · Cl, because of their short distances and the tetrahedral arrangement of chlorine atoms referred to the C–N bond. As the hydrobromide was found to be isomorphous with the hydrochloride, this might lead to a hydrogen-bond formation, NH · · · Br, in the former. In this respect, it will be interesting to have additional information on these two compounds, using infra-red absorption.