Refinement of the Crystal and Molecular Structure of Cyclohexylammonium Chloride (Cyclohexylamine Hydrochloride)

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The present refinement of the crystal structure of cyclohexylammonium chloride represents an accurate determination of the simplest cyclohexane derivative known to date. Crystals of cyclohexylammonium chloride belong to the orthorhombic space group $Pca2_1$, with four molecules in the unit cell of dimensions $a = 9\cdot313 \pm 0\cdot001$, $b = 11\cdot442 \pm 0\cdot002$ and $c = 7\cdot554 \pm 0\cdot001$ Å, $D_m = 1\cdot14$ g.cm^{-3}, $D_x = 1\cdot13$ g.cm^{-3}. Intensities of 615 reflections were measured on a Picker four-circle diffractometer with Ni-filtered Cu radiation. All of the fourteen hydrogen atoms were unambiguously located on a difference electron density map. The structure was refined by full-matrix least-squares to an R value of $0\cdot039$ from 610 observed reflections, excluding five extinguished reflections. The cyclohexane ring is in the chair form with an equatorially substituted ammonium group. The average values of the bond distances, bond angles and the torsion angles in the ring are $1\cdot523 \pm 0\cdot007$ Å, $111\cdot3 \pm 0\cdot6°$ and $55\cdot2 \pm 1\cdot2°$ respectively. The ammonium group is staggered to the ring; it is hydrogen bonded to three neighboring chloride ions and forms the stabilizing force in the crystal lattice. The average $\overset{+}{N}$–H$\cdots$Cl$^-$ hydrogen-bond distance is 3·18 Å.

Introduction

In this paper is reported the redetermination of the crystal structure of cyclohexylammonium chloride whose structure was originally derived by Shimada, Okaya & Nakamura (1955) with the use of projection data. The difficulty in obtaining adequate single crystals and the possibility of disorder in the crystal have remained obstacles to the solution of the crystal structure of cyclohexane itself by X-ray diffraction techniques. Current interest in the accurate geometry and conformation of cyclohexane and its derivatives prompted us to carry out this precise X-ray analysis of the simplest cyclohexane derivative known to date.

Experimental

Crystals of cyclohexylammonium chloride, grown from aqueous ethanol solution, were in the form of plates. The lattice parameters were determined from six reflections with $2\theta > 60°$ carefully measured on a Picker four-circle diffractometer using nickel-filtered Cu radiation ($\lambda = 1\cdot5418$ Å). The crystal data are given in Table 1. The cell edges a, b are shorter than those of the earlier investigation by about 0·5%, while that of c is about 2% greater. The crystal was mounted with the c axis parallel to the φ axis of the goniostat and 716 intensity data were scanned with Ni-filtered Cu radiation on a Picker four-circle diffractometer equipped

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Table 1. *Crystallographic data*

	This work Diffractometric	Shimada *et al.* (1955) Photographic
a	$9\cdot313 \pm 0\cdot001$ Å	$9\cdot36 \pm 0\cdot03$ Å
b	$11\cdot442 \pm 0\cdot002$	$11\cdot47 \pm 0\cdot03$
c	$7\cdot554 \pm 0\cdot001$	$7\cdot41 \pm 0\cdot03$
Crystal system	Orthorhombic	
Systematic absences	$0kl$, $l = 2n+1$	
	$h0l$, $h = 2n+1$	
Space group	$Pca2_1$ or $Pcam$; $Pca2_1$ confirmed by intensity statistics and structure analysis	
Z	4	
D_x	1·13 g.cm^{-3}	
D_m	1·14 g.cm^{-3}	

with a scintillation counter and a pulse-height discriminator out to $2\theta = 134°$. Inspection of the systematically absent reflections ($0kl$, l odd; $h0l$, h odd) indicated that a reflection count is significant if $I > 1\cdot40$ (I), where

$$\sigma(I) = [I_{scan} + I_{bkg}]^{1/2} .$$

On this criterion, 615 reflections were considered observed, and were used in the structure analysis. The total number of reflections accessible to Cu $K\alpha$ radiation is about 930. The data were corrected for the Lorentz and polarization factors. The anisotropy of absorption was roughly accounted for by observing the intensity of a reflection at $\chi = 90°$ as a function of φ. The maximum variation in the intensity was 2%. Absorption corrections were not applied because the crystal used was small, $0\cdot1 \times 0\cdot25$ mm² in cross-section and $0\cdot4$ mm long. The distribution of the intensities (normalized structure amplitudes) showed that the space group is acentric. Therefore, the space group $Pca2_1$ was assigned and the structure analysis and refinement were carried out on this basis (Shimada et al., 1955).

Structure determination and refinement

The structure was redetermined to confirm the results obtained by Shimada et al. (1955) who used two-dimensional data.

The x and y coordinates of the chloride were found from a gradient-sharpened three-dimensional Patterson diagram (Jacobson, Wunderlich & Lipscomb, 1961) and the z coordinate, which is arbitrary, was set equal to $0\cdot0$. A three-dimensional electron density distribution phased on this atom contained the spurious mirror symmetry. The nitrogen atom could be easily located and a second round of calculation using both the chloride and the nitrogen atoms revealed the entire structure, which was essentially the same as that obtained in the earlier work.

Four cycles of full-matrix least-squares refinement (Busing, Martin & Levy, 1962) using Hughes's (1941) weighting scheme lowered the R value from $0\cdot350$ to $0\cdot104$. The quantity minimized in the least-squares refinement was $\Sigma w(|F_o| - k|F_c|)^2$. At this point, a three-dimensional difference electron density map revealed the approximate positions of all the fourteen hydrogen atoms (Fig.1). The hydrogen atoms were assigned a uniform thermal parameter of 5 Å² which was held fixed throughout the refinement. An additional three cycles of isotropic least-squares with the same weighting scheme reduced the R value to $0\cdot064$. Further cycles of

refinement were made in which the overall scale factor, positional parameters of the hydrogen atoms and the positional and anisotropic thermal parameters of the heavy atom were varied.
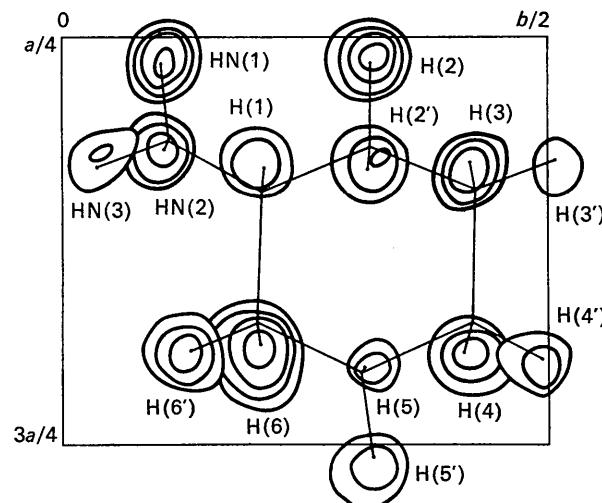

Fig. 1. The difference electron density map showing the hydrogen atoms. Contours are at intervals of $0\cdot1$ e.Å⁻³ starting from $0\cdot2$ e.Å⁻³.
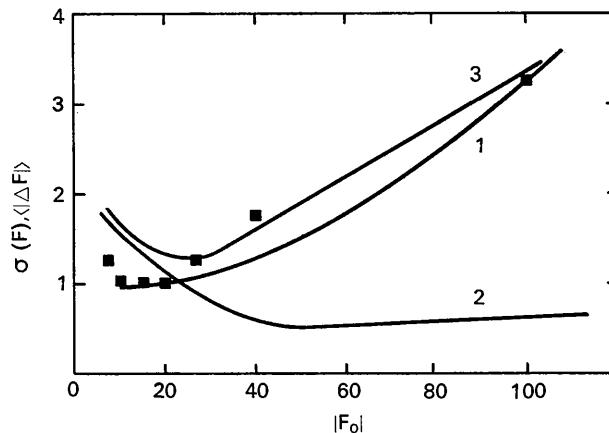

Fig. 2. A plot of the three different error schemes as a function of $|F|$ used in the refinement. They are (1) $\sigma_1(F) = [1\cdot1 + |F| + 0\cdot008|F|^2]^{1/2}$, (2) $\sigma_2(F) = \dfrac{F}{2} \cdot \dfrac{[I + B + 0\cdot01(I+B)^2]^{1/2}}{I - B}$,

(3) $\sigma_3(F) = \sigma_2(F) + 0\cdot027|F|$. The actual values of $\langle \Delta|F_o - F_c|\rangle$ are shown by rectangles. Scheme 1 underestimates the errors in the weak reflections while scheme 2 underestimates the errors in the strong reflections. Scheme 3 reflects the proper errors.

Table 2. *Some results of the refinement based on the three different weighting schemes*

	Δ/δ Average shift/standard deviation in positional parameters	R	wR	$\sqrt{\dfrac{w(\Delta F^2)}{m-n}}$	Average standard deviation in carbon atom positions	C(4)–C(5)
Scheme 1	0·38	0·042	0·054	1·28	0·006 Å	1·484 Å
Scheme 2	0·19	0·041	0·036	2·16	0·005	1·486
Scheme 3	0·16	0·039	0·050	1·02	0·006	1·493

Table 3. *Positional and thermal parameters of the atoms*

Standard deviations are in parentheses.

The anisotropic temperature factor is of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	$x/a \times 10^4$	$y/b \times 10^4$	$z/c \times 10^4$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
C(1)	4404 (5)	2064 (4)	39 (13)	107 (5)	67 (3)	143 (8)	−2 (3)	−2 (12)	1 (9)
C(2)	3834 (6)	3203 (5)	−710 (11)	107 (7)	65 (4)	247 (14)	17 (4)	−13 (8)	3 (6)
C(3)	4460 (7)	4244 (6)	275 (14)	137 (6)	75 (4)	271 (24)	7 (4)	23 (13)	−33 (9)
C(4)	6091 (7)	4210 (5)	276 (11)	139 (7)	69 (4)	222 (20)	−17 (4)	9 (11)	−21 (8)
C(5)	6662 (7)	3075 (6)	951 (12)	121 (8)	87 (5)	242 (14)	−7 (5)	−18 (9)	25 (8)
C(6)	6033 (5)	2029 (4)	−26 (15)	104 (5)	71 (4)	238 (11)	11 (3)	−1 (15)	8 (11)
N	3800 (5)	1058 (4)	−962 (8)	114 (5)	55 (3)	191 (9)	1 (3)	−8 (6)	15 (5)
Cl	455 (1)	1305 (1)	0	107 (1)	72 (1)	164 (2)	−9 (1)	−7 (3)	4 (2)

	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$
HN(1)*	262 (6)	108 (4)	−78 (9)
HN(2)	404 (7)	113 (5)	−228 (9)
HN(3)	415 (6)	32 (6)	−63 (8)
H(1)	407 (7)	208 (6)	114 (9)
H(2)	411 (7)	317 (6)	−196 (9)
H(2')	274 (6)	316 (4)	−73 (9)
H(3)	430 (7)	425 (6)	141 (10)
H(3')	405 (6)	497 (5)	−58 (8)
H(4)	634 (7)	433 (6)	−116 (9)
H(4')	650 (6)	487 (5)	83 (10)
H(5)	646 (7)	293 (6)	203 (11)
H(5')	776 (7)	307 (5)	64 (8)
H(6)	634 (7)	199 (6)	−133 (10)
H(6')	635 (6)	133 (5)	36 (9)

* All hydrogen atoms are isotropic with $B=5$ Å².

The final stages of the anisotropic refinement were carried out with a Cruickshank type of weighting scheme (scheme 1), where

$$\frac{1}{\sqrt{w}} = \sigma_1(F) = [1 \cdot 1 + |F| + 0 \cdot 008|F|^2]^{1/2}.$$

After four cycles, convergence was reached, Table 2. However, it was found that the C(4)–C(5) bond distance was only 1·484 Å, significantly shorter than the remaining endocyclic bonds, which averaged 1·519 ±0·003 Å. A plot of $|\Delta F|$ *vs.* $|F|$ indicated that the weighting scheme, although satisfactory for medium and strong reflections, underestimated the errors in the weakest group of reflections, Fig.2. A plot of $\sigma(F)$, based on counting statistics and electronic instability of 1% *vs.* $|F|$ also shown in Fig.2. Since scheme 2 does not account for systematic errors due primarily to secondary extinction effects, the errors in the strong reflections are underestimated. Nevertheless, two cycles of refinement were carried out using weighting scheme 2. The results are listed in Table 2. Now scheme 2 was modified to yield scheme 3 which reflects the correct relative error in the data. This was done by adding a linear term in $|F|$ so as to bring the $\sigma(F)$ to the same level as $\langle|\Delta F|\rangle$ for strong reflections. $\sigma_3(F)$ is given by

$$\sigma_3(F) = \sigma_2(F) + 0 \cdot 027|F|.$$

Results of the refinement based on scheme 3 are shown in Table 2. It is seen that the R index and the Δ/σ value are the lowest for the latter refinement. The parameters obtained from weighting scheme 3 are listed in Table 3, together with the standard deviations estimated from

the diagonal terms of the inverse normal matrix. The analysis of the thermal ellipsoids in terms of the principal axes is given in Table 4. The observed and calculated structure factors are listed in Table 5. A perspective view of the electron density is shown in Fig.3. An *ORTEP* plot (Johnson, 1965) of the molecule is shown in Fig.4.

Table 4. *Analysis of the thermal ellipsoids in terms of the principal axes*

	i	u_i	l_i	m_i	n_i
C(1)	1	0·216 Å	−0·989	0·150	0·004
	2	0·210	−0·145	−0·954	−0·261
	3	0·203	−0·035	−0·259	0·965
C(2)	1	0·266	0·088	−0·019	−0·996
	2	0·224	0·804	0·592	0·060
	3	0·200	0·588	−0·806	0·067
C(3)	1	0·284	−0·161	0·201	−0·966
	2	0·245	−0·964	−0·241	0·110
	3	0·217	−0·211	0·949	0·233
C(4)	1	0·256	0·545	−0·316	0·778
	2	0·247	0·806	−0·058	−0·589
	3	0·209	0·231	0·947	0·223
C(5)	1	0·268	−0·188	0·346	0·919
	2	0·236	−0·109	0·923	−0·370
	3	0·229	−0·976	−0·169	−0·136
C(6)	1	0·263	−0·006	−0·079	−0·997
	2	0·221	−0·653	−0·755	0·063
	3	0·209	−0·758	0·651	−0·047
N	1	0·237	0·217	−0·158	−0·963
	2	0·224	0·976	0·050	0·211
	3	0·189	0·015	−0·986	0·165
Cl	1	0·225	−0·600	0·656	0·458
	2	0·216	−0·269	0·373	−0·888
	3	0·212	−0·753	−0·656	−0·048

The scattering factors for Cl⁻, N and C were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965).

Discussion

The bond lengths, bond angles (and their standard errors) and the torsion angles involving the nonhydrogen atoms are given in Table 6. For comparison, the bond lengths and angles obtained by Shimada *et al.* (1955) are also tabulated. The bond lengths and angles involving the hydrogen atoms are listed in Table 7. The average errors in these are: $\sigma(C-H) = \sigma(N-H) = 0.07$ Å, $\sigma(C-C-H) = \sigma(N-C-H) = 2.8°$, $\sigma(H-C-H) = 3.5°$. A rigid body analysis of the thermal motion (Schomaker & Trueblood, 1968) has been made and the **T** and **ω** tensors are listed in Table 8. It is found that the translation is nearly isotropic whereas there is a libration of 6.5° about an axis roughly along the line joining C(1)–C(4). This is a reasonable mode of libration in view
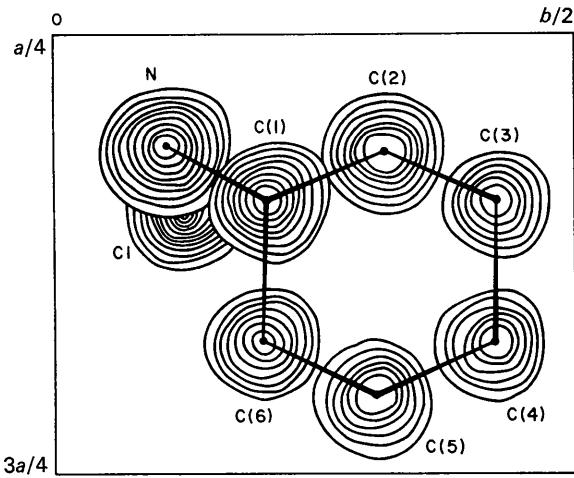
Fig. 3. A perspective view of the electron density as viewed along the *c* axis. The contours around Cl⁻ start at 5 e.Å⁻³ and are at intervals of 2 e.Å⁻³; those around other atoms start at 1 e.Å⁻³ and are at intervals of 1 e.Å⁻³.

Table 5. *Observed and calculated structure factors*

Each line gives the running index *k*, 10|F_o| and 10|F_c|.

projection work are 1·55 Å and 110° respectively (Shimada et al., 1955). Although the present results are more accurate, the differences between our values and those of Shimada et al. (1955) are probably within the

Fig. 4. *ORTEP* plot of the molecule.

Table 7. *Bond lengths and angles involving the hydrogen atoms*

	Distance		Angle
C(1)–H(1)	0·89 Å	H(1)——C(1)–N	111°
C(2)–H(2)	0·98	H(1)——C(1)–C(2)	102
C(2)–H(2')	1·02	H(1)——C(1)–C(6)	112
C(3)–H(3)	0·87	H(2)——C(2)–C(1)	104
C(3)–H(3')	1·13	H(2)——C(2)–C(3)	114
C(4)–H(4)	1·12	H(2)——C(2)–H(2')	104
C(4)–H(4')	0·95	H(2')——C(2)–C(1)	108
C(5)–H(5)	0·85	H(2')——C(2)–C(3)	115
C(5)–H(5')	1·05	H(3)——C(3)–C(2)	115
C(6)–H(6)	1·03	H(3)——C(3)–C(4)	100
C(6)–H(6')	0·90	H(3)——C(3)–H(3')	120
N——HN(1)	1·10	H(3)——C(3)–C(2)	100
N——HN(2)	1·02	H(3')——C(3)–C(4)	111
N——HN(3)	0·94	H(4)——C(4)–C(3)	102
		H(4)——C(4)–C(5)	112
		H(4)——C(4)–H(4')	104
		H(4')——C(4)–C(3)	113
		H(4')——C(4)–C(5)	113
		H(5)——C(5)–C(4)	114
		H(5)——C(5)–C(6)	103
		H(5)——C(5)–H(5')	115
		H(5')——C(5)–C(4)	106
		H(5')——C(5)–C(6)	105
		H(6)——C(6)–C(5)	113
		H(6)——C(6)–C(1)	108
		H(6)——C(6)–H(6')	101
		H(6')——C(6)–C(5)	114
		H(6')——C(6)–C(1)	111
		HN(1)-N——C(1)	107
		HN(1)-N——HN(2)	110
		HN(1)-N——HN(3)	109
		HN(2)-N——C(1)	110
		HN(2)-N——HN(3)	105
		HN(3)-N——C(1)	115

of the hydrogen-bonding scheme involving the amino group. The values corrected for librational motion are given in parentheses in Table 6. It is found that the C(4)–C(5) bond is still short, differing from the remaining ring bonds by about 2·5 σ, although chemically the C(4)–C(5) bond is similar to the C(3)–C(4) bond. The average corrected values of the endocyclic bond distance, bond angle, and torsional angle are 1·523 ± 0·007 Å, 111·3 ± 0·6° and 55·0 ± 1·2°, respectively. The average bond distance and bond angle obtained in the

Table 6. *Bond lengths, bond angles and torsion angles involving the nonhydrogen atoms*

Values in parentheses are those corrected for librational motion of the molecule.

	Bond length					Bond angle			
	This work	σ(l)	Shimada et al. (1955) (±0·05 Å)			This work	σ(θ)	Shimada et al. (1955) (±5°)	
C(1)–C(2)	1·516 Å (1·526)	0·008 Å	1·55 Å		C(1)–C(2)–C(3)	110·8° (110·7)	0·5°	113°	
C(2)–C(3)	1·521 (1·526)	0·010	1·55		C(2)–C(3)–C(4)	111·3 (111·1)	0·5	108	
C(3)–C(4)	1·520 (1·529)	0·009	1·54		C(3)–C(4)–C(5)	112·2 (112·4)	0·5	109	
C(4)–C(5)	1·493 (1·502)	0·009	1·55		C(4)–C(5)–C(6)	112·4 (112·2)	0·5	110*	
C(5)–C(6)	1·523 (1·528)	0·010	1·55*		C(5)–C(6)–C(1)	110·4 (110·2)	0·5	111*	
C(6)–C(1)	1·518 (1·527)	0·006	1·54		C(6)–C(1)–C(2)	111·1 (111·3)	0·5	106*	
C(1)–N	1·488 (1·493)	0·008	1·45		C(2)–C(1)–N	110·0 (109·9)	0·5	102*	
					C(6)–C(1)–N	109·9 (109·7)	0·5	109	

Atoms	Torsion angle	
C(5)–C(6)–C(1)–C(2)	56·3°	(56·5)
C(6)–C(1)–C(2)–C(3)	−57·0	(−57·2)
C(1)–C(2)–C(3)–C(4)	54·8	(54·8)
C(4)–C(5)–C(6)–C(1)	−54·7	(−54·7)
C(2)–C(3)–C(4)–C(5)	−53·3	(−53·5)
C(3)–C(4)–C(5)–C(6)	53·5	(53·7)
N——C(1)–C(2)–C(3)	−179·0	(−179·0)
N——C(1)–C(6)–C(5)	178·4	(178·4)

* Values not in agreement with those published.

probable errors of the earlier work. Davis & Hassel (1963) have found, from electron diffraction studies on cyclohexane systems, values which are very similar to those obtained in the present investigation. It is noteworthy that the valency angle is significanthy larger than the ideal tetrahedral value of 109°28′.

The cyclohexane ring is in the chair form with the amino group equatorially substituted. The average value of the torsional angle in this compound agrees well with the value of 55·2° expected for a regular cyclohexane ring with C–C–C valence angles of 111·3°. Table 6 shows that the torsional angles around the bonds C(6)–C(1) and C(1)–C(2) involving the substituted atom are approximately equal and are about 3° greater than those at the opposite end, involving C(4). The departure of the individual torsional angles from the mean value is such that there is a greater puckering involving the equatorially substituted atom,

while a reduction in puckering occurs at the opposite end.

Drawings showing the crystal packing have already been given in the earlier paper by Shimada *et al.* (1955). The ammonium group has three neighboring chloride ions at characteristic distances of 3·21, 3·14 and 3·20 Å, Table 9. A view of the surroundings of the ammonium group as viewed down the C(1)–N bond is given in Fig. 5. The hydrogen bonds are not all linear, the angles at the hydrogen atoms being 169, 179 and 168°. Each NH_3^+ group is surrounded by three Cl^- ions forming a distorted triangular pyramid and *vice versa*. The structure is quite loosely packed as is evident from the low density, and there are no unusually short intermolecular contacts. An interesting comparison of the crystal structures of the higher- and lower-membered alkylamine hydrohalides with those of the alkali halides has been presented by Shimada *et al.* (1955).

Table 8. τ *and* ω *tensors and their eigenvalues and eigenvectors*

Standard deviations are given in parentheses.

$$T = (Å)^2 \quad \begin{bmatrix} 0·046 & 0·002 & 0·004 \\ (0·002) & (0·001) & (0·002) \\ & 0·043 & 0·001 \\ & (0·001) & (0·003) \\ & & 0·047 \\ & & (0·003) \end{bmatrix}$$

$$\omega = (deg)^2 \quad \begin{bmatrix} 19·9 & 17·0 & 5·6 \\ (3·8) & (2·4) & (2·6) \\ & 34·2 & 4·2 \\ & (6·2) & (3·4) \\ & & 9·6 \\ & & (2·7) \end{bmatrix}$$

Principal values and components of eigenvectors

		T					ω		
Å²	Å	*l*	*m*	*n*	(deg)²	(deg)	*l*	*m*	*n*
0·051	0·23	−0·657	−0·187	−0·730	46·7	6·8	0·554	0·814	0·176
0·043	0·21	−0·341	−0·790	0·509	10·8	3·3	0·523	−0·504	0·617
0·042	0·20	−0·672	0·584	0·455	6·2	2·5	0·647	−0·289	−0·705

Table 9. *Hydrogen bond distances and angles*

The first atom is in the list given in Table 3 and the second atom is symmetry-related according to the following code:

I	x, y, z
II	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
III	$\frac{1}{2} + x, y, z$

Atom	Code	Distance	Atom	Angle
N——Cl	I	3·21 Å	C(1)–N——Cl	100·6°
H(1)–Cl	I	2·12	H(1)–N——Cl	7·2
			N——H(1)–Cl	169·1
N——Cl	II	3·14	C(1)–N——Cl	109·9
H(2)–Cl	II	2·12	H(2)–N——Cl	0·5
			N——H(2)–Cl	179·2
N——Cl	III	3·20	C(1)–N——Cl	110·9
H(3)–Cl	III	2·27	H(3)–N——Cl	8·8
			N——H(3)–Cl	167·5
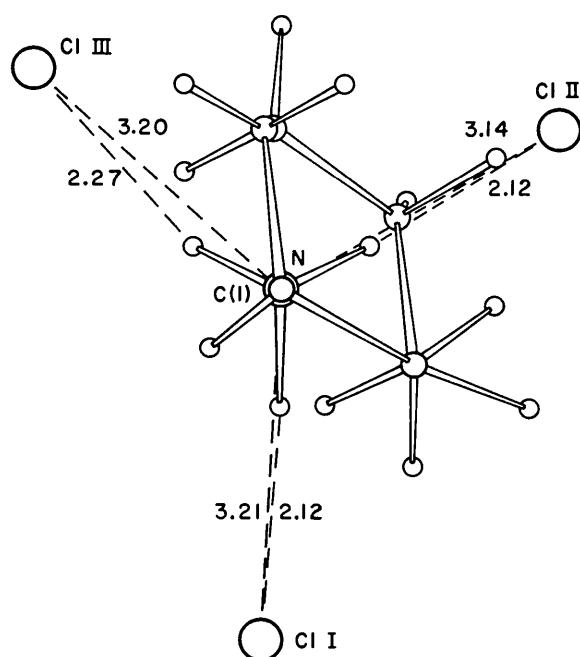
Fig. 5. The surroundings of the NH_3^+ group as viewed along the bond N–C(1).

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Modifications and Transitions of Solid Oxygen

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Thin films of solid oxygen were investigated by electron diffraction and electron microscopy. New information was obtained about the formation of the modifications of solid oxygen and the transitions between the modifications. In particular, the phase which is formed on helium-cooled substrates by deposition of oxygen gas at a low flow rate was examined.

Introduction

The author has shown in previous papers (Hörl, 1959, 1962; Hörl & Marton, 1961) how electron diffraction can be applied to problems of crystal structure, crystal growth and crystal faults of solidified permanent gases. The present paper presents a further study of the modifications of solid oxygen with the aim of investigating the transitions between these modifications in thin films.

The technique described in the previous papers (see also Hörl & Marton, 1958) was extended by the use of an electron microscope as diffraction apparatus. A special stage (Hörl, 1968) for cooling specimens with liquid helium was constructed, which also allowed magnetic studies (not discussed in this paper) by the application of a transverse magnetic field. With this stage it was possible to obtain, in addition to the electron diffraction patterns, electron micrographs of the deposits of interest. Direct observation of the crystals also allowed selected area diffraction.

Oxygen modifications

Ten years ago there were three known modifications of solid oxygen: an α modification, stable up to 23·9 °K, a β modification stable between 23·9° and 43·6 °K and a γ modification stable between 43·6 °K and the melting point at 54·4 °K. Today we have to add two additional modifications, one (we will call it α') which is formed in the temperature range of the α phase when oxygen gas is deposited in the form of a very thin film on a cold substrate, and an amorphous phase, which can be ob-