

X-ray structural characterization of dicyclohexylammonium chloride and its conversion to bromo-, iodo- and hexafluorophosphate derivatives

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Single crystal X-ray structural determination of dicyclohexylammonium chloride, prepared easily in quantitative yield by a modified procedure, reveals it to be strongly and intermolecularly hydrogen bonded. While its bromide derivative is readily obtained in nearly quantitative yield, the iodide and hexafluorophosphate salts are formed slowly in moderate yields.

Amine hydrochlorides, in general, are high melting solids¹ and find use in synthesis² as source of corresponding amines especially if the amine considered is either volatile or highly reactive. Relatively very less is reported on the structure and reactivity of these³ unlike amines. A detailed structural information of amine hydrochlorides have also been considered important for studies on hydrogen bonding. Very few single crystal X-ray structural data on them are available in literature^{4a,b}. It is likely that their high hygroscopic nature and consequent difficulty in handling have contributed to this scenario.

We report herein (i) a modified procedure suitable for large scale synthesis of dicyclohexylammonium chloride (DCA.HCl) which is highly stable towards air and moisture, (ii) its single crystal X-ray structure, and (iii) its reaction with potassium salts, K [X = Br, I, PF₆].

Experimental Section

Reagents, Instrumentation and General Procedures. Dicyclohexylamine (E. Merck), KBr (S.D.), KI (S.D.), KPF₆ (Aldrich) and conc. HCl (Ranbaxy) were used as received. CH₃OH, CHCl₃ and C₆H₆ were freshly distilled and dried according to literature procedures⁵.

Spectral facilities used for characterization have been described earlier⁶. X-ray powder pattern was recorded using Cu K_α radiation with Ni filter and Ge monochromator on SRD 3000P SEIFERT diffractometer.

Synthesis of DCA.HCl. Slow addition of conc. HCl (3.5 g, 96 mmoles) to a stirred solution of di-

cyclohexylamine (17.4 g, 96 mmoles) in C₆H₆ (50 mL) at 20°C resulted in the formation of DCA.HCl as a white precipitate which was washed with C₆H₆ (15 mL) and dried (quantitative yield). Its ¹H NMR spectrum in CD₃OD gave multiplets centred at δ 1.31 (10H), 1.90 (10H) and 3.20 (2H). The corresponding values for the free amine appear at δ 1.13 (10H), 1.72 (10H) and 2.50 (2H).

Reactions of DCA.HCl with KX [X = Br, I, PF₆]. An equimolar reflux reaction (16 hr) of DCA.HCl (1.0 g in each case) with powdered KX [X = Br, I, PF₆] in CH₃OH (30 mL) led to the isolation of the byproduct KCl as the precipitate (identified by X-ray powder pattern). The solid residue obtained after removing CH₃OH from the filtrate was quickly washed with water (2 × 20 mL) to obtain DCA.HX as colourless to pale yellow crystalline solid.

DCA.HBr (84% yield): IR: 2960(s), 2860(s), 2780(s), 2520(s), 2420(s), 2360(w), 2160(w), 2060(w), 1930(w), 1460(vs), 1440(s), 1380(s), 1310(s), 1270(w), 1050(vs), 1030(vs), 960(m), 920(m), 900(s), 869(m), 550(w), 480(s) and 440(m) cm⁻¹.

DCA.HI (50% yield): IR: 2960(s), 2850(s), 2740(m), 2530(s), 2430(s), 2365(m), 2165(w), 2060(w), 1960(w), 1460(vs), 1440(s), 1380(s), 1320(s), 1050(vs), 1040(vs), 975(s), 960(m), 925(m), 900(w), 860(m), 560(m), 480(s) and 450(m) cm⁻¹.

DCA.HPF₆ (50% yield, m.p. 250-53°C, dec.): IR: 2940(s), 2860(s), 2800(s), 2760(m), 2530(s), 2430(s), 2360(w), 1460(vs), 1440(m), 1390(s), 1315(m), 1060(m), 1040(m), 970(w), 850(br, s),

560(vs), 470(m) and 440(w) cm^{-1} ; ^{31}P NMR (CH_3OH soln, δ in ppm): -145.9 (septet).

X-ray analyses. Needle shaped crystals of $[(\text{C}_6\text{H}_{11})_2\text{NH}_2]^+\text{Cl}^-$ were grown from a methanol solution. The crystal data and experimental conditions are summarized in Table I. The crystal was glued at its sharpest point on to a glass fiber. The cell constants were obtained from preliminary photographic examination and the extinctions observed are (oko), $k=2n+1$, (hol), $l=2n+1$, identified the space group at $\text{P}2_1/\text{C}$. All the data were collected on an Enraf-Nonius CAD-4 diffractometer using MoK_α radiation ($\lambda=0.71069$ Å) at room temperature. The cell constants and orientation matrix were determined by Least-squares refinement for 25 reflections in the range $9 \leq \theta \leq 14$. Totally, 2612 reflections were measured using the ω - 2θ scan technique. The data were collected for background, Lorentz and polarization effects. 1908 reflections were observed with $I \geq 3\sigma(I)$ and 1713 unique reflections were used for structure refinement. Absorption corrections were made using an in-built software of the diffractometer.

The structure was solved by direct methods using the programme package SHELXS-86⁷. All the hydrogen atoms could be located from the difference electron density maps during the refinement. All the non-hydrogen atoms were refined with anisotropic thermal parameters using the pro-

gramme SHELXL-93⁸. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, where, $w = 1/[2(F_o^2) = 0.040 \text{P}^2 + 0.2850 \text{P}]$, $\text{P} = [F_o^2 + 2 F_c^2]/3$. The maximum and minimum electron densities in the final difference map are 0.143 and -0.149 respectively. The final residual factors are $\text{R}1 = 0.0283$ and $\text{wR}2 = 0.0737$. All the atomic scattering factors were those incorporated in SHELXL-93.

Results and Discussion

Dicyclohexylamine reacts exothermically at ambient conditions to produce dicyclohexylammonium chloride in quantitative yield. It is thermally quite stable (does not melt even upto 250°C) and is not attacked by air or moisture. High basic nature [$\text{pK}_a = 11.25$; pK_a of $(\text{C}_2\text{H}_5)_3\text{N} = 10.72^9$] of dicyclohexylamine and steric protection of the chloride ion provided by the bulky dicyclohexylammonium ion could possibly be the reason for this unusual stability observed unlike amine hydrochlorides in general^{4b}.

The amino proton as well as the acidic proton are not detected in the ^1H NMR spectra (400 MHz) of the amine and the salt recorded in deuterated methanol. However, the methyne proton of the cyclohexyl group is substantially deshielded by 0.7 δ in the salt, as expected.

Reactions of DCA.HCl. Amine hydrochlorides have been used as a source of amines for condensation reactions¹⁰. As the present X-ray structure revealed highly stable nature of dicyclohexylammonium ion, only chloride ion exchange reactions were considered in this study. It was found that DCA.HCl could be converted smoothly to the bromide, iodide and hexafluorophosphate salts by reflux reaction in methanol. The reactions are favoured by the formation of stable KCl lattice in each case. KI and KPF_6 are found to be comparatively less reactive. All these derivatives are air and thermally stable crystalline solids and are soluble in chloroform under hot conditions.

The ^1H NMR spectral features were found to be very similar for bromo, iodo and hexafluorophosphate derivatives.

X-ray structure of DCA.HCl. The ORTEP plot¹¹, packing diagram and important bond length, bond angle data for DCA.HCl are given in Figures 1, 2 and Table II respectively. The main feature of the structure is the significant intermolecular and unsymmetrical type of hydrogen bonding. Identical and noticeably shorter than usual N-H distances of the dicyclohexylammonium ion supports its high pK_a value. The hydrogen bond distance N-H...Cl was observed to be 3.151 Å which is typical of those observed for amine hydrochloro-

Table I—Crystallographic parameters for $[(\text{C}_{16}\text{H}_{34})_2\text{NH}_2]^+\text{Cl}^-$

Empirical formula	$\text{C}_{12}\text{H}_{24}\text{ClN}$
Formula weight	217.77
Crystal system	Monoclinic
Space group	$\text{P}2_1/\text{C}$
Unit cell constants	
a, Å	5.3988 (11)
b, Å	11.7333 (11)
c, Å	20.0734 (2)
α , deg	90
β , deg	95.45 (3)
γ , deg	90
Volume, (Å) ³	1265.82 (3)
Z	4
Density (calcd), mgm^{-3}	1.143
Absorption coefficient, mm^{-1}	0.269
F (000)	480
Crystal dimensions, mm	$0.1 \times 0.12 \times 0.32$
" θ " range scanned, deg.	2-25
Index ranges	$0 \leq h \leq 6, -2 \leq k \leq 13, -23 \leq l \leq 23$
min/max abs. corr, %	86.4, 99.8

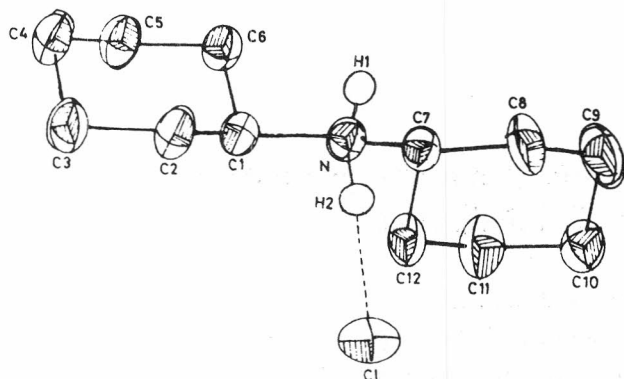


Fig. 1—ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $[(C_6H_{11})_2NH_2]^+ Cl^-$.

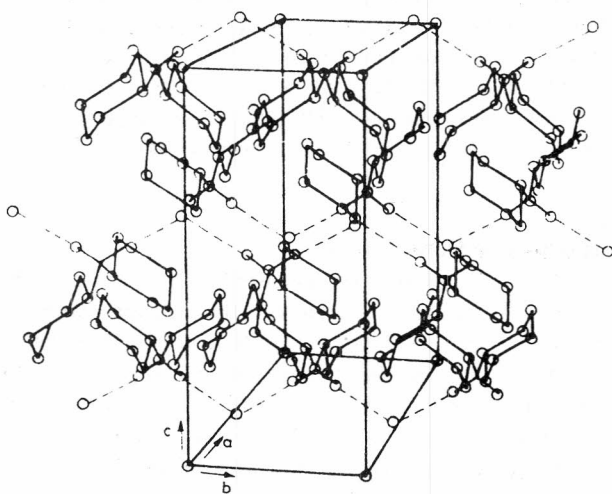


Fig. 2—Molecular packing of $[(C_6H_{11})_2NH_2]^+ Cl^-$ in the unit cell.

rides¹². This distance is shorter by 0.151 Å when compared to their Van der Waals' contact. The bonds N-H...Cl expected to be linear, is found to be bent by 5° which may be due to the effect of cyclohexyl groups that conform to chair conformation. The chloride ion bridging the two dicyclohexylammonium units is found to be equidistant from both the groups and makes an angle of 120.5° which is a substantial deviation from the expected near tetrahedral angle. This seems to highlight the predominance of the steric bulk of dicyclohexylammonium units over the lone pair effects of chloride ion. This has been further exemplified by enlarged angle at nitrogen defined by the two cyclohexyl groups [$\angle C_1NC_7$: 118.5°].

Table II—Selected bond lengths (Å) and bond angles (deg.) for $[(C_6H_{11})_2NH_2]^+ Cl^-$

C (1)-N (1)	1.502 (2)	N (1)-H (2)	0.880 (2)
C (7)-N (1)	1.505 (2)	H (2)-Cl	2.27 (2)
N (1)-H (1)	0.891 (2)	H (1)-Cl	2.29 (2)
H (1)-N (1)-H (2)	108.8 (9)	C (1)-N (1)-C (7)	118.5 (1)
H (1)-N (1)-C (1)	107.2 (8)	N (1)-H (2)-Cl	173.3 (15)
H (1)-N (1)-C (7)	106.8 (9)	N (1)-H (1)-Cl	174.8 (15)
H (2)-N (1)-C (1)	107.4 (9)	H (1)-Cl-H (2)	120.5 (9)
H (2)-N (1)-C (7)	107.9 (9)		

Conclusions

High yield synthesis, air and moisture stability and different reaction possibilities of dicyclohexylammonium chloride offer it to be synthetically useful as revealed by the derivatives with desirable properties prepared in this study.

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