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The crystal structure of 4-chloro-1-methylpiperidin-1-ium chloride, $C_6H_{13}Cl_2N$

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Abstract

$C_6H_{13}Cl_2N$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 6.0087(3)$ Å, $b = 10.1176(6)$ Å, $c = 14.3532(7)$ Å, $V = 872.58(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0304$, $wR_{ref}(F^2) = 0.0632$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Fluka).

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å for methylene groups and C–H 1.00 Å

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	$0.25 \times 0.12 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.67 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8227, 2165, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1874
$N(\text{param})_{\text{refined}}$:	88
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

for methine groups) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$. The H atoms of the methyl group were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [3]), with $U(H)$ set to $1.5U_{eq}(C)$. The nitrogen-bound H atom was located on a difference Fourier map and refined freely. The compound was refined as an inversion twin with volume ratios of 6.64 and 93.36%.

Comment

Among the many effects that can be attributed to the spatial requirements of counterions have been the glass transition temperature in ionomers [7], surfactant modifying properties [8], the charge transfer in radical ions [9] and polymer-modified electrodes [10] as well as the structural and vibrational spectroscopic behaviour of DNA building blocks [11]. Furthermore, the benefit of choosing the adequate size of counterions to crystallize ionic compounds has been confirmed on many occasions [12]. In continuation of our interest in metrical features of large cations [13–15] the structure of the title compound has been determined. A comparable molecular connectivity pattern has been characterized structurally previously in form of the chloride [16] and perchlorate [17] salts of 4-chloro quinuclidinium.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cl1	0.75355 (13)	−0.11634 (8)	0.47932 (5)	0.0507 (2)
N1	0.4071 (3)	0.05003 (19)	0.28772 (13)	0.0261 (4)
H71	0.313 (4)	0.123 (3)	0.2987 (18)	0.037 (7)*
C1	0.6381 (4)	0.0916 (2)	0.31382 (17)	0.0298 (5)
H1A	0.683904	0.167620	0.274846	0.036*
H1B	0.742808	0.017970	0.301932	0.036*
C2	0.6483 (4)	0.1300 (2)	0.41544 (16)	0.0329 (5)
H2A	0.559491	0.211334	0.425013	0.039*
H2B	0.804464	0.150234	0.432189	0.039*
C3	0.5619 (4)	0.0230 (3)	0.47933 (18)	0.0347 (6)
H3	0.550928	0.059112	0.544029	0.042*
C4	0.3342 (4)	−0.0237 (3)	0.44861 (17)	0.0340 (6)
H4A	0.224460	0.047712	0.459387	0.041*
H4B	0.289568	−0.100670	0.486867	0.041*
C5	0.3302 (4)	−0.0623 (2)	0.34651 (17)	0.0309 (5)
H5A	0.428250	−0.139662	0.336430	0.037*
H5B	0.177013	−0.087551	0.328336	0.037*
C6	0.3910 (5)	0.0191 (3)	0.18688 (16)	0.0377 (6)
H6A	0.501090	−0.048640	0.170801	0.057*
H6B	0.419939	0.099239	0.150517	0.057*
H6C	0.241342	−0.013786	0.172744	0.057*
Cl2	0.12300 (10)	0.29376 (6)	0.30651 (5)	0.03429 (15)

The structure shows the presence of the chloride salt of a piperidinium derivative. The nitrogen atom is methylated while the intracyclic carbon atom in *para* position to the pnicogen atom features a chlorine substituent. N–C bond lengths span a range of 1.484(3)–1.498(3) Å with the shortest bond apparent to the exocyclic carbon atom. The C–Cl distance of 1.820(3) Å is in good agreement with the common values deposited with the Cambridge Structural Database [18]. While the methyl group on the tetrahedral nitrogen atom adopts an equatorial position on the central six-membered ring the chlorine atom is found to occupy an axial position. A conformational analysis of the heterocycle according to Cremer & Pople [19] shows the ring to adopt a ¹C₄ conformation on atoms N1 and C3 [20].

In the crystal, classical hydrogen bonds of the N–H...Cl type are observed next to C–H...Cl contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. While the acceptor for all aforementioned interactions is invariably found in the chloride counterion, the C–H...Cl contacts are only supported by one hydrogen atom of the methyl group as well as the hydrogen atom of the chlorine-substituted intracyclic methylene group. In terms of graph-set analysis [21, 22], the descriptor for these contacts is *DDD* on the unary level.

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