

4-Methylbenzylammonium chloride hemihydrate

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Received 10 August 2017

Accepted 22 August 2017

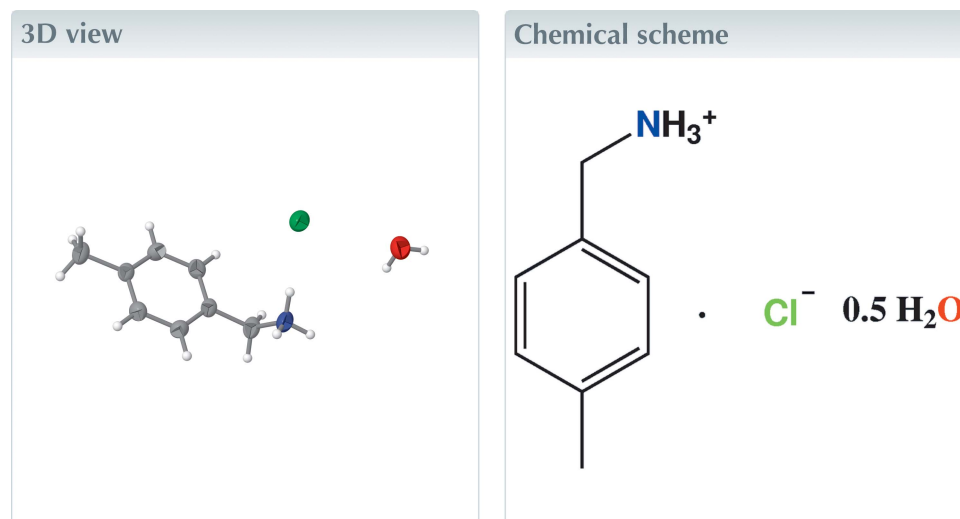
Edited by R. J. Butcher, Howard University, USA

Keywords: crystal structure; hydrated salt; hydrogen bonds; C—H··· π interactions.

CCDC reference: 1570202

Structural data: full structural data are available from iucrdata.iucr.org

In the title hydrated salt, $C_8H_{12}N^+ \cdot Cl^- \cdot 0.5H_2O$, the water O atom lies on a crystallographic twofold axis. In the crystal, the cation, anion and water molecule are linked to one another *via* C—H···Cl, O—H···Cl, N—H···O and N—H···Cl hydrogen bonds. The crystal structure is further stabilized by two weak C—H··· π interactions involving the benzene ring to form a three-dimensional network.



Structure description

We report here the growth and single-crystal X-ray structure of 4-methylbenzylammonium chloride hemihydrate, prepared by the slow evaporation method. Derivatives of benzylamine act as good inhibitors for proteolytic enzymes, such as trypsin, plasmin and thrombin (Markwardt *et al.*, 2005). These derivatives are also used in the field of microelectronics (Sahbani *et al.*, 2017).

In the title hydrated salt (Fig. 1), the water O atom lies on a crystallographic twofold axis. In the crystal, the cation, anion and water molecule are linked to one another *via* C8—H8B···Cl1ⁱ, O1—H1···Cl1ⁱ, N1—H1D···O1ⁱⁱ, N1—H1E···Cl1, N1—H1F···Cl1ⁱ and N1—H1F···Cl1ⁱⁱⁱ hydrogen bonds (see Fig. 2 and Table 1), generating layers lying parallel to the *bc* plane. Furthermore, the crystal structure is stabilized by C1—H1B··· π ⁱⁱⁱ and C8—H8A··· π ⁱ weak interactions involving the C2—C7 benzene ring, to form a three-dimensional network (see Table 1).

Souissi *et al.* (2010) have reported the crystal structure of (4-chlorophenyl)-methanaminium chloride hemihydrate, in which the water O atom lies on a crystallographic twofold axis.

Table 1
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C2–C7 benzene ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C8–H8 <i>B</i> ...Cl1 ⁱ	0.97	2.96	3.5656 (16)	122
O1–H1...Cl1 ⁱ	0.86 (1)	2.27 (1)	3.1231 (13)	177 (2)
N1–H1 <i>D</i> ...O1 ⁱⁱ	0.92 (1)	1.98 (2)	2.8707 (18)	163 (2)
N1–H1 <i>E</i> ...Cl1	0.93 (1)	2.22 (1)	3.1531 (15)	177 (2)
N1–H1 <i>F</i> ...Cl1 ⁱ	0.91 (1)	2.85 (2)	3.4430 (15)	124 (2)
N1–H1 <i>F</i> ...Cl1 ⁱⁱ	0.91 (1)	2.52 (2)	3.2733 (13)	141 (2)
C1–H1 <i>B</i> ...Cg1 ⁱⁱⁱ	0.96	2.64	3.5656 (16)	162
C8–H8 <i>A</i> ...Cg1 ⁱ	0.97	2.91	3.4693 (16)	118

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y + 1, z$.

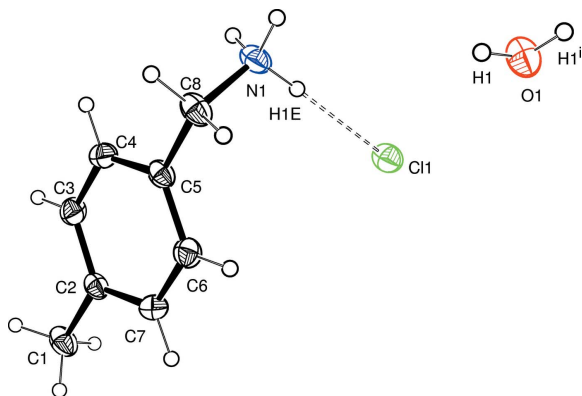


Figure 1
A view of the components of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

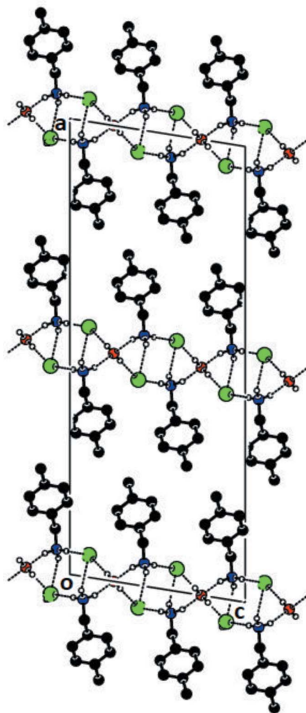


Figure 2
The crystal structure of (I), viewed down the *b* axis, showing the formation of hydrogen bonding. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{12}N^+ \cdot Cl^- \cdot 0.5H_2O$
<i>M_r</i>	166.65
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	296
<i>a, b, c</i> (Å)	30.5325 (14), 4.8966 (2), 11.8973 (5)
β (°)	99.067 (2)
<i>V</i> (Å ³)	1756.49 (13)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.37
Crystal size (mm)	0.20 × 0.20 × 0.15
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
<i>T_{min}</i> , <i>T_{max}</i>	0.703, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	14479, 2985, 2030
<i>R_{int}</i>	0.029
(sin θ/λ) _{max} (Å ⁻¹)	0.761
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.041, 0.118, 1.04
No. of reflections	2985
No. of parameters	112
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.26, -0.25

Computer programs: *APEX2* (Bruker, 2004), *SAINT* (Bruker, 2004), *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1993), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2015), *SHELXL2017* (Sheldrick, 2015) and *pubCIF* (Westrip, 2010).

Synthesis and crystallization

A solution of 4-methylbenzylamine (2 mmol, 0.242 g) was dissolved in dilute HCl (10 ml, 1 mol) and CaCl₂ (1 mmol, 0.147 g) was added. The resulting clear solution was stirred for 3 h and left to stand at room temperature. Colourless single crystals of the title compound were obtained after 15 d.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. ‘DFIX 0.85 0.02 O1 H1’ was used to fix the water O–H distance. ‘DFIX 0.90 0.02 N1 H1*D* N1 H1*E* N1 H1*F*’ was used to fix the N–H distances in the –NH₃ group. ‘DFIX 1.48 0.02 H1*D* H1*E* H1*E* H1*F* H1*F* H1*D*’ was used to fix the three H...H distances in the –NH₃ group. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93 (aromatic), 0.97 (–CH₂–) and 0.96 Å (–CH₃), and with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C).

Acknowledgements

The authors are thankful to the Sophisticated Analytical Instrument Facility (SAIF), IITM, Chennai, Tamilnadu, India, for the single-crystal X-ray diffraction data.

Funding information

Funding for this research was provided by: Council of Scientific and Industrial Research (CSIR), New Delhi, India (grant No. 03(1301)13/EMR II to CR).

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full crystallographic data

IUCrData (2017). **2**, x171213 [<https://doi.org/10.1107/S2414314617012135>]

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Crystal data

$C_8H_{12}N^+ \cdot Cl^- \cdot 0.5H_2O$

$M_r = 166.65$

Monoclinic, $C2/c$

$a = 30.5325$ (14) Å

$b = 4.8966$ (2) Å

$c = 11.8973$ (5) Å

$\beta = 99.067$ (2)°

$V = 1756.49$ (13) Å³

$Z = 4$

$F(000) = 712$

$D_x = 1.260$ Mg m⁻³

Melting point: 533(3) K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3525 reflections

$\theta = 2.7$ – 27.2 °

$\mu = 0.37$ mm⁻¹

$T = 296$ K

Block, colourless

$0.20 \times 0.20 \times 0.15$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scan

Absorption correction: multi-scan

(SADABS; Bruker, 2004)

$T_{\min} = 0.703$, $T_{\max} = 0.747$

14479 measured reflections

2985 independent reflections

2030 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 32.7$ °, $\theta_{\min} = 2.7$ °

$h = -43 \rightarrow 44$

$k = -7 \rightarrow 7$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.118$

$S = 1.04$

2985 reflections

112 parameters

7 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 1.1506P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.26$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.27846 (5)	1.1363 (3)	0.66526 (16)	0.0457 (4)
H1A	0.250753	1.104215	0.616561	0.069*
H1B	0.289350	1.314261	0.650098	0.069*
H1C	0.274153	1.126064	0.743349	0.069*
C2	0.31162 (5)	0.9233 (3)	0.64291 (13)	0.0329 (3)
C3	0.34309 (5)	0.8260 (3)	0.73017 (13)	0.0381 (3)
H3	0.343895	0.894951	0.803292	0.046*
C4	0.37344 (5)	0.6277 (3)	0.71083 (13)	0.0370 (3)
H4	0.394078	0.564484	0.771108	0.044*
C5	0.37334 (4)	0.5229 (3)	0.60280 (12)	0.0317 (3)
C6	0.34264 (5)	0.6250 (3)	0.51457 (13)	0.0380 (3)
H6	0.342469	0.560761	0.440939	0.046*
C7	0.31220 (5)	0.8218 (3)	0.53477 (13)	0.0385 (3)
H7	0.291774	0.886742	0.474401	0.046*
C8	0.40494 (5)	0.2992 (3)	0.58295 (16)	0.0409 (4)
H8A	0.406778	0.167653	0.644475	0.049*
H8B	0.393489	0.205408	0.512626	0.049*
N1	0.44988 (4)	0.4038 (3)	0.57608 (13)	0.0409 (3)
O1	0.500000	0.2659 (4)	0.250000	0.0520 (4)
Cl1	0.45068 (2)	0.86388 (8)	0.39101 (4)	0.04364 (13)
H1	0.4865 (6)	0.151 (3)	0.2865 (16)	0.052*
H1D	0.4625 (7)	0.492 (4)	0.6416 (12)	0.066 (6)*
H1E	0.4504 (7)	0.535 (4)	0.5197 (14)	0.073 (7)*
H1F	0.4686 (6)	0.265 (3)	0.5654 (16)	0.071 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0397 (8)	0.0368 (8)	0.0643 (11)	0.0070 (7)	0.0201 (8)	0.0028 (7)
C2	0.0297 (6)	0.0284 (6)	0.0425 (8)	−0.0003 (5)	0.0118 (6)	0.0024 (6)
C3	0.0424 (8)	0.0394 (8)	0.0335 (7)	0.0055 (6)	0.0094 (6)	−0.0025 (6)
C4	0.0359 (7)	0.0396 (8)	0.0348 (7)	0.0062 (6)	0.0033 (6)	0.0029 (6)
C5	0.0282 (6)	0.0269 (6)	0.0413 (7)	−0.0016 (5)	0.0102 (5)	−0.0008 (6)
C6	0.0388 (8)	0.0425 (8)	0.0334 (7)	0.0013 (6)	0.0079 (6)	−0.0050 (6)
C7	0.0339 (7)	0.0425 (8)	0.0379 (8)	0.0057 (6)	0.0022 (6)	0.0041 (6)
C8	0.0372 (8)	0.0296 (7)	0.0590 (10)	0.0006 (6)	0.0173 (7)	−0.0025 (7)
N1	0.0312 (6)	0.0389 (7)	0.0543 (8)	0.0075 (6)	0.0117 (6)	0.0026 (6)
O1	0.0542 (11)	0.0444 (10)	0.0619 (11)	0.000	0.0227 (9)	0.000
Cl1	0.0389 (2)	0.0404 (2)	0.0523 (2)	0.00223 (16)	0.00932 (16)	0.00296 (17)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.506 (2)	C6—C7	1.386 (2)
C1—H1A	0.9600	C6—H6	0.9300
C1—H1B	0.9600	C7—H7	0.9300

C1—H1C	0.9600	C8—N1	1.479 (2)
C2—C7	1.382 (2)	C8—H8A	0.9700
C2—C3	1.383 (2)	C8—H8B	0.9700
C3—C4	1.386 (2)	N1—H1D	0.921 (13)
C3—H3	0.9300	N1—H1E	0.931 (14)
C4—C5	1.384 (2)	N1—H1F	0.911 (14)
C4—H4	0.9300	O1—H1	0.855 (14)
C5—C6	1.386 (2)	O1—H1 ⁱ	0.855 (14)
C5—C8	1.503 (2)		
C2—C1—H1A	109.5	C7—C6—H6	119.6
C2—C1—H1B	109.5	C5—C6—H6	119.6
H1A—C1—H1B	109.5	C2—C7—C6	121.25 (14)
C2—C1—H1C	109.5	C2—C7—H7	119.4
H1A—C1—H1C	109.5	C6—C7—H7	119.4
H1B—C1—H1C	109.5	N1—C8—C5	112.37 (12)
C7—C2—C3	117.75 (13)	N1—C8—H8A	109.1
C7—C2—C1	121.40 (14)	C5—C8—H8A	109.1
C3—C2—C1	120.85 (14)	N1—C8—H8B	109.1
C2—C3—C4	121.34 (14)	C5—C8—H8B	109.1
C2—C3—H3	119.3	H8A—C8—H8B	107.9
C4—C3—H3	119.3	C8—N1—H1D	112.5 (13)
C5—C4—C3	120.70 (14)	C8—N1—H1E	113.5 (14)
C5—C4—H4	119.7	H1D—N1—H1E	103.5 (16)
C3—C4—H4	119.7	C8—N1—H1F	110.9 (13)
C4—C5—C6	118.15 (13)	H1D—N1—H1F	106.4 (15)
C4—C5—C8	120.61 (14)	H1E—N1—H1F	109.6 (16)
C6—C5—C8	121.22 (14)	H1—O1—H1 ⁱ	98 (3)
C7—C6—C5	120.77 (14)		
C7—C2—C3—C4	-1.8 (2)	C8—C5—C6—C7	176.79 (14)
C1—C2—C3—C4	179.25 (14)	C3—C2—C7—C6	1.3 (2)
C2—C3—C4—C5	0.6 (2)	C1—C2—C7—C6	-179.75 (15)
C3—C4—C5—C6	1.1 (2)	C5—C6—C7—C2	0.4 (2)
C3—C4—C5—C8	-177.28 (14)	C4—C5—C8—N1	-80.09 (18)
C4—C5—C6—C7	-1.6 (2)	C6—C5—C8—N1	101.57 (17)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of the (C2-C7) benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8B \cdots C11 ⁱⁱ	0.97	2.96	3.5656 (16)	122
O1—H1 \cdots C11 ⁱⁱ	0.86 (1)	2.27 (1)	3.1231 (13)	177 (2)
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N1—H1E \cdots C11	0.93 (1)	2.22 (1)	3.1531 (15)	177 (2)
N1—H1F \cdots C11 ⁱⁱ	0.91 (1)	2.85 (2)	3.4430 (15)	124 (2)

N1—H1F...Cl1 ⁱⁱⁱ	0.91 (1)	2.52 (2)	3.2733 (13)	141 (2)
C1—H1B...Cg1 ^{iv}	0.96	2.64	3.5656 (16)	162
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