1-Allyl-2-methylpyridinium chloride

Gino Bentivoglio,[a] Gerhard Laus,[a] Volker Kahlenberg,[b] Thomas Röder[c] and Herwig Schottenberger[a]*

[a]University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 80, 6020 Innsbruck, Austria, [b]University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52, 6020 Innsbruck, Austria, and [c]Lenzing AG, Global R&D, Werkstrasse 2, 4860 Lenzing, Austria. *Correspondence e-mail: herwig.schottenberger@uibk.ac.at

The title molecular salt, $C_9H_{12}N^+ \cdot Cl^-$, was obtained by reaction of 2-methylpyridine and allyl chloride. A network of C—H$\cdots$Cl hydrogen bonds is observed in the crystal structure.

3D view
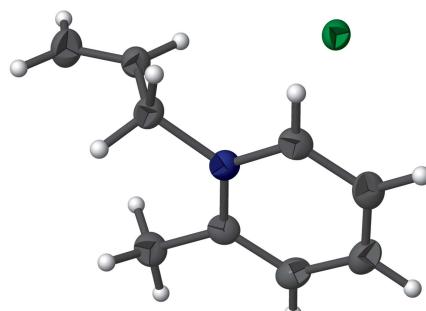
Chemical scheme
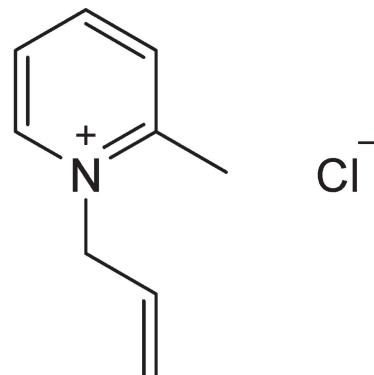
Structure description

Chloride-based ionic liquids (salts melting below 373 K) are suitable solvents for cellulose dissolution (Wang *et al.*, 2012; Liu *et al.*, 2016) and for fibre spinning. The numerous advantages of ionic liquids, such as non-volatility, thermal stability, chemical modifiability, and low melting points are countervailed by their disadvantages, such as aquatic toxicity, corrosivity, and a high energy input required for pulp preparation and removal of water (Bentivoglio *et al.*, 2006). In particular, it has been found that some ionic liquids promote degradation of cellulose. The molecular mass distribution of the reconstituted cellulose samples was determined by gel permeation chromatography (Schelosky *et al.*, 1999). Degradation was exceptionally strong (from 200 kDa down to 24 kDa) in the present ionic liquid. The solubility of cellulose in a series of pyridinium chlorides was studied by quantum-chemical calculations (Sashina *et al.*, 2012).

The title compound has been described as a 'sirupy liquid' (Ramsay, 1876). It has now been crystallized but still qualifies as an ionic liquid (melting at 367 K). In the crystal structure, the allyl group is twisted out of the plane of the heterocyclic ring. Weak C—H$\cdots$Cl hydrogen bonds (Fig. 1, Table 1) create a three-dimensional network in which the chloride ions are sixfold coordinated toward the pyridinium cations (Fig. 2).

Related structures with similar hydrogen bond networks include *N*-allylpyrrolidinium chloride (Laus *et al.*, 2008), *N*-allylpyridinium bromide (Seethalakshmi *et al.*, 2013) and *N*-allylimidazolium iodides (Fei *et al.*, 2006).
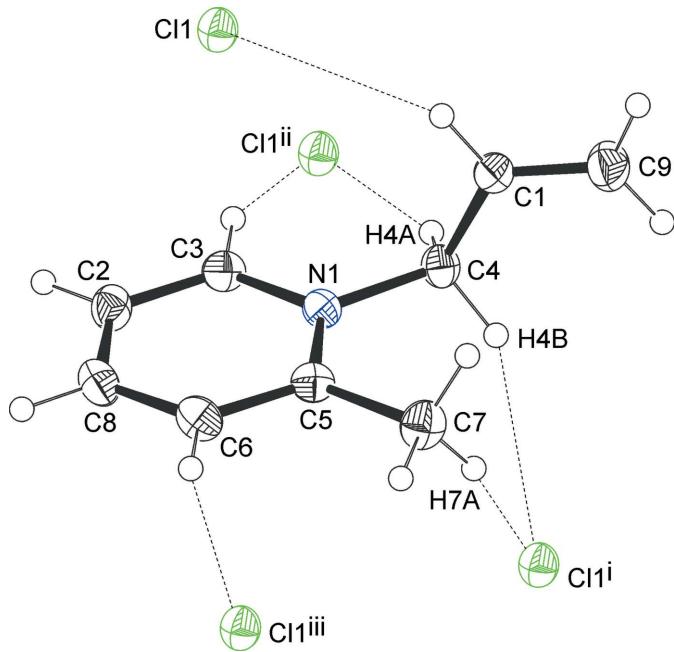
Figure 1
The molecular structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. The C—H···Cl hydrogen bonds are shown as dashed lines. Symmetry codes: (i) x, $y + 1$, z; (ii) $-x + 2$, $-y$, $-z + 1$; (iii) $-x + 2$, $-y$, $-z + 2$.

Synthesis and crystallization

To 2-methylpyridine (18.9 g, 0.20 mol) was added an excess of allyl chloride (18.6 g, 0.24 mol). The reaction mixture was refluxed for 72 h. Excess allyl chloride was removed under reduced pressure. The crude product was washed with Et_2O (50 ml) and dried on a high vacuum line giving 1-allyl-2-methylpyridinium chloride as a brown powder (17.4 g, 51%), m.p. 364–367 K. Colourless plates were recrystallized from a solvent mixture of acetone/CH_2Cl_2. ^1H NMR (300 MHz, DMSO-d_6): δ 2.93 (3H, s), 5.10 (1H, d, $J = 17.2$ Hz), 5.35 (1H, d, $J = 10.6$ Hz), 5.66 (2H, d, $J = 5.6$ Hz), 6.00 (1H, m), 7.92 (1H, t, $J = 6.8$ Hz), 8.00 (1H, d, $J = 7.9$ Hz), 8.41 (1H, t, $J = 7.6$ Hz),
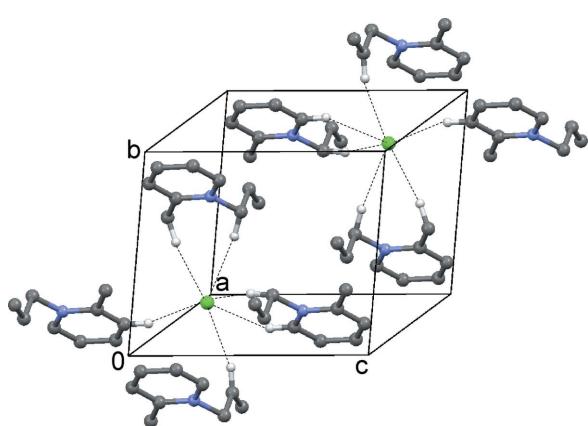

Figure 2
Sixfold-coordinated chloride ions in the unit cell of the title compound. Only hydrogen atoms involved in contacts are shown.

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···Cl1	0.95	2.82	3.701 (2)	155
C7—H7A···Cl1^i	0.98	2.78	3.695 (2)	157
C4—H4A···Cl1^{ii}	0.99	2.76	3.698 (2)	159
C4—H4B···Cl1^i	0.99	2.72	3.609 (2)	149
C6—H6···Cl1^{iii}	0.95	2.64	3.545 (2)	161
C3—H3···Cl1^{ii}	0.95	2.57	3.454 (2)	155

Symmetry codes: (i) x, $y + 1$, z; (ii) $-x + 2$, $-y$, $-z + 1$; (iii) $-x + 2$, $-y$, $-z + 2$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}N^+·Cl^-$
M_r	169.65
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	6.9617 (17), 7.5941 (19), 9.464 (2)
α, β, γ (°)	86.06 (2), 82.118 (19), 67.102 (18)
V (Å^3)	456.48 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.35
Crystal size (mm)	$0.4 \times 0.38 \times 0.1$
Data collection	
Diffractometer	Stoe *IPDS* 2
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.904, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3066, 1616, 1465
R_{int}	0.017
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.067, 1.05
No. of reflections	1616
No. of parameters	101
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.17

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 1997), *SIR2002* (Burla *et al.*, 2003), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

9.70 (1H, d, $J = 5.9$) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.5, 60.0, 120.9, 126.2, 130.0, 130.1, 145.5, 146.9, 155.0 p.p.m. IR (neat): ν 3009, 2921, 2438, 1622, 1573, 1503, 1478, 1455, 1421, 1296, 1158, 1141, 1053, 1004, 930, 829, 794, 770, 710, 663 cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

References

Bentivoglio, G., Röder, T., Fasching, M., Buchberger, M., Schottenberger, H. & Sixta, H. (2006). *Lenz. Ber.* **86**, 154–161.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Fei, Z., Kuang, D., Zhao, D., Klein, C., Ang, W. H., Zakeeruddin, S. M., Grätzel, M. & Dyson, P. J. (2006). *Inorg. Chem.* **45**, 10407–10409.

Laus, G., Bentivoglio, G., Kahlenberg, V., Griesser, U. J., Schottenberger, H. & Nauer, G. (2008). *CrystEngComm*, **10**, 748–752.

Liu, Y.-R., Thomsen, K., Nie, Y., Zhang, S.-J. & Meyer, A. S. (2016). *Green Chem.* **18**, 6246–6254.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Ramsay, W. (1876). *Philos. Mag. Ser. 5*, **2**, 269–281.

Sashina, E. S., Kashirskii, D. A. & Martynova, E. V. (2012). *Russ. J. Gen. Chem.* **82**, 729–735.

Schelosky, N., Röder, T. & Baldinger, T. (1999). *Papier* 53, 728–738.

Seethalakshmi, T., Venkatesan, P., Nallu, M., Lynch, D. E. & Thamotharan, S. (2013). *Acta Cryst.* E**69**, o884.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stoe & Cie (1997). *X-AREA* and *X-RED*. Stoe & Cie GmbH, Darmstadt, Germany.

Wang, H., Gurau, G. & Rogers, R. D. (2012). *Chem. Soc. Rev.* **41**, 1519–1537.

full crystallographic data

1-Allyl-2-methylpyridinium chloride

Gino Bentivoglio, Gerhard Laus, Volker Kahlenberg, Thomas Röder and Herwig Schottenberger

1-Allyl-2-methylpyridinium chloride

Crystal data

$C_9H_{12}N^+ \cdot Cl^-$	$Z = 2$
$M_r = 169.65$	$F(000) = 180$
Triclinic, $P\overline{1}$	$D_x = 1.234$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.9617$ (17) Å	Cell parameters from 3556 reflections
$b = 7.5941$ (19) Å	$\theta = 2.2–27.2°$
$c = 9.464$ (2) Å	$\mu = 0.35$ mm^{-1}
$\alpha = 86.06$ (2)°	$T = 173$ K
$\beta = 82.118$ (19)°	Fragment of a plate, colorless
$\gamma = 67.102$ (18)°	$0.4 \times 0.38 \times 0.1$ mm
$V = 456.48$ (19) Å^3	

Data collection

Stoe IPDS 2 diffractometer	$T_{min} = 0.904$, $T_{max} = 0.985$
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	3066 measured reflections
	1616 independent reflections
Graphite monochromator	1465 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.017$
rotation method scans	$\theta_{max} = 25.4°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -8 \rightarrow 8$
	$k = -8 \rightarrow 9$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.067$	
$S = 1.05$	H-atom parameters constrained
1616 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 0.1555P]$ where $P = (F_o^2 + 2F_c^2)/3$
101 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.19$ e Å^{-3}
	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.89617 (6)	−0.22917 (5)	0.72298 (4)	0.02896 (12)
N1	1.00030 (18)	0.21870 (17)	0.71106 (12)	0.0243 (3)
C1	0.6310 (2)	0.2941 (2)	0.67241 (16)	0.0294 (3)
H1	0.6544	0.1621	0.6801	0.035*
C2	1.3379 (2)	−0.0309 (2)	0.68650 (17)	0.0314 (3)
H2	1.4525	−0.1182	0.6277	0.038*
C3	1.1628 (2)	0.0914 (2)	0.62917 (16)	0.0281 (3)
H3	1.1553	0.0868	0.5301	0.034*
C4	0.8179 (2)	0.3488 (2)	0.63906 (15)	0.0272 (3)
H4A	0.8591	0.3451	0.5346	0.033*
H4B	0.7789	0.4814	0.67	0.033*
C5	1.0027 (2)	0.2277 (2)	0.85415 (15)	0.0268 (3)
C6	1.1772 (2)	0.1022 (2)	0.91430 (16)	0.0322 (3)
H6	1.1808	0.1042	1.0141	0.039*
C7	0.8237 (3)	0.3733 (2)	0.94055 (16)	0.0350 (4)
H7A	0.8066	0.5014	0.9031	0.052*
H7B	0.8518	0.3622	1.0401	0.052*
H7C	0.6948	0.352	0.9352	0.052*
C8	1.3453 (2)	−0.0254 (2)	0.83142 (17)	0.0331 (3)
H8	1.4654	−0.1089	0.8734	0.04*
C9	0.4376 (2)	0.4194 (2)	0.69139 (19)	0.0394 (4)
H9A	0.4102	0.5522	0.6842	0.047*
H9B	0.3246	0.3776	0.7123	0.047*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02934 (19)	0.02856 (19)	0.02593 (19)	−0.00806 (14)	−0.00311 (14)	0.00060 (13)
N1	0.0225 (6)	0.0264 (6)	0.0247 (6)	−0.0108 (5)	−0.0011 (5)	0.0002 (5)
C1	0.0283 (7)	0.0250 (7)	0.0353 (8)	−0.0100 (6)	−0.0063 (6)	0.0000 (6)
C2	0.0242 (7)	0.0315 (8)	0.0357 (8)	−0.0093 (6)	0.0026 (6)	−0.0024 (6)
C3	0.0279 (7)	0.0321 (8)	0.0254 (7)	−0.0137 (6)	0.0012 (6)	−0.0032 (6)
C4	0.0262 (7)	0.0275 (7)	0.0258 (7)	−0.0083 (6)	−0.0038 (6)	0.0022 (6)
C5	0.0283 (7)	0.0299 (7)	0.0245 (7)	−0.0149 (6)	−0.0001 (6)	0.0003 (6)
C6	0.0328 (8)	0.0390 (8)	0.0269 (8)	−0.0162 (7)	−0.0059 (6)	0.0040 (6)
C7	0.0368 (8)	0.0370 (9)	0.0269 (8)	−0.0108 (7)	0.0006 (7)	−0.0024 (6)
C8	0.0256 (7)	0.0358 (8)	0.0378 (9)	−0.0117 (6)	−0.0071 (7)	0.0055 (7)
C9	0.0288 (8)	0.0333 (8)	0.0542 (11)	−0.0108 (7)	−0.0037 (7)	0.0015 (7)

Geometric parameters (Å, º)

N1—C3	1.351 (2)	C4—H4B	0.9900
N1—C5	1.364 (2)	C5—C6	1.385 (2)
N1—C4	1.4882 (19)	C5—C7	1.489 (2)
C1—C9	1.307 (2)	C6—C8	1.376 (2)
C1—C4	1.502 (2)	C6—H6	0.9500
C1—H1	0.9500	C7—H7A	0.9800
C2—C3	1.368 (2)	C7—H7B	0.9800
C2—C8	1.383 (2)	C7—H7C	0.9800
C2—H2	0.9500	C8—H8	0.9500
C3—H3	0.9500	C9—H9A	0.9500
C4—H4A	0.9900	C9—H9B	0.9500
C3—N1—C5	121.20 (13)	N1—C5—C6	118.28 (14)
C3—N1—C4	117.55 (13)	N1—C5—C7	119.86 (14)
C5—N1—C4	121.25 (13)	C6—C5—C7	121.84 (14)
C9—C1—C4	123.20 (15)	C8—C6—C5	120.98 (15)
C9—C1—H1	118.4	C8—C6—H6	119.5
C4—C1—H1	118.4	C5—C6—H6	119.5
C3—C2—C8	118.97 (15)	C5—C7—H7A	109.5
C3—C2—H2	120.5	C5—C7—H7B	109.5
C8—C2—H2	120.5	H7A—C7—H7B	109.5
N1—C3—C2	121.21 (15)	C5—C7—H7C	109.5
N1—C3—H3	119.4	H7A—C7—H7C	109.5
C2—C3—H3	119.4	H7B—C7—H7C	109.5
N1—C4—C1	112.07 (12)	C6—C8—C2	119.33 (15)
N1—C4—H4A	109.2	C6—C8—H8	120.3
C1—C4—H4A	109.2	C2—C8—H8	120.3
N1—C4—H4B	109.2	C1—C9—H9A	120.0
C1—C4—H4B	109.2	C1—C9—H9B	120.0
H4A—C4—H4B	107.9	H9A—C9—H9B	120.0

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C1—H1⋯Cl1	0.95	2.82	3.701 (2)	155
C7—H7*A*⋯Cl1[i]	0.98	2.78	3.695 (2)	157
C4—H4*A*⋯Cl1[ii]	0.99	2.76	3.698 (2)	159
C4—H4*B*⋯Cl1[i]	0.99	2.72	3.609 (2)	149
C6—H6⋯Cl1[iii]	0.95	2.64	3.545 (2)	161
C3—H3⋯Cl1[ii]	0.95	2.57	3.454 (2)	155

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+2, −*y*, −*z*+1; (iii) −*x*+2, −*y*, −*z*+2.