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1-Methyl-1-propylpyrrolidinium chloride

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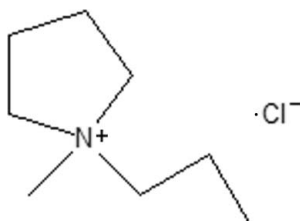
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 Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.031; wR factor = 0.080; data-to-parameter ratio = 21.3.

The asymmetric unit of the title compound, $\text{C}_8\text{H}_{18}\text{N}^+\cdot\text{Cl}^-$, consists of one crystallographically independent 1-methyl-1-propylpyrrolidinium cation and one chloride anion, both of which lie in general positions. Minor hydrogen-bonded $\text{C}-\text{H}\cdots\text{Cl}$ interactions occur. However, no classical hydrogen bonding is observed.

Related literature

For bond-length data, see: Allen *et al.* (1987). For comparative thermal and crystallographic analysis of four crystallized *N*-alkyl-*N*-methylpyrrolidinium and piperidinium bis(trifluoromethanesulfonyl)imide salts and an insight into why these salts form room-temperature ionic liquids, see: Henderson *et al.* (2006). For the synthesis and analysis of *N*-butyl-*N*-methylpyrrolidinium chloride, an analogue of the title compound, see: Lancaster *et al.* (2002). For the first synthesis and analysis of the new pyrrolidinium family of molten salts, see: MacFarlane *et al.* (1999). For the quantitative comparison of intermolecular interactions using Hirshfeld surfaces, see: McKinnon *et al.* (2007). For the first synthesis and analysis of 1-alkyl-2-methylpyrrolidinium ionic liquids involving the bis(trifluoromethanesulfonyl)imide anion, see: Sun *et al.* (2003).



Experimental

Crystal data

 $\text{C}_8\text{H}_{18}\text{N}^+\cdot\text{Cl}^-$
 $M_r = 163.68$

 Orthorhombic, *Pbcn*
 $a = 14.5863$ (5) Å

 $b = 13.2196$ (4) Å
 $c = 9.9779$ (3) Å
 $V = 1923.99$ (11) Å³
 $Z = 8$

 Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹
 $T = 123$ (2) K
 $0.30 \times 0.30 \times 0.30$ mm

Data collection

 Bruker Kappa APEXII
 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2005)
 $T_{\min} = 0.907$, $T_{\max} = 0.907$

 11550 measured reflections
 1982 independent reflections
 1800 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.079$
 $S = 1.04$
 1982 reflections

 93 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³

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

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C1—H1B···Cl1 ⁱ | 0.99 | 2.79 | 3.607 (1) | 141 |
| C2—H2A···Cl1 ⁱⁱ | 0.99 | 2.77 | 3.630 (2) | 146 |
| C5—H5A···Cl1 | 0.98 | 2.77 | 3.648 (1) | 149 |
| C5—H5C···Cl1 ⁱⁱⁱ | 0.98 | 2.71 | 3.656 (1) | 163 |
| C6—H6A···Cl1 ⁱ | 0.99 | 2.76 | 3.672 (1) | 153 |
| C6—H6B···Cl1 | 0.99 | 2.77 | 3.666 (1) | 151 |

 Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $-y + 2, z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *POV-RAY* (Persistence of Vision, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2101).

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supplementary materials

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1-Methyl-1-propylpyrrolidinium chloride

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Comment

The title compound, (I), is commonly used as a precursor in ionic liquid synthesis (MacFarlane *et al.*, 1999, Sun *et al.*, 2003). Pyrrolidinium-based ionic liquids have been a subject of intense investigation recently (Henderson *et al.*, 2006), whereby with understanding of the fundamental molecular-level interactions, a desired product with predicted physico-chemical properties could be designed. Additionally, a particular emphasis has been placed on whether hydrogen bonding occurs between the cation and a potential electron-pair donor (hydrogen bond acceptor) and its influence on the ionic liquids' overall properties. This paper briefly reports the structural determination and analysis of 1-methyl-1-propyl pyrrolidinium chloride (Figure 1).

The bond distances and angles of the pyrrolidinium cation are all within normal ranges (as is tabulated in Allen *et al.*, 1987), with the propyl substituent adopting the energetically preferred *anti* conformation (torsional angle N1—C6—C7—C8: $-177.0(2)^\circ$) and the ring adopting the energetically preferred envelope (*Cs*) conformation. The extended structure packs in layers of groups of anions and cations (Figure 2) which are interconnected by an extended network of weak hydrogen bonds (C—H \cdots Cl interactions), where each cation is hydrogen bonded to four anions and each anion is weakly hydrogen bonded to four cations [C1—H1B \cdots C11ⁱ [3.607 (2) Å], C2—H2A \cdots C11ⁱⁱ [3.630 (2) Å], C5—H5A \cdots C11 [3.648 (1) Å], C5—H5C \cdots C11ⁱⁱⁱ [3.656 (1) Å], C6—H6A \cdots C11ⁱ [3.672 (2) Å] and C6—H6B \cdots C11 [3.666 (1) Å] (symmetry operators: $i=1/2 - x, 3/2 - y, 1/2 + z$; $ii=1 - x, y, 1/2 - z$; $iii=x, 2 - y, 1/2 + z$) -see Table 1]. Analysis of the salts' Hirshfeld surface, reveals that the short range inter-cationic H—H intermolecular contact contribution to the Hirshfeld surface area predominates (McKinnon *et al.*, 2007).

Experimental

The compound was synthesized following the procedure of Lancaster *et al.* (2002) for the analogous *N*-butyl-*N*-methyl pyrrolidinium chloride species: 1-methyl-1-propylpyrrolidinium chloride was synthesized by heating a solution of chloropropane (28 ml, 0.315 moles) and methyl pyrrolidine (20 ml, 0.287 moles) in 2-propanol at 323 K under nitrogen for 48 h. The resultant white solid was recrystallized from 2-propanol at 273 K. Crystals resulted after 2 days. Crystals were coated with Paratone N oil (Exxon Chemical Co., TX, USA) immediately after isolation and cooled in a stream of nitrogen vapour on the diffractometer. Melting point: 323.5 K.

Refinement

All H atoms were initially located in a difference Fourier map. Thereafter, all H atoms were placed in geometrically fixed idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

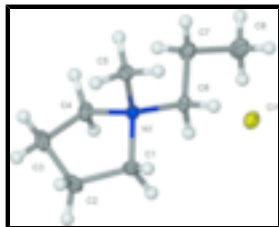


Fig. 1. Diagram of the unique component of (I) shown with 50% thermal ellipsoids and hydrogen atoms as spheres of arbitrary size.

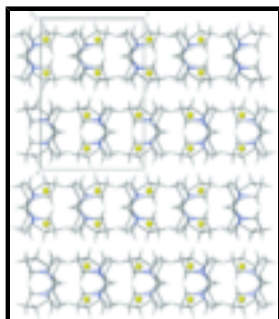


Fig. 2. Extended packing diagram of the unit-cell contents of (I) as viewed down the *b* axis.

1-Methyl-1-propylpyrrolidinium chloride

Crystal data

$C_8H_{18}N^+Cl^-$

$M_r = 163.68$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 14.5863$ (5) Å

$b = 13.2196$ (4) Å

$c = 9.9779$ (3) Å

$V = 1923.99$ (11) Å³

$Z = 8$

$F_{000} = 720$

$D_x = 1.130$ Mg m⁻³

Melting point: 323.5 K

Mo *K*α radiation

$\lambda = 0.71073$ Å

Cell parameters from 4825 reflections

$\theta = 2.8$ – 26.4°

$\mu = 0.33$ mm⁻¹

$T = 123$ (2) K

Cubic, colourless

$0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker X8 APEX KappaCCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 123$ (2) K

0.5° frames in φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.907$, $T_{\max} = 0.907$

11550 measured reflections

1982 independent reflections

1800 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 26.4^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -18 \rightarrow 18$

$k = -15 \rightarrow 16$

$l = -11 \rightarrow 12$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | H-atom parameters constrained |
| $wR(F^2) = 0.079$ | $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.834P]$ |
| $S = 1.04$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1982 reflections | $(\Delta/\sigma)_{\max} = 0.001$ |
| 93 parameters | $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$ |
| | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Cl1 | 0.36024 (2) | 0.82436 (2) | 0.05218 (3) | 0.02423 (12) |
| N1 | 0.32912 (7) | 0.86923 (8) | 0.43497 (10) | 0.0179 (2) |
| C1 | 0.35707 (9) | 0.75928 (10) | 0.41992 (14) | 0.0241 (3) |
| H1A | 0.3939 | 0.7496 | 0.3376 | 0.029* |
| H1B | 0.3023 | 0.7152 | 0.4152 | 0.029* |
| C2 | 0.41390 (11) | 0.73488 (12) | 0.54424 (15) | 0.0323 (3) |
| H2A | 0.4793 | 0.7268 | 0.5202 | 0.039* |
| H2B | 0.3922 | 0.6714 | 0.5863 | 0.039* |
| C3 | 0.40131 (10) | 0.82444 (12) | 0.64053 (15) | 0.0309 (3) |
| H3A | 0.3884 | 0.8004 | 0.7326 | 0.037* |
| H3B | 0.4569 | 0.8674 | 0.6423 | 0.037* |
| C4 | 0.32014 (9) | 0.88251 (11) | 0.58455 (13) | 0.0242 (3) |
| H4A | 0.2616 | 0.8540 | 0.6174 | 0.029* |
| H4B | 0.3234 | 0.9549 | 0.6097 | 0.029* |
| C5 | 0.40372 (8) | 0.93610 (10) | 0.38042 (13) | 0.0209 (3) |
| H5A | 0.4045 | 0.9315 | 0.2824 | 0.031* |
| H5B | 0.4631 | 0.9141 | 0.4161 | 0.031* |
| H5C | 0.3922 | 1.0063 | 0.4072 | 0.031* |

supplementary materials

| | | | | |
|-----|--------------|--------------|--------------|------------|
| C6 | 0.23958 (8) | 0.88722 (10) | 0.36358 (13) | 0.0198 (3) |
| H6A | 0.1941 | 0.8374 | 0.3962 | 0.024* |
| H6B | 0.2487 | 0.8750 | 0.2666 | 0.024* |
| C7 | 0.20062 (9) | 0.99281 (11) | 0.38223 (14) | 0.0254 (3) |
| H7A | 0.1931 | 1.0073 | 0.4789 | 0.031* |
| H7B | 0.2433 | 1.0434 | 0.3442 | 0.031* |
| C8 | 0.10858 (10) | 0.99984 (12) | 0.31221 (18) | 0.0372 (4) |
| H8A | 0.1173 | 0.9926 | 0.2153 | 0.056* |
| H8B | 0.0806 | 1.0657 | 0.3313 | 0.056* |
| H8C | 0.0683 | 0.9458 | 0.3447 | 0.056* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C11 | 0.02343 (18) | 0.02619 (19) | 0.02308 (18) | -0.00399 (13) | -0.00151 (13) | -0.00178 (12) |
| N1 | 0.0162 (5) | 0.0191 (5) | 0.0185 (5) | -0.0015 (4) | -0.0013 (4) | 0.0004 (4) |
| C1 | 0.0246 (7) | 0.0178 (6) | 0.0299 (7) | 0.0005 (5) | -0.0008 (6) | 0.0012 (5) |
| C2 | 0.0282 (7) | 0.0287 (8) | 0.0401 (9) | 0.0006 (6) | -0.0051 (6) | 0.0123 (6) |
| C3 | 0.0273 (7) | 0.0406 (9) | 0.0247 (7) | -0.0068 (6) | -0.0067 (6) | 0.0100 (6) |
| C4 | 0.0232 (6) | 0.0322 (8) | 0.0172 (6) | -0.0044 (6) | -0.0004 (5) | -0.0005 (5) |
| C5 | 0.0163 (6) | 0.0223 (7) | 0.0241 (6) | -0.0031 (5) | 0.0008 (5) | 0.0023 (5) |
| C6 | 0.0157 (6) | 0.0231 (6) | 0.0206 (6) | -0.0019 (5) | -0.0035 (5) | -0.0014 (5) |
| C7 | 0.0208 (6) | 0.0257 (7) | 0.0298 (7) | 0.0018 (5) | -0.0037 (6) | -0.0049 (6) |
| C8 | 0.0258 (7) | 0.0314 (8) | 0.0543 (10) | 0.0050 (6) | -0.0138 (7) | -0.0065 (7) |

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

| | | | |
|----------|-------------|------------|-------------|
| N1—C5 | 1.5038 (16) | C4—H4B | 0.9900 |
| N1—C6 | 1.5066 (16) | C5—H5A | 0.9800 |
| N1—C4 | 1.5085 (16) | C5—H5B | 0.9800 |
| N1—C1 | 1.5171 (17) | C5—H5C | 0.9800 |
| C1—C2 | 1.526 (2) | C6—C7 | 1.5185 (18) |
| C1—H1A | 0.9900 | C6—H6A | 0.9900 |
| C1—H1B | 0.9900 | C6—H6B | 0.9900 |
| C2—C3 | 1.536 (2) | C7—C8 | 1.5163 (19) |
| C2—H2A | 0.9900 | C7—H7A | 0.9900 |
| C2—H2B | 0.9900 | C7—H7B | 0.9900 |
| C3—C4 | 1.518 (2) | C8—H8A | 0.9800 |
| C3—H3A | 0.9900 | C8—H8B | 0.9800 |
| C3—H3B | 0.9900 | C8—H8C | 0.9800 |
| C4—H4A | 0.9900 | | |
| C5—N1—C6 | 111.31 (10) | N1—C4—H4B | 111.0 |
| C5—N1—C4 | 110.64 (10) | C3—C4—H4B | 111.0 |
| C6—N1—C4 | 111.98 (10) | H4A—C4—H4B | 109.0 |
| C5—N1—C1 | 109.44 (10) | N1—C5—H5A | 109.5 |
| C6—N1—C1 | 109.72 (10) | N1—C5—H5B | 109.5 |
| C4—N1—C1 | 103.46 (10) | H5A—C5—H5B | 109.5 |
| N1—C1—C2 | 105.54 (11) | N1—C5—H5C | 109.5 |

| | | | |
|-------------|--------------|-------------|--------------|
| N1—C1—H1A | 110.6 | H5A—C5—H5C | 109.5 |
| C2—C1—H1A | 110.6 | H5B—C5—H5C | 109.5 |
| N1—C1—H1B | 110.6 | N1—C6—C7 | 114.30 (10) |
| C2—C1—H1B | 110.6 | N1—C6—H6A | 108.7 |
| H1A—C1—H1B | 108.8 | C7—C6—H6A | 108.7 |
| C1—C2—C3 | 106.30 (12) | N1—C6—H6B | 108.7 |
| C1—C2—H2A | 110.5 | C7—C6—H6B | 108.7 |
| C3—C2—H2A | 110.5 | H6A—C6—H6B | 107.6 |
| C1—C2—H2B | 110.5 | C8—C7—C6 | 109.34 (11) |
| C3—C2—H2B | 110.5 | C8—C7—H7A | 109.8 |
| H2A—C2—H2B | 108.7 | C6—C7—H7A | 109.8 |
| C4—C3—C2 | 104.66 (11) | C8—C7—H7B | 109.8 |
| C4—C3—H3A | 110.8 | C6—C7—H7B | 109.8 |
| C2—C3—H3A | 110.8 | H7A—C7—H7B | 108.3 |
| C4—C3—H3B | 110.8 | C7—C8—H8A | 109.5 |
| C2—C3—H3B | 110.8 | C7—C8—H8B | 109.5 |
| H3A—C3—H3B | 108.9 | H8A—C8—H8B | 109.5 |
| N1—C4—C3 | 103.74 (11) | C7—C8—H8C | 109.5 |
| N1—C4—H4A | 111.0 | H8A—C8—H8C | 109.5 |
| C3—C4—H4A | 111.0 | H8B—C8—H8C | 109.5 |
| C5—N1—C1—C2 | 85.97 (12) | C1—N1—C4—C3 | 40.98 (12) |
| C6—N1—C1—C2 | -151.63 (11) | C2—C3—C4—N1 | -33.99 (14) |
| C4—N1—C1—C2 | -31.99 (13) | C5—N1—C6—C7 | -63.82 (14) |
| N1—C1—C2—C3 | 10.96 (15) | C4—N1—C6—C7 | 60.62 (14) |
| C1—C2—C3—C4 | 14.09 (15) | C1—N1—C6—C7 | 174.90 (11) |
| C5—N1—C4—C3 | -76.14 (13) | N1—C6—C7—C8 | -177.02 (12) |
| C6—N1—C4—C3 | 159.05 (10) | | |

Hydrogen-bond geometry (Å, °)

| <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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| C1—H1B...C11 ⁱ | 0.99 | 2.79 | 3.607 (1) | 141 |
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| C6—H6B...C11 | 0.99 | 2.77 | 3.666 (1) | 151 |

Symmetry codes: (i) $-x+1/2, -y+3/2, z+1/2$; (ii) $-x+1, y, -z+1/2$; (iii) $x, -y+2, z+1/2$.

Fig. 1

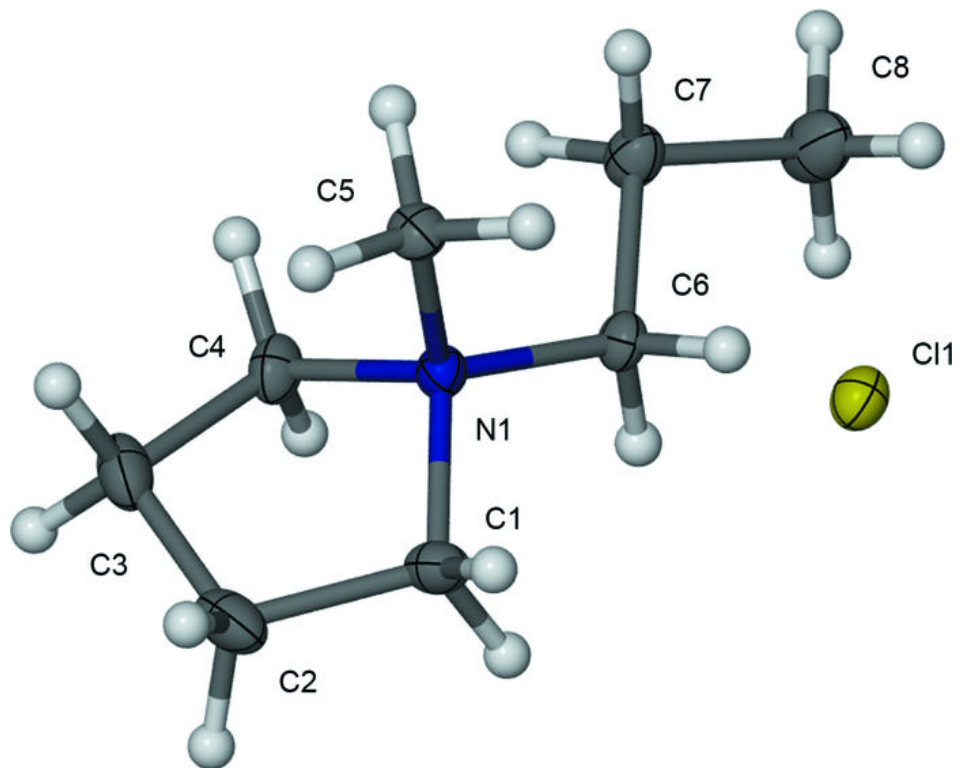


Fig. 2

