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4-hydrazinopyridinium chloride

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4-Hydrazinopyridinium chloride

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Key indicators: single-crystal X-ray study; T = 173 K, P = 0.0 kPa; mean |C–C| = 0.002 Å; R factor = 0.022; wR factor = 0.060; data-to-parameter ratio = 13.6.

In the title compound, C₅H₈N₃⁺Cl⁻, the cation and the anion lie on a mirror plane and are hydrogen bonded in a three-dimensional network via the H atoms of the two hydrazine N atoms. The pyridine N atom is protonated and hydrogen bonded to the terminal hydrazine N atom.

Related literature

For related structures, see: Lima et al. (2008); Hammerl et al. (2001). For background to the synthesis, see: Mann et al. (1959).

Experimental

Crystal data

C₅H₈N₃⁺Cl⁻
Mᵣ = 145.59
Monoclinic, P₂₁/m
a = 6.9526 (11) Å
b = 6.434 (1) Å
c = 7.7432 (12) Å
β = 95.316 (1)°
V = 344.89 (9) Å³
Z = 2
Mo Kα radiation
µ = 0.46 mm⁻¹
T = 173 K
0.27 x 0.19 x 0.18 mm

Data collection

Bruker APEXII CCD area-detector
Absorption correction: multi-scan (SADABS; Bruker, 2006)
Tmin = 0.884, Tmax = 0.920
4968 measured reflections
855 independent reflections
840 reflections with I > 2σ(I)
Rint = 0.016

Refinement

R[F² > 2σ(F²)] = 0.022
wR(F²) = 0.060
S = 1.13
855 reflections
63 parameters

H atoms treated by a mixture of independent and constrained refinement
Δρmax = 0.32 e Å⁻³
Δρmin = −0.20 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D–H···A   D–H   H···A   D···A   D–H···A
N7—H7···Cl1 0.89 (2) 2.25 (2) 3.1358 (14) 176.7 (19)
N8—H8···Cl1i 0.849 (14) 2.905 (14) 3.1970 (14) 102.4 (11)
N1—H1···N8ii 0.89 (2) 1.92 (2) 2.8069 (19) 172.0 (19)

Symmetry codes: (i) x, y, z; (ii) x, y, z.

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 2006); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXD (Sheldrick, 2008); program(s) used to refine structure: SHELXTL (Sheldrick, 2008); molecular graphics: Mercury (Macrae et al., 2006); software used to prepare material for publication: pubICIF (Westrip, 2009).

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for a Discovery Grant and the Alberta Ingenuity Fund for a studentship (MRH). The diffractometer was purchased with the help of NSERC and the University of Lethbridge.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2178).

References

4-Hydrazinopyridinium chloride

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S1. Comment
In the structure of the title compound, (I), (Figure 1.) both ions crystallize on the mirror plane perpendicular to b with a separation of b/2 (3.217 Å). In consequence, the N7, N8 and N7—H atom are coplanar with the aromatic ring, and thus the out-of-plane H atoms on N8 are in a staggered conformation with respect to the N7—H atom. The local conformation of the aryl-hydrazine is similar to that observed in only two known crystal structures, both of phenylhydrazine, namely [(C₆H₅NHNH₂)₂(N₇)(II), Hammerl et al. (2001) and [C₆H₅NHNH₃]Cl, (III), Lima et al. (2008). The former contains both PhNHNH₂ and PhNHNH₃⁺ in the lattice. However, in (I) it is the more basic pyridine N1 that is protonated, but which also forms a strong H bond to the terminal hydrazinyl N8 (D···A = 2.8069 (19) Å). This bond is comparable in strength to the linking H bond between PhNHNH₂ and PhNHNH₃⁺ in (II). The structures of (II) and (III) are also composed of essentially flat sheets of Aryl—N units, with inter-planar separations of 3.497 and 3.378 Å, respectively.

There are additional H bonds between the N7—H and the N8—H atoms and the chloride anion which, in conjunction with the infinite chains of N1—H to N8 bonds, result in the formation of planar hydrogen-bonded sheets (Figure 2), with N···Cl distances very comparable to those found in (III).

In summary, the structure of (I) has a higher symmetry than (II) and (III) and is tightly packed due to a network of strong H bonds.

S2. Experimental
4-Chloropyridine (1.1 mmol, 4.20 g) and pure hydrazine hydrate (1.1 mmol, 1.63 g) were added to 10 ml of 1-propanol. After refluxing for 48 h, the mixture was cooled to 273 K and washed with cold 1-propanol. Recrystallization from methanol yielded 3.6 g of the title compound (I) as colorless needles in 65% yield. The compound (I) has a melting point of 516–517 K, which was in agreement with published values (Mann et al. 1959).

S3. Refinement
Space group determination was ambiguous between P2₁ and P2₁/m because of poor E-statistics. However, the structure was successfully solved using the SHELXD procedure (Sheldrick, 2008) and refined in P2₁/m. The origin of the ambiguous E-statistics became obvious after structure solution, as every atom except for the two N8 hydrogen atoms are found on a crystallographic mirror plane. All H atoms were located in a difference map. N-bound H atoms were freely refined with the constraint U_{iso}(H) = 1.2U_{eq}(N). The C-bound H atoms were placed in calculated positions (C—H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C).
Figure 1
A view of (I) plotted with displacement ellipsoids at 50% probability level.
Figure 2
Packing diagram of (I) showing the network of H-bonds.

4-Hydrazinopyridinium chloride

Crystal data

\[ C_5H_8N_3^+ \cdot Cl^- \]

\( M_r = 145.59 \)

Monoclinic, \( P2_1/m \)

Hall symbol: -P 2yb

\( a = 6.9526 (11) \) Å

\( b = 6.434 (1) \) Å

\( c = 7.7432 (12) \) Å

\( \beta = 95.316 (1) \)^\circ

\( V = 344.89 (9) \) Å\(^3\)

\( Z = 2 \)

\( F(000) = 152 \)

\( D_x = 1.402 \) Mg m\(^{-3}\)

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 4500 reflections

\( \theta = 2.6–27.5^\circ \)

\( \mu = 0.46 \) mm\(^{-1}\)

\( T = 173 \) K

Block, colourless

0.27 × 0.19 × 0.18 mm

Data collection

Bruker APEXiII CCD area-detector diffractometer

4968 measured reflections

855 independent reflections

840 reflections with \( I > 2\sigma(I) \)

\( \theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.6^\circ \)

\( h = -9 \rightarrow 9 \)

\( k = -8 \rightarrow 8 \)

\( l = -10 \rightarrow 10 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.022 \)

\( wR(F^2) = 0.060 \)

\( S = 1.13 \)

855 reflections

63 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: notdet

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

\( w = 1/[\sigma^2(F_c^2) + (0.0256P)^2 + 0.1361P] \)

where \( P = (F_c^2 + 2F_i^2)/3 \)

\( \langle \Delta\sigma/\sigma \rangle_{\text{max}} < 0.001 \)

\( \Delta\rho_{\text{max}} = 0.32 \) e Å\(^{-3}\)

\( \Delta\rho_{\text{min}} = -0.20 \) e Å\(^{-3}\)

Extinction correction: \( SHELXTL \) (Sheldrick, 2008), \( Fe = kF_c[1+0.001xFe^2\lambda^2\sin(2\theta)]^{1/4} \)

Extinction coefficient: 0.038 (6)
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 $F^2 > \sigma(F^2)$ 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 ($\AA^2$)

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Atomic displacement parameters ($\AA^2$)

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<tr>
<td>N1</td>
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<td>N8</td>
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<td>0.0151 (6)</td>
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<td>C3</td>
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Geometric parameters ($\AA$, °)

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### Hydrogen-bond geometry (Å, °)

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<thead>
<tr>
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<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tr>
<td>N7—H7···Cl1</td>
<td>0.89 (2)</td>
<td>2.25 (2)</td>
<td>3.1358 (14)</td>
<td>177 (2)</td>
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<td>N8—H8···Cl1'</td>
<td>0.849 (14)</td>
<td>2.905 (14)</td>
<td>3.1970 (14)</td>
<td>102.4 (11)</td>
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<tr>
<td>N1—H1···N8#</td>
<td>0.89 (2)</td>
<td>1.92 (2)</td>
<td>2.8069 (19)</td>
<td>172 (2)</td>
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Symmetry codes: (i) x, y, z; (ii) x, y, z+1.