

4-[*N,N*-Bis(2-cyanoethyl)amino]pyridinium perchlorate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.049

w R factor = 0.118

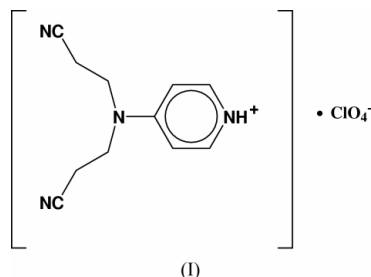
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{11}\text{H}_{13}\text{N}_4^+\cdot\text{ClO}_4^-$, the planar geometry around the amino N atom in the cation suggests conjugation with the π -system of the pyridine ring. $\text{N}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen-bonding interactions play a key role in the crystal packing.

Comment

The synthesis of 4-(*N,N*-dimethylamino)pyridine (DMAP) has attracted much attention for its excellent catalytic properties in many organic reactions (Höfle *et al.*, 1978; Scriven, 1983; Steglich & Hoefle, 1969). Its derivatives also display catalytic properties (Huang *et al.*, 1994; Scriven, 1983). In our present research, we find that 4-[*N,N*-bis(2-cyanoethyl)-amino]pyridine (CEAP) can catalyse an acylation reaction. As part of our research on CEAP and its derivatives, we prepared the title compound, (I). As a derivative of DMAP, compound (I) also has potential catalytic properties in organic reactions.



The title compound, (I), consists of a protonated 4-[*N,N*-bis(2-cyanoethyl)amino]pyridinium cation and a ClO_4^- anion (Fig. 1). The sum of the bond angles around amino atom N2 is 360° (Table 1), as observed in aminopyridines and their derivatives (Chao *et al.*, 1977; Ohms & Guth, 1983). The N2—C3 bond length of $1.340(3)\text{ \AA}$ is shorter than the corresponding bond length in CEAP [$1.374(3)\text{ \AA}$; Ni, Li, Qi *et al.*, 2003] and in its Ag complex [$1.358(5)$ – $1.385(5)\text{ \AA}$; Ni, Li, Xue *et al.*, 2003]. This geometric conformation reflects conjugation between the lone pair of N2 and the π system of the pyridine ring (Chao & Schempp, 1977). The protonation makes this conjugation more strong. The Cl—O distances in the ClO_4^- are in the range $1.403(3)$ – $1.430(3)\text{ \AA}$, which is within the range of typical values (Riera *et al.*, 1998). The ClO_4^- anion and the cation are connected by $\text{C5}-\text{H5}\cdots\text{O4}$ and $\text{N1}-\text{H11}\cdots\text{O2}$ interactions.

Atoms H9a and H10a on the cation interact with N4 on an adjacent cation at $(x-1, y, z)$ through $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds (Table 2). Furthermore, atom H7a also interacts with N3 on an adjacent cation at $(x+1, y, z)$. The propagation of

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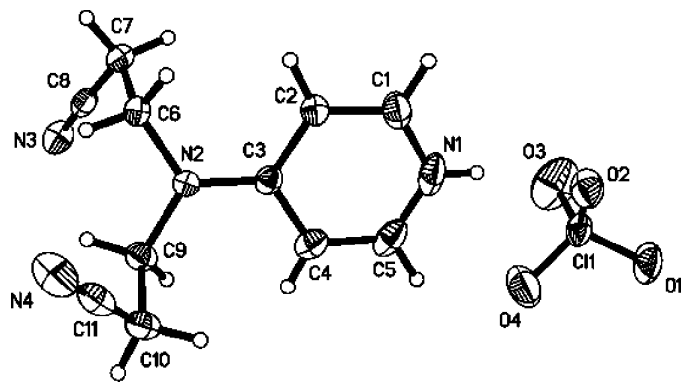


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids.

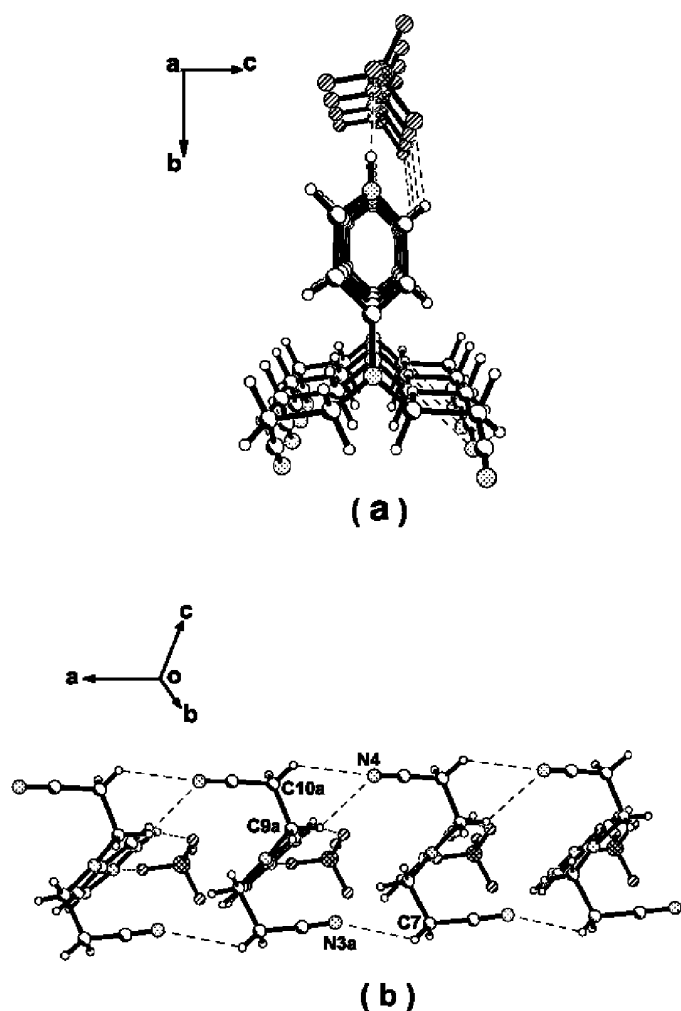


Figure 2
(a) View of one molecular chain down the *a* axis. (b) View of one molecular chain along the *a* axis. [Symmetry code: (a) $x + 1, y, z$.]

molecules and the hydrogen bonds produces a chain along the *a* axis (Fig. 2). The molecules in a chain are parallel with each other and the angle between the molecular chain and the pyridine plane is $40.6(2)^\circ$. Many chains are arranged along the

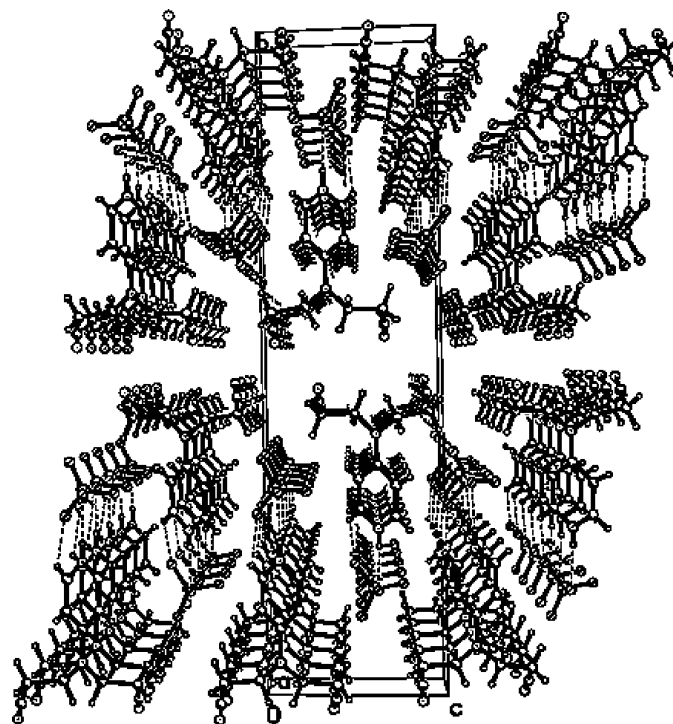


Figure 3
The crystal packing of (I), viewed along the *a* axis.

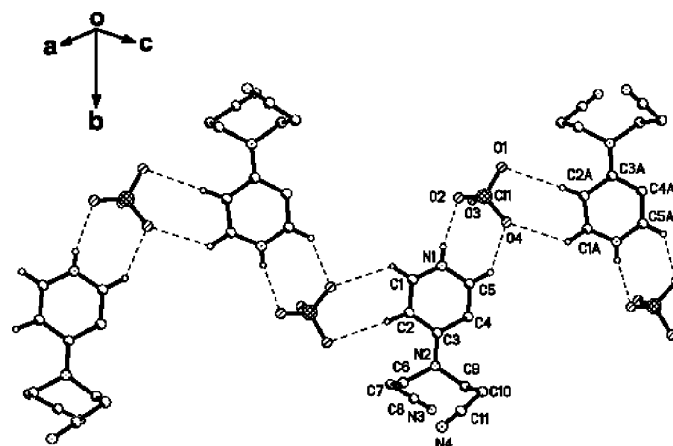


Figure 4
The hydrogen-bond interactions between adjacent chains. H atoms not participating in the hydrogen bonds have been omitted for clarity. [Symmetry code: (A) $x - 1, \frac{3}{2} - y, \frac{1}{2} + z$.]

c axis forming a layer. We can see in Fig. 3 that all chains in a layer are parallel with each other. The molecules in adjacent chains have the opposite direction and the dihedral angle between the pyridine planes in adjacent chains is $8.5(2)^\circ$. This makes it easy for them to bond together through C—H \cdots O hydrogen bonds between cations and ClO_4^- anions. As shown in Fig. 4, atoms H1 and H2 on the cation interact with O4 and O1 of the ClO_4^- anion at $(1 + x, \frac{3}{2} - y, z - \frac{1}{2})$ through C1—H1 \cdots O4 and C2—H2 \cdots O1 hydrogen bonds. The adjacent layers are also linked by a C6—H6b \cdots N4($1 - x, 2 - y, 2 - z$) hydrogen bond.

Experimental

FeSO₄ (152 mg, 1 mmol) and 4-[*N,N*-bis(2-cyanoethyl)amino]-pyridine (200 mg, 1 mmol) were added to 40 ml ethanol. The reaction mixture was refluxed for 1.5 h. NaClO₄ (122.5 mg) was then added to the reaction mixture and stirred for 15 min. White powder of (I) was filtered, washed with ethanol and dried in a vacuum desiccator, yielding 246 mg (82%). Colorless crystals of (I) were obtained by recrystallization from ethanol. The elemental analysis data for C₁₁H₁₃N₄⁺·ClO₄⁻ are as follows, calculated: C 43.90, H 4.23, N 18.62%; found: C 43.78, H 4.27, N 18.49%.

Crystal data

C ₁₁ H ₁₃ N ₄ ⁺ ·ClO ₄ ⁻	<i>D</i> _x = 1.493 Mg m ⁻³
<i>M</i> _r = 300.70	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 2473 reflections
<i>a</i> = 5.403 (1) Å	<i>θ</i> = 2.6–25.9°
<i>b</i> = 30.252 (5) Å	<i>μ</i> = 0.31 mm ⁻¹
<i>c</i> = 8.293 (2) Å	<i>T</i> = 293 (2) K
<i>β</i> = 99.24 (1)°	Needle, colorless
<i>V</i> = 1337.9 (5) Å ³	0.40 × 0.20 × 0.15 mm
<i>Z</i> = 4	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2345 independent reflections
<i>φ</i> and <i>ω</i> scans	1848 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2000)	<i>R</i> _{int} = 0.062
<i>T</i> _{min} = 0.925, <i>T</i> _{max} = 0.957	<i>θ</i> _{max} = 25.0°
6812 measured reflections	<i>h</i> = -6 → 6
	<i>k</i> = -35 → 35
	<i>l</i> = -8 → 9

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.044 <i>P</i>) ² + 0.8 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.118	(Δ/ <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.00	Δ <i>ρ</i> _{max} = 0.36 e Å ⁻³
2345 reflections	Δ <i>ρ</i> _{min} = -0.35 e Å ⁻³
185 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

Cl1–O1	1.403 (2)	N1–C1	1.331 (4)
Cl1–O3	1.406 (3)	N2–C3	1.340 (3)
Cl1–O4	1.426 (2)	N3–C8	1.134 (3)
Cl1–O2	1.430 (2)	N4–C11	1.134 (4)
N1–C5	1.329 (4)		
O1–Cl1–O3	111.29 (18)	O4–Cl1–O2	108.38 (14)
O1–Cl1–O4	108.99 (15)	C5–N1–C1	120.8 (3)
O3–Cl1–O4	108.6 (2)	C3–N2–C9	121.3 (2)
O1–Cl1–O2	110.28 (14)	C3–N2–C6	121.92 (19)
O3–Cl1–O2	109.26 (19)	C9–N2–C6	116.71 (19)

Table 2

Hydrogen-bonding 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>
N1–H11···O2	0.84 (3)	2.09 (3)	2.913 (4)	164 (3)
C1–H1···O4 ⁱ	0.93	2.69	3.326 (4)	126
C2–H2···O1 ⁱ	0.93	2.66	3.579 (3)	168
C5–H5···O4	0.93	2.44	3.169 (4)	135
C6–H6b···N4 ⁱⁱ	0.97	2.65	3.487 (3)	145
C7–H7a···N3 ⁱⁱⁱ	0.97	2.73	3.407 (4)	127
C9–H9a···N4 ^{iv}	0.97	2.65	3.163 (4)	113
C10–H10a···N4 ^{iv}	0.97	2.57	3.257 (4)	128

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

Atom H11 am bonded to N1 was located in a difference Fourier map and refined isotropically. The positions of the other H atoms were fixed geometrically (C–H = 0.93–0.97 Å) and refined using the riding-model approximation (*U*_{iso} = 1.2 times *U*_{eq} of the parent atom).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (2000). *SMART, SAINT, SADABS and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chao, M. & Schempp, E. (1977). *Acta Cryst.* **B33**, 1557–1564.
- Chao, M., Schempp, E. & Rosenstein, R. D. (1977). *Acta Cryst.* **B33**, 1820–1823.
- Höfle, G., Steglich, W. & Vorbrüggen, H. (1978). *Angew. Chem. Int. Ed. Engl.* **17**, 569–583.
- Huang, J. T., Cao, A. H., Shao, S. X., Sun, J. W. & Liu, Z. H. (1994). *Huaxue Shijie*, **4**, 188–190. (In Chinese.)
- Ni, J., Li, Y. Z., Qi, W. B., Liu, Y. J., Chen, H. L. & Wang, Z. L. (2003). *Acta Cryst.* **C59**, o470–o472.
- Ni, J., Li, Y. Z., Xue, Z., Chen, H. L. & Wang, Z. L. (2003). *Acta Cryst.* **C59**, m201–m203.
- Ohms, U. & Guth, H. (1983). *Z. Kristallogr.* **162**, 174.
- Riera, X., Moreno, V., Font-Bardia, M. & Solans, X. (1998). *Polyhedron*, **18**, 65–78.
- Scriven, E. F. V. (1983). *Chem. Soc. Rev.* **12**, 129–161.
- Steglich, W. & Hoefle, G. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 981.