Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2823 measured reflections
2698 independent reflections
1821 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.0106$
$\theta_{\text{max}} = 25.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.111$
$S = 1.065$
2698 reflections
191 parameters
H-atom coordinates fixed, one common U
$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2 + 0.9295P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = -0.001$
$\Delta\rho_{\text{max}} = 0.197$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.194$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.349 (3)	O4—C4	1.457 (3)
O1—C8a	1.469 (3)	C2—C2a	1.516 (4)
O2—C2	1.197 (3)	C3—C4	1.469 (3)
O3—C10	1.208 (3)	C5—C8c	1.329 (3)
O4—C3	1.446 (3)		
C2—O1—C8a	109.7 (2)	O4—C4—C5	117.0 (2)
C3—O4—C4	60.81 (15)	C3—C4—C5	118.2 (2)
O4—C3—C4	59.93 (15)	O4—C4—C10	114.1 (2)
O4—C3—C9	115.5 (2)	C3—C4—C10	120.7 (2)
C4—C3—C9	123.5 (2)	C5—C4—C10	115.4 (2)
O4—C3—C2a	112.5 (2)	C5—C8c—C6	121.7 (2)
C4—C3—C2a	114.4 (2)	C5—C8c—C8b	119.0 (2)
C9—C3—C2a	117.2 (2)	C6—C8c—C8b	119.2 (2)
O4—C4—C3	59.26 (15)		

The H atoms were found from difference Fourier maps and included as fixed contributors. Only an overall isotropic displacement parameter was refined and converged to $U = 0.075\,(2)$ Å^2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1275). Services for accessing these data are described at the back of the journal.

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N-(2-Pyridinium)urea Perchlorate†

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Abstract

The *N*-(2-pyridinium)urea cation of the title compound, $C_6H_8N_3O^+.ClO_4^-$, is planar within 0.022 (2) Å and adopts an *s-cis-s-cis* conformation with respect to the imino C—N bonds. The structure consists of centrosymmetric dimers of cations ordered in layers parallel to the $(\bar{1}03)$ plane, and hydrogen-bonded anions.

Comment

This article is part of a project investigating adducts of urea derivatives and inorganic salts unsymmetrically substituted by π-conjugated substituents as potential non-linear materials. The adduct of *N*-(2-pyridyl)urea (2pU) with $HReO_4$ was found to crystallize in the centrosymmetric space group $P\bar{1}$ (Velikova, Petrova & Angelova, 1997) and contain cationic hydrogen-bonded dimers. Here we changed the counter ion to a tetrahedral but smaller ClO_4^- anion in order to investigate its effect on the cationic geometry and arrangement.

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† Alternative name: 2-ureidopyridinium perchlorate.

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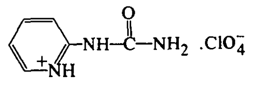

(1)

Bond lengths and angles in *N*-(2-pyridinium)urea perchlorate (1) are similar to those found for 2pU (Velikova, Angelova & Kossev, 1997) and derivatives (Magueres, Ouahab, Hocquet & Fournier, 1994; Velikova, Petrova & Angelova, 1997). The intramolecular hydrogen bond between the protonated *endo* N atom and the carbonyl O atom is crucial for the planarity and conformation of the molecule. The cation is planar with the largest deviation of 0.022 (2) Å at both the N1 and C5 atoms. The overall conformation of the molecule can be described as *s-cis-s-cis* with respect to the imino C1—N2—C2 bonds. The same conformation is realised in the structure of *N*-(2-pyridinium)urea perrhenate (Velikova, Petrova & Angelova, 1997).

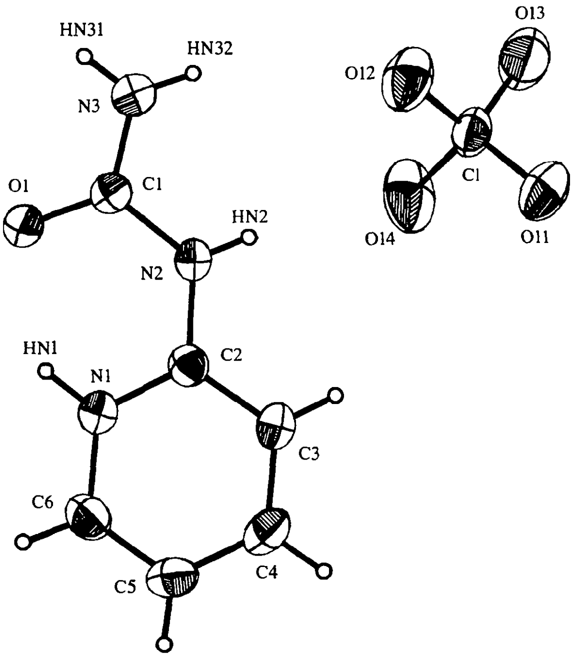

Fig. 1. The ions with the atom-numbering scheme; 50% probability displacement ellipsoids.

The ions are organized in layers parallel to ($\bar{1}03$) by an extensive hydrogen-bonding network (Table 2). The cations are dimerized through centrosymmetric eight-membered hydrogen-bonded rings similar to those found in the structures of 2pU and $2pUH^+.ReO_4^-$. In addition, the *cisoid* imino HN2 and amino HN32 atoms take part in another type of eight-membered hydrogen-bonded ring to O12 and O14 atoms (Fig. 2). An analogous interionic interaction has been found in the structure of guanidinium perchlorate (Pajak, Grottel & Koziol, 1982). In the structure of $2pUH^+.ReO_4^-$ the same H atoms are bonded to one acceptor only, thus forming a six-membered ring. The layers are held together by weak van der Waals forces only.

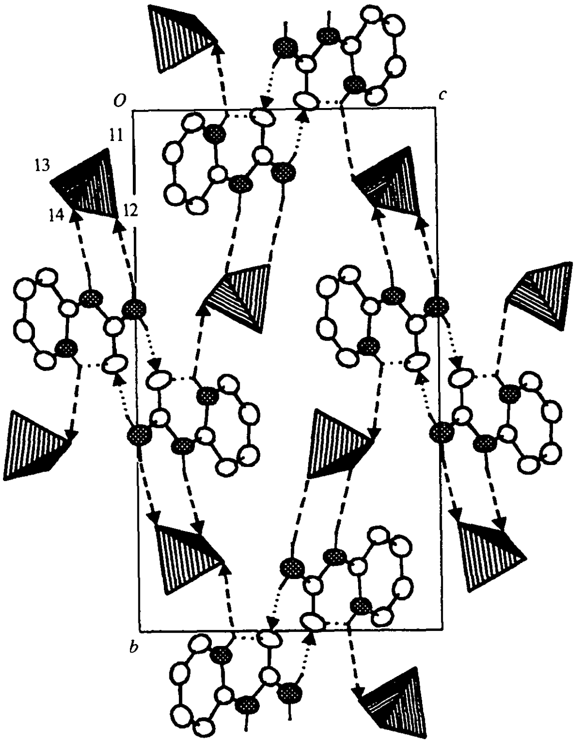

Fig. 2. Projection of the structure down the *a* axis.

Experimental

The compound was obtained by mixing equimolar amounts of *N*-(2-pyridinyl)urea and perchloric acid (70%) in water and recrystallized from ethanol.

Crystal data

$C_6H_8N_3O^+.ClO_4^-$
$M_r = 237.60$
Monoclinic
$P2_1/n$
$a = 5.946\ (2)$ Å
$b = 16.441\ (4)$ Å
$c = 9.582\ (2)$ Å
$\beta = 100.14\ (2)°$
$V = 922.1\ (8)$ Å^3
$Z = 4$
$D_x = 1.712$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 19.93–21.08°$
$\mu = 0.42$ mm^{-1}
$T = 292$ K
Prismatic
0.40 × 0.39 × 0.26 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 28.0°$

$\omega/2\theta$ scans
Absorption correction: none
4848 measured reflections
2025 independent reflections
1392 reflections with
$I > 2\sigma(I)$

$h = 0 \rightarrow 7$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1.4%

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.074$
$S = 1.042$
2026 reflections
161 parameters
H-atom positional parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.225$ e Å^{-3}
$\Delta\rho_{\min} = -0.248$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.017 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cl—O11	1.417 (2)	C2—N1	1.339 (2)
Cl—O13	1.425 (2)	C2—N2	1.366 (3)
Cl—O14	1.425 (2)	C2—C3	1.397 (3)
Cl—O12	1.432 (2)	C3—C4	1.363 (3)
O1—C1	1.228 (2)	C4—C5	1.387 (3)
C1—N3	1.326 (3)	C5—C6	1.359 (3)
C1—N2	1.386 (2)	C6—N1	1.351 (3)
O11—Cl—O13	109.43 (11)	O1—C1—N2	120.7 (2)
O11—Cl—O14	110.22 (12)	N3—C1—N2	115.3 (2)
O13—Cl—O14	109.76 (13)	N1—C2—N2	120.2 (2)
O11—Cl—O12	109.63 (11)	N2—C2—C3	121.4 (2)
O13—Cl—O12	109.51 (11)	C4—C3—C2	119.1 (2)
O14—Cl—O12	108.28 (11)	C2—N1—C6	122.9 (2)
O1—C1—N3	124.0 (2)	C2—N2—C1	125.9 (2)

Table 2. *Hydrogen-bond parameters (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	*A*···H···*A*
N1—HN1···O1	0.85 (2)	1.92 (2)	2.606 (2)	137 (2)	
N1—HN1···O13^{i}	0.87 (3)	2.47 (2)	3.105 (3)	132 (2)	90 (1)
N2—HN2···O14	0.79 (2)	2.17 (2)	2.950 (2)	170 (2)	
N3—HN31···O1^{ii}	0.83 (2)	2.15 (3)	2.950 (3)	164 (2)	
N3—HN32···O12	0.81 (2)	2.21 (3)	3.002 (3)	168 (3)	

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

All H atoms have been localized from difference Fourier maps and refined with fixed isotropic thermal displacement parameters.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1081). Services for accessing these data are described at the back of the journal.

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Isomerism/Tautomerism in Hydrazones Derived from Thiophenaldehydes and 2-Hydrazinoquinoline

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Abstract

The structures of 2-thiophenecarbaldehyde 2-quinolylhydrazone, $C_{14}H_{11}N_3S$, (1), 2-acetylthiophene 2-quinolylhydrazone, $C_{15}H_{13}N_3S$, (2), 2(1*H*)-quinolone 5-bromo-2-thienylmethylidenehydrazone, $C_{14}H_{10}BrN_3S$, (3), and 5-chloro-2-thiophenecarbaldehyde 2-quinolylhydrazone, $C_{14}H_{10}ClN_3S$, (4), show that (1), (2) and (4) exist as the *anti–E* isomer, while (3) is the tautomer of the *syn–Z* isomer, being protonated on the quinoline nitrogen rather than on the exocyclic nitrogen. The photochemical isomerization/tautomerization of (3) to the *anti–E* isomer is discussed.

Comment

Hydrazones have been widely studied as chelating ligands for the spectrophotometric and fluorimetric determination of trace metal ions (Geldard & Lyons, 1964; Katyal & Dutt, 1975; Singh, Jain & Singh, 1972; Galiano-Roth & Collum, 1988; Desgupta, Zhang, Schulze & Marx, 1994). Less studied are those de-

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