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Phenazinium perchlorate

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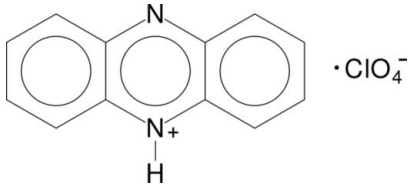
Key indicators: single-crystal X-ray study; T = 297 K; mean σ(C–C) = 0.003 Å; R factor = 0.034; wR factor = 0.101; data-to-parameter ratio = 11.8.

In the crystal structure of the title compound, $C_{12}H_9N_2^+\cdot ClO_4^-$, paired C—H···N interactions link the phenazinium cations into centrosymmetric $R_2^2(8)$ dimers. The cations are also associated by nearly symmetrical bifurcated N—H···O hydrogen bonds *via* perchlorate anions. The resulting hydrogen-bond system generates sheets running parallel to the $(12\bar{1})$ plane.

Related literature

For related literature, see: Allen *et al.* (1987); Etter *et al.* (1990); Sieroń (2005, 2007*a*, 2007*b*).



Experimental

Crystal data

$C_{12}H_9N_2^+\cdot ClO_4^-$
M_r = 280.66
Triclinic, $P\bar{1}$
a = 7.2025 (5) Å
b = 7.8494 (4) Å
c = 11.1564 (8) Å
α = 81.463 (5)°
β = 80.539 (6)°
γ = 74.005 (5)°
V = 594.52 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 297 K
0.45 × 0.25 × 0.15 mm

Data collection

Kuma KM-4-CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.865, T_{max} = 0.950
6587 measured reflections
2097 independent reflections
1900 reflections with $I > 2\sigma(I)$
R_{int} = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.101
S = 1.07
2097 reflections
177 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—O1	1.420 (3)	N1—C1	1.344 (3)
Cl1—O2	1.4188 (15)	N1—C12	1.345 (3)
Cl1—O3	1.411 (2)	N2—C6	1.340 (2)
Cl1—O4	1.4109 (16)	N2—C7	1.332 (2)
O1—Cl1—O2	107.90 (11)	N1—C1—C2	122.11 (16)
O1—Cl1—O3	110.73 (14)	N1—C1—C6	117.11 (18)
O1—Cl1—O4	108.76 (13)	N1—C12—C7	116.80 (18)
O2—Cl1—O3	108.73 (11)	N1—C12—C11	122.19 (17)
O2—Cl1—O4	111.68 (10)	N2—C6—C1	121.92 (18)
O3—Cl1—O4	109.05 (13)	N2—C6—C5	120.04 (16)
C1—N1—C12	123.35 (16)	N2—C7—C8	120.05 (16)
C6—N2—C7	118.69 (15)	N2—C7—C12	122.13 (18)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88 (2)	2.16 (2)	2.936 (3)	148 (2)
N1—H1···O1^{i}	0.88 (2)	2.22 (2)	2.903 (3)	135 (2)
C8—H8···N2^{ii}	0.93	2.58	3.497 (3)	170

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2240).

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  doi:10.1107/S160053680701759X

supplementary materials

Acta Cryst. (2007). E**63**, o2508 [**doi:10.1107/S160053680701759X**]

Phenazinium perchlorate

L. Sieron

Comment

The title compound, (I), was investigated as part of a structural study on hydrogen-bonding patterns in N-heterocyclic perchlorate salts (Sieroń, 2005, 2007a,b).

In (I), the asymmetric unit is composed of one monoprotonated phenazinium cation and one perchlorate anion (Fig. 1). The bond lengths and angles are within normal ranges (Allen *et al.*, 1987) (Table 1). In the crystal structure, pairs of cations are connected into centrosymmetric dimers of $R_2^2(8)$ graph-set (Etter *et al.*, 1990) *via* C–H···N hydrogen bonds (Table 2). In addition the perchlorate ions involve phenazinium cations into bifurcated N–H···O hydrogen bonds, generating a ring of graph-set motif $R_2^2(4)$. The combination of N–H···O and C–H···O hydrogen bonds forms sheets parallel to the $(12\bar{1})$ plane, as shown in Fig. 2.

Experimental

Phenazine was dissolved in hot perchloric acid (60%). The solution was allowed to cool to room temperature, and crystals formed after a few days.

Refinement

H bonded to N atom was located in a difference Fourier map and refined isotropically. Remaining H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å and with U_{iso}(H) = 1.2 times U_{eq}(C).

Figures

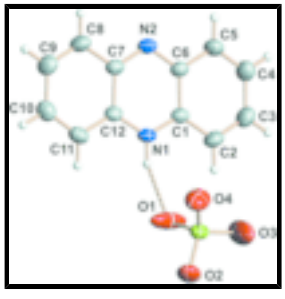

Fig. 1. The molecular structure of (I), with atom labels and 40% probability displacement ellipsoids for non-H atoms. The dashed line indicates a hydrogen bond.

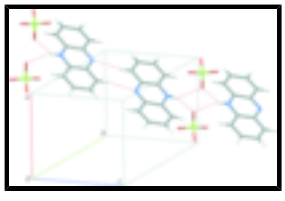

Fig. 2. The packing of (I), showing molecules connected by N—H···O and C—H···N hydrogen bonds (dashed lines) into sheets approximately parallel to the $(12\bar{1})$ plane.

Phenazinium perchlorate

Crystal data

$C_{12}H_9N_2^+ \cdot ClO_4^-$	$Z = 2$
$M_r = 280.66$	$F_{000} = 288$
Triclinic, $P\overline{1}$	$D_x = 1.568$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.2025$ (5) Å	Cell parameters from 5148 reflections
$b = 7.8494$ (4) Å	$\theta = 1.8$–28.1º
$c = 11.1564$ (8) Å	$\mu = 0.33$ mm^{-1}
$\alpha = 81.463$ (5)º	$T = 297$ K
$\beta = 80.539$ (6)º	Prism, orange
$\gamma = 74.005$ (5)º	0.45 × 0.25 × 0.15 mm
$V = 594.52$ (7) Å^3	

Data collection

Kuma KM-4-CCD diffractometer	2097 independent reflections
Radiation source: CX-Mo12x0.4-S Seifert Mo tube	1900 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.013$
Detector resolution: 8.2356 pixels mm^{-1}	$\theta_{max} = 25.0$º
$T = 297$ K	$\theta_{min} = 2.7$º
ω scans	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	$k = -9 \rightarrow 9$
$T_{min} = 0.865$, $T_{max} = 0.950$	$l = -13 \rightarrow 13$
6587 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.2208P]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
$wR(F^2) = 0.101$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
$S = 1.07$	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
2097 reflections	Extinction coefficient: 0.022 (4)
177 parameters	
Primary atom site location: structure-invariant direct methods	
Hydrogen site location: difference Fourier map	
H atoms treated by a mixture of	

independent and constrained refinement

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating -R-factor-obs 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}
N1	0.6217 (2)	0.8228 (2)	0.81292 (14)	0.0418 (5)
N2	0.7501 (2)	0.6529 (2)	0.60495 (13)	0.0443 (5)
C1	0.4979 (3)	0.8473 (2)	0.73018 (16)	0.0395 (5)
C2	0.3079 (3)	0.9601 (3)	0.74564 (19)	0.0515 (7)
C3	0.1933 (3)	0.9828 (3)	0.6566 (2)	0.0581 (7)
C4	0.2608 (3)	0.8939 (3)	0.5497 (2)	0.0578 (7)
C5	0.4414 (3)	0.7845 (3)	0.53331 (18)	0.0521 (7)
C6	0.5686 (3)	0.7577 (2)	0.62308 (16)	0.0402 (6)
C7	0.8674 (3)	0.6333 (2)	0.68953 (16)	0.0399 (5)
C8	1.0604 (3)	0.5229 (3)	0.67312 (19)	0.0529 (7)
C9	1.1803 (3)	0.5048 (3)	0.7581 (2)	0.0568 (7)
C10	1.1178 (3)	0.5957 (3)	0.86372 (19)	0.0530 (7)
C11	0.9341 (3)	0.7022 (3)	0.88447 (18)	0.0488 (6)
C12	0.8059 (3)	0.7209 (2)	0.79850 (16)	0.0381 (5)
Cl1	0.31140 (6)	0.76238 (6)	1.13972 (4)	0.0419 (2)
O1	0.4337 (4)	0.8615 (3)	1.06518 (17)	0.1046 (9)
O2	0.3034 (2)	0.7936 (2)	1.26274 (13)	0.0665 (6)
O3	0.1211 (3)	0.8186 (3)	1.1070 (2)	0.1135 (10)
O4	0.3889 (3)	0.5803 (2)	1.12356 (17)	0.0731 (7)
H1	0.579 (3)	0.875 (3)	0.880 (2)	0.061 (7)*
H2	0.26200	1.01810	0.81570	0.0620*
H3	0.06810	1.05780	0.66570	0.0700*
H4	0.17920	0.91150	0.49000	0.0690*
H5	0.48290	0.72630	0.46310	0.0630*
H8	1.10440	0.46310	0.60380	0.0630*
H9	1.30600	0.43130	0.74690	0.0680*
H10	1.20390	0.58230	0.92010	0.0640*
H11	0.89440	0.76150	0.95420	0.0590*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0466 (9)	0.0448 (9)	0.0345 (8)	−0.0086 (7)	−0.0008 (7)	−0.0169 (7)
N2	0.0458 (9)	0.0518 (9)	0.0327 (8)	−0.0059 (7)	−0.0011 (7)	−0.0134 (7)
C1	0.0427 (10)	0.0418 (9)	0.0345 (9)	−0.0115 (8)	−0.0001 (7)	−0.0098 (7)
C2	0.0454 (11)	0.0575 (12)	0.0478 (11)	−0.0046 (9)	0.0026 (9)	−0.0195 (9)
C3	0.0400 (11)	0.0689 (14)	0.0597 (13)	−0.0029 (10)	−0.0037 (9)	−0.0133 (11)
C4	0.0459 (11)	0.0786 (15)	0.0480 (12)	−0.0101 (10)	−0.0119 (9)	−0.0092 (10)
C5	0.0518 (11)	0.0679 (13)	0.0368 (10)	−0.0104 (10)	−0.0063 (8)	−0.0153 (9)
C6	0.0417 (10)	0.0450 (10)	0.0326 (9)	−0.0094 (8)	0.0000 (7)	−0.0092 (7)
C7	0.0444 (10)	0.0418 (9)	0.0324 (9)	−0.0092 (8)	−0.0019 (7)	−0.0077 (7)
C8	0.0488 (11)	0.0608 (12)	0.0431 (11)	−0.0006 (9)	−0.0013 (9)	−0.0176 (9)
C9	0.0457 (11)	0.0633 (13)	0.0555 (13)	−0.0012 (10)	−0.0088 (9)	−0.0096 (10)
C10	0.0539 (12)	0.0579 (12)	0.0492 (12)	−0.0125 (10)	−0.0164 (9)	−0.0054 (9)
C11	0.0579 (12)	0.0524 (11)	0.0400 (10)	−0.0144 (9)	−0.0105 (9)	−0.0126 (8)
C12	0.0429 (10)	0.0369 (9)	0.0351 (9)	−0.0113 (7)	−0.0011 (7)	−0.0084 (7)
Cl1	0.0474 (3)	0.0426 (3)	0.0362 (3)	−0.0103 (2)	−0.0031 (2)	−0.0113 (2)
O1	0.180 (2)	0.0876 (13)	0.0610 (11)	−0.0859 (14)	0.0580 (13)	−0.0385 (9)
O2	0.0791 (11)	0.0886 (12)	0.0354 (8)	−0.0252 (9)	−0.0031 (7)	−0.0162 (7)
O3	0.0760 (13)	0.143 (2)	0.1173 (18)	0.0260 (13)	−0.0527 (12)	−0.0599 (15)
O4	0.0818 (12)	0.0451 (9)	0.0905 (13)	−0.0117 (8)	−0.0028 (9)	−0.0197 (8)

Geometric parameters (Å, °)

Cl1—O1	1.420 (3)	C7—C8	1.420 (3)
Cl1—O2	1.4188 (15)	C7—C12	1.432 (2)
Cl1—O3	1.411 (2)	C8—C9	1.351 (3)
Cl1—O4	1.4109 (16)	C9—C10	1.414 (3)
N1—C1	1.344 (3)	C10—C11	1.360 (3)
N1—C12	1.345 (3)	C11—C12	1.403 (3)
N2—C6	1.340 (2)	C2—H2	0.9300
N2—C7	1.332 (2)	C3—H3	0.9300
N1—H1	0.88 (2)	C4—H4	0.9300
C1—C2	1.409 (3)	C5—H5	0.9300
C1—C6	1.426 (2)	C8—H8	0.9300
C2—C3	1.355 (3)	C9—H9	0.9300
C3—C4	1.420 (3)	C10—H10	0.9300
C4—C5	1.348 (3)	C11—H11	0.9300
C5—C6	1.421 (3)		
O1—Cl1—O2	107.90 (11)	N2—C7—C12	122.13 (18)
O1—Cl1—O3	110.73 (14)	C7—C8—C9	120.1 (2)
O1—Cl1—O4	108.76 (13)	C7—C12—C11	121.01 (19)
O2—Cl1—O3	108.73 (11)	C8—C7—C12	117.82 (18)
O2—Cl1—O4	111.68 (10)	C8—C9—C10	121.1 (2)
O3—Cl1—O4	109.05 (13)	C9—C10—C11	121.3 (2)
C1—N1—C12	123.35 (16)	C10—C11—C12	118.67 (19)

C6—N2—C7	118.69 (15)	C1—C2—H2	121.00
C12—N1—H1	118.7 (15)	C3—C2—H2	121.00
C1—N1—H1	118.0 (15)	C2—C3—H3	119.00
N1—C1—C2	122.11 (16)	C4—C3—H3	119.00
N1—C1—C6	117.11 (18)	C5—C4—H4	119.00
C2—C1—C6	120.76 (18)	C3—C4—H4	120.00
C1—C2—C3	118.85 (19)	C4—C5—H5	120.00
C2—C3—C4	121.2 (2)	C6—C5—H5	120.00
C3—C4—C5	121.0 (2)	C7—C8—H8	120.00
C4—C5—C6	120.15 (19)	C9—C8—H8	120.00
C1—C6—C5	118.04 (18)	C10—C9—H9	119.00
N1—C12—C7	116.80 (18)	C8—C9—H9	119.00
N1—C12—C11	122.19 (17)	C9—C10—H10	119.00
N2—C6—C1	121.92 (18)	C11—C10—H10	119.00
N2—C6—C5	120.04 (16)	C12—C11—H11	121.00
N2—C7—C8	120.05 (16)	C10—C11—H11	121.00

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88 (2)	2.16 (2)	2.936 (3)	148 (2)
N1—H1···O1^{i}	0.88 (2)	2.22 (2)	2.903 (3)	135 (2)
C8—H8···N2^{ii}	0.93	2.58	3.497 (3)	170

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

Fig. 1

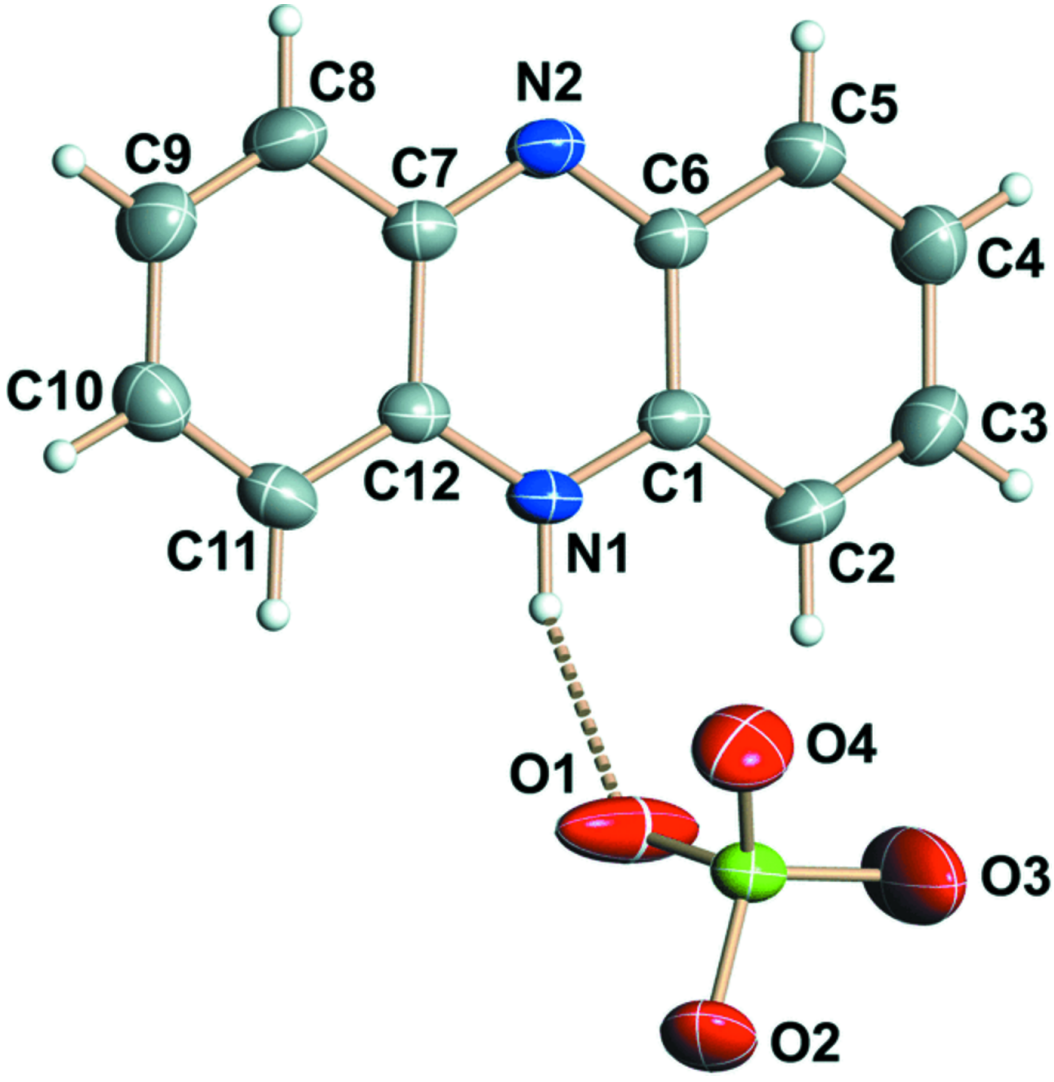

Fig. 2