3,6-Diaminoacridinium perchlorate

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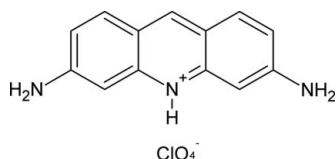
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The structure of the title compound, $C_{13}H_{12}N_3^+ \cdot ClO_4^-$, reveals a twofold axis through the ring N and *para*-C atoms; a twofold rotation axis also passes through the Cl atom. The structure of the organic fragment is similar to that of homologous heterocyclic systems. The organic cations and perchlorate anions self-assemble in the solid state through C—H···O and N—H···O hydrogen bonds, leading to a two-dimensional layer parallel to the (112) plane. The layers are stacked along the c axis through offset π–π interactions between cations from different layers (the distance between the planes through two cations is 3.35 Å), resulting in a three-dimensional supramolecular architecture.

Related literature

For similar structures, see: Obendorf *et al.* (1974); Jones & Neidle (1975); Achari & Neidle (1976). For related literature, see: Berceanu *et al.* (2002); Diop *et al.* (2002). For synthesis, see: Rus *et al.* (2001).

Experimental

Crystal data

$C_{13}H_{12}N_3^+ \cdot ClO_4^-$	V = 1337.8 (5) Å^3
M_r = 309.71	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 15.122 (3) Å	μ = 0.31 mm^{-1}
b = 13.477 (3) Å	T = 297 (2) K
c = 6.6922 (13) Å	0.33 × 0.29 × 0.19 mm
β = 101.21 (3)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	7044 measured reflections
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)	1378 independent reflections
	1271 reflections with $I > 2\sigma(I)$
T_{min} = 0.906, T_{max} = 0.934	R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.132	
S = 1.12	
1378 reflections	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
107 parameters	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
3 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86 (2)	2.51 (2)	3.296 (3)	152 (1)
N1—H1···O1[i]	0.86 (2)	2.51 (2)	3.296 (3)	152 (1)
C2—H2···O1[i]	0.93	2.44	3.274 (3)	150
N2—H2B···O2[ii]	0.85 (2)	2.35 (3)	3.174 (3)	164 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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supplementary materials

3,6-Diaminoacridinium perchlorate

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Comment

Nitrogen containing heterocycles, along with aromatic amines, are valuable candidates for building supramolecular archi-tectures (Berceanu *et al.*, 2002 and Diop *et al.*, 2002). The structural investigation of acridinium-3,6-diamine perchlorate, $(C_{13}H_{12}N_3)^+(ClO_4)^-$ (I), is a result of our constant interest in this field. The asymmetric unit of the title compound consists of two independent halves of each molecular ion. The remainder of the molecules are generated by twofold axes through atoms C7 and N1 for $(C_{13}H_{12}N_3)^+$ and the Cl1 atom, bisecting the O—Cl—O angles, for $(ClO_4)^-$ (Fig. 1). All metric data for the organic unit are consistent with the corresponding values found in homologous derivatives [*cf.* $(C_{13}H_{13}N_3)Cl_2\cdot 2H_2O$; $(C_{13}H_{12}N_3)_2(SO_4)\cdot 3.5H_2O$ and $C_{13}H_{11}N_3\cdot H_2O$: C—C = 1.32—1.45 Å, C—N = 1.33—1.39 Å, C—N—C = 118—123° (Obendorf *et al.*, 1974; Jones & Neidle, 1975 and Achari & Neidle, 1976)]. The perchlorate unit is essentially tetrahedral.

The molecules associate in the solid state into a two-dimensional network *via* N—H···O and C—H···O hydrogen bonding (Fig. 2). Thus, each perchlorate unit links three organic units, which in turn is connected to three other perchlorates through the NH$_2$ group interacting with the O2 atoms from two ClO$_4^-$ cations (Table 1).

The two-dimensional layers along the (112) plane are stacked in the third dimension due to off-set π-π interactions between organic molecules facing in alternating directions [distances between centroids: $Cg1$—$Cg1^{vi}$ = 3.69 Å, $Cg2$—$Cg2^{iii}$ = 3.72 Å, $Cg1^i$—$Cg1^{iii}$ = 3.69 Å, symmetry codes: (i) −x + 2, y, −z + 1/2; (iii) 2 − x, −y, −z; (iv) x, −y, z − 1/2; distance between the planes of two interacting cations 3.35 Å] (Fig. 3).

All these interactions lead to the formation of a three-dimensional supramolecular architecture built up by interlocking layers (Fig. 4).

Experimental

The title compound was obtained by decomposition of [FeL(ClO$_4$)$_2$(H$_2$O)$_2$](ClO$_4$), *L* = 4-(3-aminoacridine-6-imino)pentane-2-one, in 70% HClO$_4$ solution (Rus *et al.*, 2001). Slow evaporation of the mother liquor at room temperature deposited the product as yellow crystals.

Refinement

All hydrogen atoms were placed in calculated positions using a riding model, with C—H = 0.93–0.97 Å and U_{iso}= 1.2U_{eq}(C) for aryl H. The H atoms bonded to N1 and N2 were found in a difference map and refined with a restrained N—H distance of 0.86 (2), 0.85 (2) and 0.87 (2) Å, respectively.
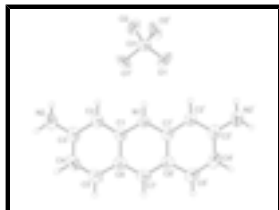
supplementary materials

Figures

Fig. 1. : View of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 2$, y, $-z + 1/2$].
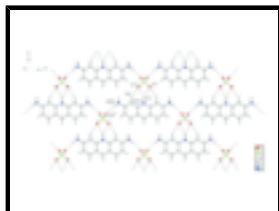
Fig. 2. : The hydrogen bonding (dashed lines) scheme in the title compound. [Symmetry codes: (i) $-x + 2$, y, $-z + 1/2$; (ii) $-x + 3/2$, $y - 1/2$, $-z + 1/2$].
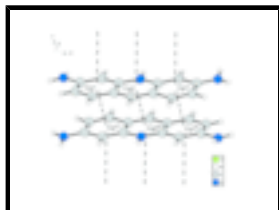
Fig. 3. : π-π interactions (dashed lines) between cations. [Symmetry codes: (i) $-x + 2$, y, $-z + 1/2$; (iii) $2 - x$, $-y$, $-z$; (iv) x, $-y$, $z - 1/2$]. $Cg1$ is the centroid of the C1—C6 ring and $Cg2$ is the centroid of the C1C6C7C6^{i}C1^{i}N1 ring.
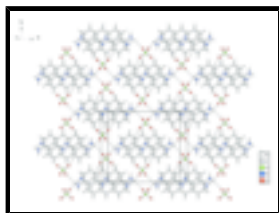
Fig. 4. : Crystal packing of the title compound along the c axis. The hydrogen bonding is shown as dashed lines.

3,6-Diaminoacridinium perchlorate

Crystal data

$C_{13}H_{12}N_3{}^+ \cdot ClO_4{}^-$	$F_{000} = 640$
$M_r = 309.71$	$D_x = 1.538$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2203 reflections
$a = 15.122$ (3) Å	$\theta = 2.8–26.3°$
$b = 13.477$ (3) Å	$\mu = 0.31$ mm^{-1}
$c = 6.6922$ (13) Å	$T = 297$ (2) K
$\beta = 101.21$ (3)°	Block, yellow
$V = 1337.8$ (5) Å^3	$0.33 \times 0.29 \times 0.19$ mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD area-detector	1378 independent reflections

diffractometer

Radiation source: fine-focus sealed tube	1271 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.034$
$T = 297(2)$ K	$\theta_{max} = 26.4º$
φ and ω scans	$\theta_{min} = 2.0º$
Absorption correction: multi-scan (SHELXTL; Bruker, 2001)	$h = -18 \rightarrow 18$
$T_{min} = 0.906$, $T_{max} = 0.934$	$k = -16 \rightarrow 16$
7044 measured reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 1.4184P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} = 0.002$
1378 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
107 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 > 2sigma(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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	1.07618 (16)	0.26928 (18)	0.3309 (4)	0.0941 (8)
Cl1	1.0000	0.32862 (5)	0.2500	0.0515 (3)
O2	0.98003 (15)	0.3883 (2)	0.4083 (4)	0.1039 (10)
H2B	0.6281 (14)	0.013 (2)	0.088 (4)	0.068 (9)*
H2A	0.6775 (19)	0.1098 (13)	0.086 (4)	0.058 (8)*
H1	1.0000	0.1045 (14)	0.2500	0.038 (8)*
C1	0.91822 (13)	−0.00693 (16)	0.2142 (3)	0.0332 (5)

C2	0.83806 (13)	0.04662 (16)	0.1780 (3)	0.0369 (5)
H2	0.8394	0.1156	0.1765	0.044*
C3	0.75599 (14)	−0.00306 (18)	0.1442 (3)	0.0409 (5)
C4	0.75544 (16)	−0.10858 (19)	0.1491 (3)	0.0482 (6)
H4	0.7007	−0.1421	0.1291	0.058*
C5	0.83282 (16)	−0.16078 (18)	0.1823 (3)	0.0472 (6)
H5	0.8305	−0.2297	0.1832	0.057*
C6	0.91832 (14)	−0.11245 (16)	0.2160 (3)	0.0379 (5)
C7	1.0000	−0.1620 (2)	0.2500	0.0422 (7)
H7	1.0000	−0.2310	0.2500	0.051*
N1	1.0000	0.04076 (17)	0.2500	0.0334 (5)
N2	0.67680 (14)	0.04645 (19)	0.1091 (3)	0.0555 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0980 (17)	0.0749 (15)	0.1176 (19)	0.0489 (13)	0.0411 (14)	0.0333 (13)
Cl1	0.0437 (5)	0.0335 (4)	0.0787 (6)	0.000	0.0151 (4)	0.000
O2	0.0599 (13)	0.1064 (18)	0.137 (2)	0.0192 (12)	−0.0019 (13)	−0.0666 (17)
C1	0.0377 (11)	0.0405 (11)	0.0216 (9)	−0.0026 (8)	0.0062 (7)	−0.0006 (7)
C2	0.0388 (11)	0.0419 (11)	0.0298 (10)	−0.0013 (9)	0.0062 (8)	0.0004 (8)
C3	0.0384 (11)	0.0574 (13)	0.0266 (10)	−0.0039 (9)	0.0058 (8)	−0.0011 (9)
C4	0.0441 (13)	0.0592 (14)	0.0411 (12)	−0.0167 (11)	0.0075 (10)	−0.0032 (11)
C5	0.0547 (14)	0.0437 (12)	0.0434 (12)	−0.0121 (10)	0.0100 (10)	−0.0017 (10)
C6	0.0442 (12)	0.0394 (11)	0.0297 (10)	−0.0043 (9)	0.0061 (8)	0.0001 (8)
C7	0.0581 (19)	0.0339 (15)	0.0350 (15)	0.000	0.0097 (13)	0.000
N1	0.0374 (13)	0.0303 (12)	0.0327 (12)	0.000	0.0072 (9)	0.000
N2	0.0354 (11)	0.0683 (16)	0.0608 (13)	−0.0036 (10)	0.0045 (9)	0.0007 (11)

Geometric parameters (Å, °)

O1—Cl1	1.420 (2)	C4—C5	1.346 (3)
Cl1—O2^i	1.409 (2)	C4—H4	0.9300
Cl1—O2	1.409 (2)	C5—C6	1.426 (3)
Cl1—O1^i	1.420 (2)	C5—H5	0.9300
C1—N1	1.373 (2)	C6—C7	1.384 (3)
C1—C2	1.391 (3)	C7—C6^i	1.384 (3)
C1—C6	1.422 (3)	C7—H7	0.9300
C2—C3	1.389 (3)	N1—C1^i	1.373 (2)
C2—H2	0.9300	N1—H1	0.859 (18)
C3—N2	1.351 (3)	N2—H2B	0.849 (17)
C3—C4	1.423 (3)	N2—H2A	0.868 (17)
Cl1—O1—H1	96.4 (2)	C5—C4—H4	119.4
O2^i—Cl1—O2	110.4 (3)	C3—C4—H4	119.4
O2^i—Cl1—O1	109.37 (14)	C4—C5—C6	121.3 (2)
O2—Cl1—O1	108.13 (15)	C4—C5—H5	119.3
O2^i—Cl1—O1^i	108.13 (15)	C6—C5—H5	119.3

O2—Cl1—O1[i]	109.37 (14)	C7—C6—C1	118.9 (2)
O1—Cl1—O1[i]	111.5 (2)	C7—C6—C5	123.9 (2)
N1—C1—C2	120.83 (19)	C1—C6—C5	117.1 (2)
N1—C1—C6	117.86 (19)	C6—C7—C6[i]	122.3 (3)
C2—C1—C6	121.31 (18)	C6—C7—H7	118.9
C3—C2—C1	119.9 (2)	C6[i]—C7—H7	118.9
C3—C2—H2	120.0	C1[i]—N1—C1	124.2 (2)
C1—C2—H2	120.0	C1[i]—N1—H1	117.92 (12)
N2—C3—C2	121.6 (2)	C1—N1—H1	117.91 (12)
N2—C3—C4	119.3 (2)	C3—N2—H2B	119 (2)
C2—C3—C4	119.1 (2)	C3—N2—H2A	118.4 (19)
C5—C4—C3	121.2 (2)	H2B—N2—H2A	122 (3)
H1—O1—Cl1—O2[i]	−119.52 (15)	N1—C1—C6—C7	−1.1 (2)
H1—O1—Cl1—O2	120.25 (15)	C2—C1—C6—C7	179.14 (15)
H1—O1—Cl1—O1[i]	0.001 (1)	N1—C1—C6—C5	178.86 (15)
N1—C1—C2—C3	−179.32 (15)	C2—C1—C6—C5	−0.9 (3)
C6—C1—C2—C3	0.4 (3)	C4—C5—C6—C7	−179.71 (18)
C1—C2—C3—N2	179.85 (19)	C4—C5—C6—C1	0.3 (3)
C1—C2—C3—C4	0.6 (3)	C1—C6—C7—C6[i]	0.55 (12)
N2—C3—C4—C5	179.6 (2)	C5—C6—C7—C6[i]	−179.4 (2)
C2—C3—C4—C5	−1.2 (3)	C2—C1—N1—C1[i]	−179.68 (19)
C3—C4—C5—C6	0.7 (3)	C6—C1—N1—C1[i]	0.55 (12)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86 (2)	2.51 (2)	3.296 (3)	152 (1)
N1—H1···O1[i]	0.86 (2)	2.51 (2)	3.296 (3)	152 (1)
C2—H2···O1[i]	0.93	2.44	3.274 (3)	150
N2—H2B···O2[ii]	0.85 (2)	2.35 (3)	3.174 (3)	164 (2)

Symmetry codes: (i) −*x*+2, *y*, −*z*+1/2; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2.

Fig. 1

Fig. 2

Fig. 3

Fig. 4