

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.066$
 $S = 0.991$
 3461 reflections
 325 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.167 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.183 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)
 Absolute structure: Flack
 (1983)
 Flack parameter = -0.09 (9)

Table 1. Selected bond lengths (\AA) for (I)

C1—O21	1.196 (3)	C4—N5	1.449 (3)
C1—N2	1.380 (3)	C4—C8	1.521 (3)
C1—C4	1.538 (4)	N5—C6	1.466 (3)
N2—C3	1.497 (3)	C6—C7	1.521 (3)
C3—C4	1.589 (4)	C7—C8	1.514 (3)

Compound (II)

Crystal data

C₂₇H₂₄N₂O₆S
 $M_r = 504.54$
 Orthorhombic
 $P2_12_12_1$
 $a = 6.237$ (1) \AA
 $b = 18.928$ (2) \AA
 $c = 21.321$ (3) \AA
 $V = 2517.0$ (6) \AA^3
 $Z = 4$
 $D_x = 1.331 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 27
 reflections
 $\theta = 2.35\text{--}7.51^\circ$
 $\mu = 0.173 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Needle
 $0.52 \times 0.22 \times 0.10 \text{ mm}$
 Colourless

Data collection

Siemens P4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3978 measured reflections
 3492 independent reflections
 2256 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

$\theta_{\max} = 23.00^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 20$
 $l = -23 \rightarrow 23$
 3 standard reflections
 every 97 reflections
 intensity decay: $<4\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.083$
 $S = 1.089$
 3492 reflections
 325 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 0.176 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.161 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)
 Absolute structure: Flack
 (1983)
 Flack parameter = 0.09 (14)

Table 2. Selected bond lengths (\AA) for (II)

C1—O21	1.185 (5)	C4—N5	1.447 (5)
C1—N2	1.422 (5)	C4—C8	1.538 (5)
C1—C4	1.535 (6)	N5—C6	1.472 (5)
N2—C3	1.516 (5)	C6—C7	1.511 (5)
C3—C4	1.571 (5)	C7—C8	1.513 (5)

Because of the bad shape of the crystals, the data collections were limited in 2θ . However, the reduced thermal motion allowed the determination of both structures with sufficient accuracy.

For both compounds, data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL93 and PARSTCIF (Nardelli, 1991). Molecular parameters were calculated using PARST (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1356). Services for accessing these data are described at the back of the journal.

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8-Ammonioquinolinium Dichloride

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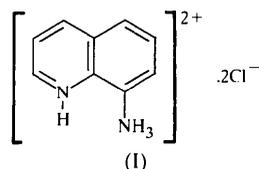
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Abstract

The crystals of C₉H₁₀N₂⁺·2Cl⁻ contain 8-ammonioquinolinium cations, which are stacked along the *c* axis, and chloride anions, which occupy the channels between the stacks. There is extensive N—H···Cl hydrogen bonding between the cations and anions, as well as weak anion–cation Cl···H—C_{sp²} interactions.

The crystal structure of the title compound, (I), was determined in a study of hydrogen bonding involving the diprotonated 8-aminoquinoline moiety. It also provides a comparison with the crystal structure of the monoprotinated analogue 8-aminoquinolinium chloride (Bengtson *et al.*, 1996).



The cation consists of an 8-aminoquinoline moiety that is protonated at both the amino and the ring N atoms (Fig. 1). Protonation of the amino group results in a lengthening of the C—N_{sp³} bond from 1.367 (6) [in 8-aminoquinolinium chloride (Bengtson *et al.*, 1996)] to 1.454 (2) Å. This reflects the loss of the conjugation between the aromatic ring and the lone pair of electrons on the amino N atom when the latter is protonated. The quinoline core (C₉N) is virtually planar, the maximum deviation from the least-squares plane being 0.014 (1) Å (C8). The ammonio N atom is almost coplanar with the quinoline plane, deviating from it by only 0.068 (2) Å.

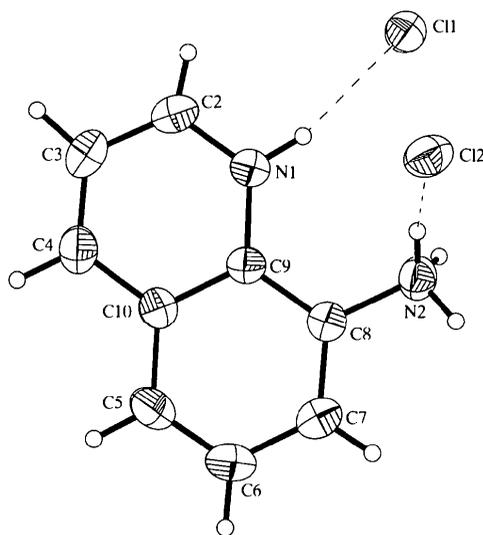


Fig. 1. The crystal structure of the title compound, showing 50% probability ellipsoids for the non-H atoms; H atoms are represented by spheres of arbitrary size.

The 8-ammonioquinolinium cations are stacked along the *c* axis, as shown in Fig. 2. The chloride anions occupy the channels between the stacks, and are engaged in extensive N—H···Cl hydrogen bonding with the cations, as indicated by the short H···Cl distances [2.16 (2)–2.26 (2) Å]. Weak anion–cation Cl···H—C_{sp²} interactions are also observed, with the Cl···H distances ranging from 2.78 (2) to 2.90 (2) Å. This unusual C_{sp²}—

H···Cl interaction in the solid state was also observed in 4,6-dimethylpyrimidine-2-thione hydrochloride monohydrate (Seth *et al.*, 1996). Overall, each chloride is engaged in four intermolecular Cl···H interactions with approximate tetrahedral geometry, as shown in Fig. 2. Thus, although there is no direct hydrogen-bonding interaction among the cations, adjacent cation stacks are interconnected through their hydrogen bonding to the chloride anions.

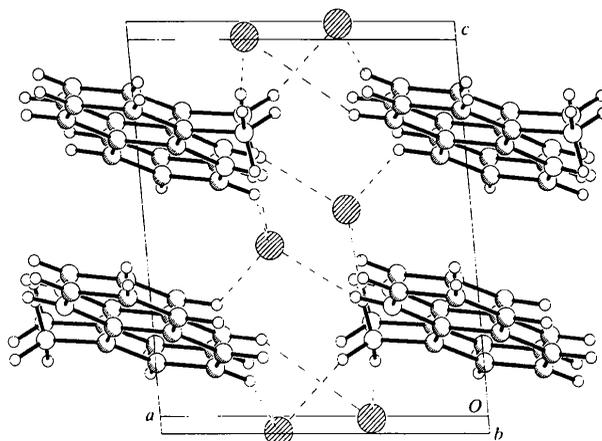


Fig. 2. Packing diagram viewed down the *b* axis. The dashed lines represent hydrogen-bonding interactions.

Experimental

Concentrated hydrochloric acid (2.5 ml) was added to a 10 ml conical flask containing 8-aminoquinoline (1 mmol, 0.144 g). The mixture was stirred and heated in a hot-water bath. When all the 8-aminoquinoline had dissolved, the solution was allowed to cool in a desiccator. Two days later, pale yellow–white crystals (0.14 g, 65%; m.p. 476–479 K) were obtained by gravitational filtration in the desiccator. Elemental analysis of the compound (observed: C 49.2, H 4.1, N 13.3%) confirms an empirical formula of C₉H₁₀Cl₂N₂, indicating the formation of a dihydrochloride salt of 8-aminoquinoline. The IR (KBr) spectrum of the compound reveals N—H absorptions at 2747 and 2548 cm⁻¹, while its ¹H NMR spectrum (DMSO-*d*₆ as solvent, TMS as internal standard) registers a downfield shift for the protons (δ = 9.46 p.p.m.) attached to the ring and the ammonio N atoms compared with 8-aminoquinolinium chloride (δ = 6.2 p.p.m.) (Bengtson *et al.*, 1996) and 8-aminoquinoline (δ = 5.0 p.p.m.) (Kook *et al.*, 1984). The crystals are very sensitive to moisture, converting to deep-orange 8-aminoquinolinium chloride (Bengtson *et al.*, 1996) within minutes of exposure to air. They were therefore sealed in glass tubes and stored in a desiccator. The crystal used for data collection was sealed in a glass capillary together with a drop of silicone oil.

Crystal data

C₉H₁₀N₂²⁺·2Cl⁻
M_r = 217.09

Mo Kα radiation
λ = 0.71073 Å

Triclinic

$P\bar{1}$
 $a = 8.0599(10) \text{ \AA}$
 $b = 8.4190(10) \text{ \AA}$
 $c = 8.4446(8) \text{ \AA}$
 $\alpha = 78.078(9)^\circ$
 $\beta = 78.886(11)^\circ$
 $\gamma = 61.473(7)^\circ$
 $V = 489.63(10) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.472 \text{ Mg m}^{-3}$
 D_m not measured

Cell parameters from 47 reflections
 $\theta = 4.96\text{--}13.60^\circ$
 $\mu = 0.615 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism
 $0.67 \times 0.30 \times 0.25 \text{ mm}$
 Pale yellow–white

The approximate positions of the chloride anions and the six atoms of the 'pyridyl' ring were obtained by the heavy-atom method, while successive Fourier syntheses yielded the positions of the remaining non-H atoms. The structure was refined by the full-matrix least-squares method to anisotropic convergence, after which the positions of the H atoms were found in a difference map calculated using low-angle data ($\theta \leq 20^\circ$). The H atoms were refined isotropically without any constraints. All computations were carried out on a Pentium PC using the Siemens *SHELXTL/PC* package (Sheldrick, 1994).

Data collection: *P4* (Siemens, 1995). Cell refinement: *P4*.
 Data reduction: *P4*.

Data collection

Siemens *P4* diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 4432 measured reflections
 2240 independent reflections
 1896 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 27.50^\circ$
 $h = -9 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -10 \rightarrow 10$
 3 standard reflections
 every 97 reflections
 intensity decay: 6%

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1080). Services for accessing these data are described at the back of the journal.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.084$
 $S = 1.051$
 2239 reflections
 158 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.0644P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.009$
 $\Delta\rho_{\text{max}} = 0.293 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.220 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

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Table 1. Selected geometric parameters (\AA , $^\circ$)

N1—C2	1.325(2)	C5—C6	1.358(2)
N1—C9	1.374(2)	C5—C10	1.415(2)
N2—C8	1.454(2)	C6—C7	1.409(2)
C2—C3	1.386(2)	C7—C8	1.367(2)
C3—C4	1.360(2)	C8—C9	1.412(2)
C4—C10	1.415(2)	C9—C10	1.413(2)
C2—N1—C9	122.63(13)	C7—C8—N2	120.16(13)
N1—C2—C3	121.08(14)	C9—C8—N2	120.09(12)
C4—C3—C2	119.15(14)	N1—C9—C8	122.32(12)
C3—C4—C10	120.67(14)	N1—C9—C10	118.11(13)
C6—C5—C10	120.31(14)	C8—C9—C10	119.57(12)
C5—C6—C7	120.56(14)	C9—C10—C4	118.35(13)
C8—C7—C6	120.74(14)	C9—C10—C5	119.07(13)
C7—C8—C9	119.74(13)	C4—C10—C5	122.58(14)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...C11	0.88(2)	2.16(2)	3.002(1)	158(2)
N2 ⁱ —H22 ⁱ ...C11	0.85(2)	2.26(2)	3.073(1)	159(2)
C2 ⁱⁱ —H2A ⁱⁱ ...C11	0.89(2)	2.89(2)	3.486(2)	126(1)
C4 ⁱⁱⁱ —H4A ⁱⁱⁱ ...C11	0.98(2)	2.78(2)	3.508(2)	131(2)
N2—H21...C12	0.91(2)	2.17(2)	3.057(2)	163(2)
N2 ^{iv} —H23 ^{iv} ...C12	0.86(2)	2.23(2)	3.090(1)	174(2)
C5 ^v —H5A ^v ...C12	0.95(2)	2.88(2)	3.640(2)	138(2)
C6 ^{vi} —H6A ^{vi} ...C12	0.92(2)	2.90(2)	3.628(2)	138(2)

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

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1-Difluoroboronyloxy-3-(*N*-methylimino)-1-phenyl-1-butene and its Two Photoproducts

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Abstract

The title compound, C₁₁H₁₂BF₂NO, was found to be converted by irradiation to the *anti* and *syn* head-to-tail dimers {1,3-bis(difluoroboronyloxy)-2,4-bis[1-(*N*-methylimino)ethyl]-1,3-diphenylcyclobutane, C₂₂H₂₄B₂F₄N₂O₂}. The enaminketone group of each complex takes a ring structure chelated through the BF₂ group.