Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Quinolizinium hexafluorophosphate

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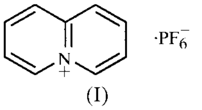
Received 14 June 2000
Accepted 30 October 2000

The crystal structure of the title compound, $C_9H_8N^+\cdot PF_6^-$, was measured at 145 K. The cationic part of the compound has crystallographically imposed 2/*m* symmetry with N/C disorder.

Comment

The quinolizinium ion, the newest of the benzenoid aromatic heterocyclic systems having only a single N atom (Bradsher, 1984), and its derivatives form a novel class of compounds whose properties have not yet been studied extensively (Arai & Hida, 1992). The first synthesis of the parent quinolizinium cation was reported by Boekelheide & Gall (1954) and the cation was assumed from its spectroscopic properties to have a planar structure resembling that of naphthalene (Boekelheide & Gall, 1954). A search of the Cambridge Structural Database (Version 5.20 of October 2000; Allen *et al.*, 1991) shows that there have been five papers on single-crystal X-ray structure determinations of the azonia derivatives of polycyclic aromatics: 2-chloro- and bromoanthracenes (Ihmels *et al.*, 1999), fluoranthene (Boubekeur *et al.*, 1989), 9-phenylanthracene (Maassarani & Pfeffer, 1990), 13-ethoxycarbonylbenzofluoranthene (Florencio *et al.*, 1984) and 2-pyridyldiazaphenanthrene (Elix *et al.*, 1971). No account of the structure of the parent quinolizinium cation has been found in the literature. We therefore decided to determine this structure using the title hexafluorophosphate salt of the cation, (I).



(I)

Data collection was undertaken at 145 K in order to minimize the thermal motion of the molecule. Analysis of a structure solution in space group *C*2 indicated a missing centre of symmetry. When refinement was attempted in the non-centrosymmetric space group, very high correlations were observed between the various parameters. For this reason, we considered a disordered structure in space group *C*2/*m* to be the correct solution. In this solution, the heterocyclic cation resides on a 2/*m* site (Wyckoff position *d*). The crystallographically imposed disorder causes the ring-shared carbon (C9a) and the ring-shared nitrogen (N5) to occupy a composite atomic site. The observed structure can be thought of as a statistical average between two orientations of the quinolizinium cation. The disorder observed in compound (I) seems to be a common feature in heterocycles which are isostructural with naphthalene. For example, disorder has also been found for quinoline (Kobayashi *et al.*, 1971) and isoquinoline (Hensen *et al.*, 1999).

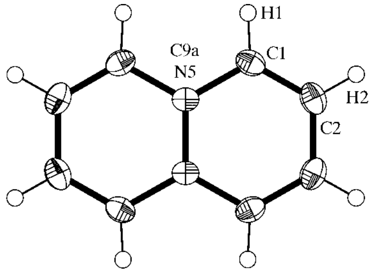


Figure 1
The molecular structure of the quinolizinium cation in (I) shown with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

An *ORTEP*III drawing (Johnson & Burnett, 1996) of the cationic part of (I), together with the atomic numbering scheme, is shown in Fig. 1. The quinolizinium ring is planar; the maximum deviation from the best plane through the non-H atoms is for atom C1, which deviates by only 0.010 (1) Å. Bond lengths and angles are listed in Table 1. The most important structural differences between this aromatic cation and naphthalene (Brock & Dunitz, 1982) are contractions of the N—C bond lengths in (I), by 0.04 Å for N5—C9a and by 0.03 Å for N5/C9a—C1.

Experimental

Quinolizinium bromide was prepared according to the method of Glover & Jones (1958) with the modifications of Miyadera & Iwai (1964). The hexafluorophosphate salt was obtained from an aqueous solution of the bromide by treatment with ammonium hexafluorophosphate. Clear colourless needles of quinolizinium hexafluorophosphate, (I) (m.p. 272.5–273 K), were obtained by slow evaporation from acetonitrile.

Crystal data

$C_9H_8N^+\cdot PF_6^-$
$M_r = 275.13$
Monoclinic, *C*2/*m*
$a = 8.505$ (3) Å
$b = 9.541$ (3) Å
$c = 6.827$ (2) Å
$\beta = 115.33$ (3)°
$V = 500.7$ (3) Å^3
$Z = 2$
$D_x = 1.825$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14$–15°
$\mu = 0.338$ mm^{-1}
$T = 145.2$ K
Needle-like, colourless
0.44 × 0.30 × 0.20 mm

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Table 1
Selected geometric parameters (Å, °).

N5/C9a—N5/C9a^{i}	1.378 (3)	C1—C2	1.352 (2)
N5/C9a—C1	1.396 (2)	C2—C2^{i}	1.408 (3)
N5/C9a^{i}—N5/C9a—C1	119.31 (8)	C2—C1—N5/C9a	121.0 (1)
C1—N5/C9a—C1^{ii}	121.4 (2)	C1—C2—C2^{i}	119.65 (9)

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

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
656 measured reflections
615 independent reflections
562 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\rm max} = 27.49°$

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -8 \rightarrow 8$
3 standard reflections
every 150 reflections
intensity decay: −0.62%

Refinement

Refinement on F^2
$R(F) = 0.025$
$wR(F^2) = 0.068$
$S = 1.086$
562 reflections
54 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.3901P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.020 (3)

All H atoms were refined isotropically. Atoms N5 and C9a were placed on the same site, each with an occupancy of 0.5, and refined with the same displacement parameters.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1998); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *TEXSAN*.

We are greatly indebted to M. Yamaguchi and M. Matsushita of Tokyo Metropolitan University for help with the preliminary measurements and computations.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1008). Services for accessing these data are described at the back of the journal.

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