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5-Dimethylamino-*N*,*N*-dimethyl-3-(4-pyridyl)-2,4-pentadieniminium tetrafluoroborate

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The crystal structure of the title salt, $C_{14}H_{20}N_3^+\cdot BF_4^-$, shows that the pentamethinecyanine moiety of the cation is essentially planar and adopts an all-*trans* conformation. The plane of the pyridyl substituent makes a dihedral angle of 60.58 (9)° with the pentamethinecyanine plane.

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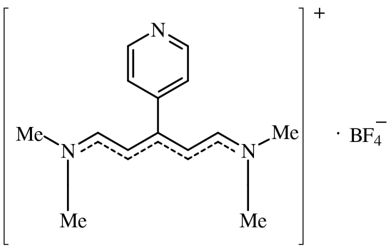
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.056
wR factor = 0.195
Data-to-parameter ratio = 16.2

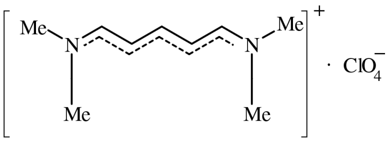
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

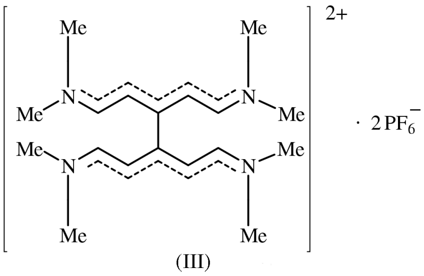
The title salt, (I), containing the relatively electron-poor 4-pyridyl substituent, was prepared in order to determine what effect (if any) the 4-pyridyl substitution at C3 would have on the conformation of the pentamethinecyanine moiety of the cation. The perchlorate salt analogue of (I) has been prepared (Hanke & Jutz, 1980), but a search of the Cambridge Structural Database (Allen & Kennard, 1993) showed that its structure had not been reported.



(I)



(II)



(III)

The crystal structure of (I) consists of discrete cations and tetrafluroborate anions, the latter being disordered over two sites. The pentamethinecyanine moiety of the cation (N1/C1–C5/N2) is essentially planar and adopts an all-*trans* confor-

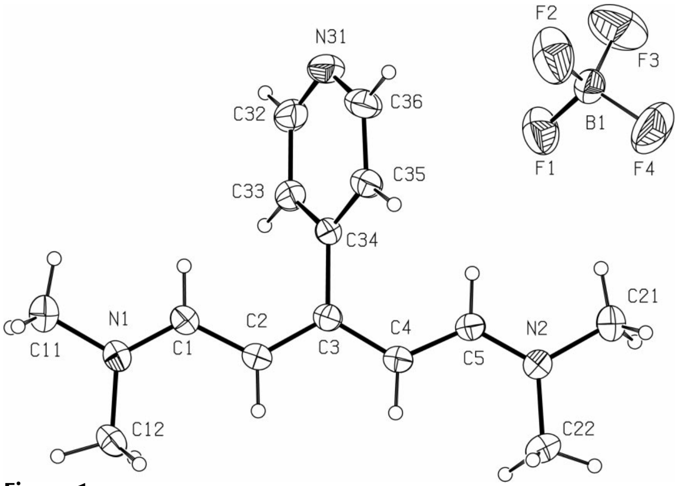


Figure 1

A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major component of the disordered tetrafluoroborate anion is shown

mation which makes a dihedral angle of 60.58 (9)° with the pyridine plane (Fig. 1). The planar terminal dimethylamino groups are rotated in opposite directions through 5.83 (12) and 6.69 (17)° out of the pentamethinecyanine plane. Bond lengths within the pentamethinecyanine fragment [C—C = 1.373 (3)–1.402 (3) Å; C—N = 1.311 (3) and 1.318 (3) Å] are similar to those reported in charge-density studies (Honda *et al.*, 1986) for the parent perchlorate salt (II), indicating minimal perturbation of the pentamethinecyanine moiety by the (4-pyridyl) substituent at C3. Bond lengths within the pyridine fragment are normal; the C3—C34 bond length [1.486 (3) Å] linking the cyanine and pyridine moieties is entirely consistent with its being a Csp^2—Csp^2 single bond. The cation dimensions and conformation are thus indicative of a lack of direct conjugative interaction between the two π systems. A coplanar arrangement of these two moieties would not be possible with the pentamethinecyanine fragment in the all-*trans* conformation because of severe steric interactions which would be present between the pyridine β-H atoms and the C1 and C5 H atoms of the cyanine moiety in the planar conformation. This situation is similar to that reported (Katoh *et al.*, 1997) for the bis(pentamethinecyanine) salt (III) in which two electron-poor pentamethinecyanine units each have an all-*trans* conformation and are linked through their central C atoms; the cation has a conformation in which the two pentamethinecyanine moieties are mutually at right angles.

The ^{1}H NMR chemical shifts found for (I) in DMSO-d_6 are similar to those reported (Hanke & Jutz, 1980) for the perchlorate analogue. However, in the present case, two closely spaced NMe signals were observed instead of one and coupling of the pyridine protons signals was resolved. In the case of the perchlorate salt, the latter signals were reported as broad multiplets. It is possible that the broadening was due to ion-pairing effects. Thus, when the spectrum of (I) was run in $CDCl_3$ [dilute solution due to low solubility of (I) in this solvent], two sets of pyridine signals were observed, while the remaining signals were unchanged. In the less polar solvent, tight ion pairing between the cations and tetrafluoroborate anions would be expected to occur. If the anion lies over one face of the pentamethinecyanine moiety, and migration of the anion between faces is slow on the NMR time scale, this would lead to discrimination between the two faces, and different environments for the α and β proton pairs of the pyridine moiety only.

Experimental

The salt (I) was prepared as described (Hanke & Jutz, 1980) for the perchlorate analogue, except that $NaBF_4$ was used instead of $NaClO_4$. Crystallization from ethanol gave (I) as orange spars, m.p. 469.0–472.5 K. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.10, 3.14 (each *s*, 6H, NMe), 6.07 (*d, J* = 12.2 Hz, 2H, C2—H + C4—H), 6.95 (*d, J* = 12.2 Hz, 2H, C1—H + C5—H), 7.28 (*d*, J_{obs} = 5.0 Hz, 2H, pyridine β-H) and 8.71 (*d*, J_{obs} = 5.0 Hz, 2H, pyridine α-H); (200 MHz, $CDCl_3$): δ = 3.19, 3.24 (each *s*, 6H, NMe), 6.28 (*d, J* = 12.2 Hz, 2H, C2—H + C4—H), 6.76 (*d, J* = 12.2 Hz, 2H, C1—H + C5—H), 7.26 (obscured by solvent peak, pyridine β-H), 7.34 (*d*, J_{obs} = 5.0 Hz, 1H, pyridine β-H), 8.71 (*d*, J_{obs} = 5.0 Hz, 1H, pyridine α-H) and 8.79 (*d*, J_{obs} = 5.0 Hz, 1H, pyridine α-H).

Crystal data

$C_{14}H_{20}N_3^+\cdot BF_4^-$
M_r = 317.14
Monoclinic, $P2_1/c$
a = 7.982 (2) Å
b = 10.492 (2) Å
c = 19.950 (3) Å
β = 106.578 (19)°
V = 1601.3 (6) Å^3
Z = 4

D_x = 1.315 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.1–11.2°
μ = 0.11 mm^{-1}
T = 293 (1) K
Needle, orange
0.38 × 0.34 × 0.20 mm

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3931 measured reflections
3482 independent reflections
2306 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.0°

$h = 0 \rightarrow 10$
$k = -13 \rightarrow 0$
$l = -25 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.195$
S = 1.04
3482 reflections
215 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0995P)^2 + 0.6393P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.311 (3)	C4—C5	1.373 (3)
N1—C11	1.450 (3)	N2—C5	1.318 (3)
N1—C12	1.460 (3)	N2—C21	1.457 (3)
C1—C2	1.390 (3)	N2—C22	1.456 (3)
C2—C3	1.390 (3)	N31—C32	1.333 (4)
C3—C4	1.402 (3)	N31—C36	1.328 (4)
C3—C34	1.486 (3)		
C11—N1—C1—C2	179.2 (2)	C2—C3—C4—C5	175.2 (2)
N1—C1—C2—C3	174.3 (2)	C3—C4—C5—N2	−178.2 (2)
C1—C2—C3—C4	177.1 (2)	C4—C5—N2—C21	−179.5 (2)

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H atoms were treated as riding atoms with C—H distances of 0.93 and 0.96 Å. All four methyl groups were allowed to rotate about their local threefold axis. The tetrafluoroborate ion is disordered by rotation about the B1—F1 bond over two sites with unequal occupancies [0.918 (5) and 0.082 (5)]. In the minor orientation, the three F atoms (F12, F13 and F14) were only allowed an overall isotropic vibration parameter; the geometry at B1 was restrained to be tetrahedral and an overall B—F distance was refined using a combination of *DFIX* and free-variable controls.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992); data reduction: *HELENA* in *PLATON* (Spek, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97.

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