| | | | |
|---|---|---|---|
| C5—N1—N2 | 106.0 (2) | N2′—N1′—C5′ | 106.8 (2) |
| C5—N1—S1 | 121.67 (19) | N2′—N1′—S1′ | 112.49 (19) |
| N2—N1—S1 | 112.2 (2) | C5′—N1′—S1′ | 122.5 (2) |
| C3—N2—N1 | 108.1 (3) | C3′—N2′—N1′ | 106.9 (3) |
| O1—C3—N2 | 121.5 (3) | N3′—C5′—C4′ | 132.1 (3) |
| O1—C3—C4 | 131.5 (3) | N3′—C5′—N1′ | 119.4 (3) |
| N2—C3—C4 | 107.0 (3) | C4′—C5′—N1′ | 108.6 (3) |
| C5—C4—C3 | 107.9 (3) | C5′—C4′—C3′ | 107.5 (3) |
| N3—C5—C4 | 130.9 (3) | O1′—C3′—N2′ | 120.3 (3) |
| N3—C5—N1 | 119.1 (3) | O1′—C3′—C4′ | 130.5 (3) |
| C4—C5—N1 | 110.0 (3) | N2′—C3′—C4′ | 109.2 (3) |
| C5—N1—N2—C3 | −9.6 (3) | C5′—N1′—N2′—C3′ | 9.2 (3) |
| N1—N2—C3—C4 | 10.5 (3) | N2′—N1′—C5′—C4′ | −3.9 (3) |
| N2—C3—C4—C5 | −7.5 (4) | N1′—C5′—C4′—C3′ | −2.9 (3) |
| C3—C4—C5—N1 | 1.4 (3) | N1′—N2′—C3′—C4′ | −11.1 (4) |
| N2—N1—C5—C4 | 5.0 (3) | C5′—C4′—C3′—N2′ | 8.8 (4) |
| N1—S1—C11—C12 | 109.5 (3) | N1′—S1′—C11′—C12′ | −73.0 (3) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O1′$^{i}$ | 0.87 (2) | 1.98 (2) | 2.852 (3) | 174 (4) |
| N3—H31···O1′$^{ii}$ | 0.86 (2) | 2.11 (2) | 2.897 (4) | 152 (3) |
| N2′—H2′···O1$^{iii}$ | 0.84 (2) | 2.02 (2) | 2.852 (3) | 171 (3) |
| N3′—H31′···O1$^{iv}$ | 0.87 (2) | 2.04 (2) | 2.900 (4) | 173 (3) |
| N3—H32···O2 | 0.84 (2) | 2.37 (3) | 2.908 (4) | 122 (2) |
| N3′—H32′···O2′ | 0.86 (2) | 2.31 (4) | 2.836 (4) | 119 (4) |

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

The true space group is $P2_1$, but automatic space-group determination suggested $P2_1/c$, in which the structure can indeed be solved and refined with a disordered phenyl group to $wR_2$ 20% and $R_1$ 8%. However, the correctness of the lower symmetry is indicated by (i) the better refinement, and (ii) the presence of several reflections $h0l$, $l$ odd, with significant intensity. The structure was refined as a racemic twin with components 0.55, 0.45 (9). A total of 1799 Friedel pairs were used. The origin was fixed by the method of Flack & Schwarzenbach (1988). H atoms bonded to N atoms were refined freely but with restrained N—H bond distances; other H atoms were refined using a riding model.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1382). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C**54**, 138–140

# 4-[2-(3,4-Dimethoxyphenyl)ethenyl]-1-methylpyridinium Tetrafluoroborate†

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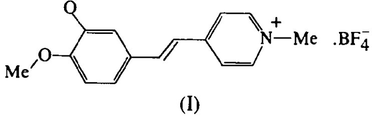
## Abstract

In the cation of the title compound, $C_{16}H_{18}NO_2^+.BF_4^-$, the pyridyl ring makes a dihedral angle of 12.4 (6)° with the phenyl ring. The cations are packed in an anti-parallel fashion along the $a$ axis through $p\pi$–$p\pi$ and dipole–dipole interactions, and form layers through C—H···O hydrogen bonds. The anions are located between the layers.

## Comment

During our systematic study of organic salts with non-linear optical properties (Marder, Perry & Tiemann, 1990; Zhang *et al.*, 1997), we isolated the title compound, (I).



(I)

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† Alternative name: *N*-methyl-3′,4′-dimethoxy-4-stilbazolium tetrafluoroborate.

In the crystal structure, every cation consists of one phenyl ring [the maximum deviation of phenyl-ring non-H atoms from their mean plane is 0.008 (2) Å] and one pyridyl ring [corresponding maximum deviation 0.008 (2) Å], which are nearly planar and make a dihedral angle of 12.4 (6)°.

Significant overlap between cations related by a centre of symmetry or *b* glide was found. The shortest distances between the mean planes (Nardelli, 1983) and between the centres of the phenyl rings (related by $1-x$, $-y$, $1-z$) are 3.45 (2) and 3.90 (2) Å, respectively. Short contacts (<3.6 Å) between parallel cations are listed in Table 2, showing the existence of strong $p\pi$–$p\pi$ interactions. Neighbouring cations, related by the translation vector **b** or by a *c* glide, are connected by hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Krishnamohan Sharma & Desiraju, 1994) (Table 3). The $BF_4^-$ anions are located between the cationic layers, being hydrogen bonded (Table 3) and adjacent to pyridyl rings (Table 2).

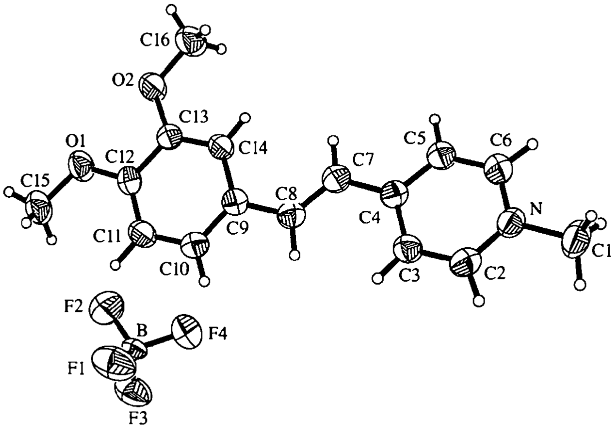

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

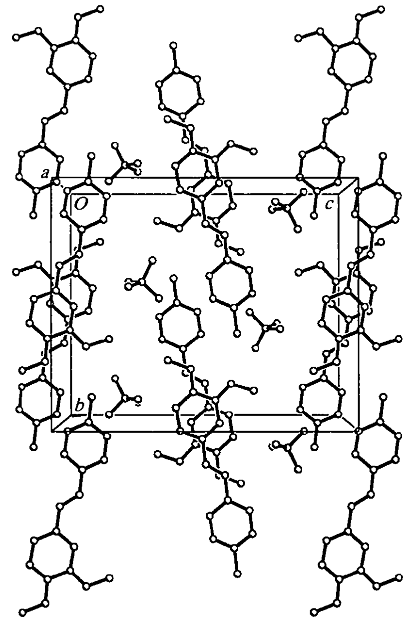

Fig. 2. Packing diagram viewed down the *a* axis.

## Experimental

1,4-Dimethylpyridinium iodide (7.05 g, 30 mmol, prepared from $CH_3I$ and $\gamma$-methylpyridine) and 3,4-dimethoxybenzaldehyde (8.14 g, 49 mmol) in 10 ml of methanol were heated at 353 K for 8 h (Okada *et al.*, 1990). The product was recrystallized twice from ethanol–water (2:1), dissolved in water (0.74 g in 100 ml) and treated with a saturated solution of sodium tetrafluoroborate. The title compound was separated, recrystallized twice from ethanol–water (4:1) and finally crystallized from *N*,*N*-dimethylformamide (m.p. 467–468 K). IR: 3400, 1643, 1615, 1600, 1520, 1460, 1338, 1305, 1050, 880, 828, 765 cm$^{-1}$. Elemental analysis: found C 55.89, H 4.52, N 4.32%; $C_{16}H_{18}BF_4NO_2$ requires C 56.22, H 4.72, N 4.68%.

*Crystal data*

$C_{16}H_{18}NO_2^+.BF_4^-$
$M_r = 343.12$
Orthorhombic
*Pbca*
$a = 13.5174\,(14)$ Å
$b = 13.9190\,(13)$ Å
$c = 17.0708\,(15)$ Å
$V = 3211.8\,(5)$ Å$^3$
$Z = 8$
$D_x = 1.419$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 4.62$–$17.86°$
$\mu = 0.123$ mm$^{-1}$
$T = 295\,(2)$ K
Plate
0.70 × 0.70 × 0.32 mm
Brown–yellow

*Data collection*

Siemens *P*4 diffractometer
$\omega$ scans
Absorption correction:
  $\psi$ scan (*SHELXL*93; Sheldrick, 1993)
  $T_{min} = 0.915$, $T_{max} = 0.981$
3569 measured reflections
2821 independent reflections
1688 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.011$
$\theta_{max} = 25°$
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 20$
3 standard reflections
  every 97 reflections
  intensity decay: 1.38%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 0.891$
2821 reflections
290 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.023$

$\Delta\rho_{max} = 0.181$ e Å$^{-3}$
$\Delta\rho_{min} = -0.142$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0026 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| F1—B | 1.360 (2) | O2—C16 | 1.429 (2) |
| F2—B | 1.368 (2) | N—C6 | 1.343 (2) |
| F3—B | 1.373 (2) | N—C2 | 1.347 (2) |
| F4—B | 1.387 (2) | N—C1 | 1.480 (3) |
| O1—C12 | 1.365 (2) | C4—C7 | 1.447 (3) |
| O1—C15 | 1.430 (3) | C7—C8 | 1.331 (3) |
| O2—C13 | 1.362 (2) | C8—C9 | 1.452 (3) |
| C12—O1—C15 | 116.3 (2) | F1—B—F4 | 110.1 (2) |
| C13—O2—C16 | 117.3 (2) | F2—B—F4 | 108.07 (15) |
| C6—N—C2 | 119.4 (2) | F3—B—F4 | 108.7 (2) |
| C6—N—C1 | 120.6 (2) | C3—C2—N | 121.9 (2) |
| C2—N—C1 | 120.0 (2) | C8—C7—C4 | 125.1 (2) |
| F1—B—F2 | 110.2 (2) | C7—C8—C9 | 127.3 (2) |
| F1—B—F3 | 109.80 (15) | C14—C9—C8 | 122.5 (2) |
| F2—B—F3 | 109.9 (2) | | |
| C5—C4—C7—C8 | 170.5 (2) | C15—O1—C12—C13 | −174.4 (2) |
| C4—C7—C8—C9 | −179.3 (2) | C16—O2—C13—C14 | 0.7 (3) |
| C7—C8—C9—C14 | −3.8 (3) | C16—O2—C13—C12 | 180.0 (2) |
| C15—O1—C12—C11 | 6.4 (3) | | |

Table 2. *Contact distances (Å)*

| | | | |
|---|---|---|---|
| N···F4$^{i}$ | 3.214 (5) | C9···C13$^{iii}$ | 3.479 (5) |
| C6···F4$^{i}$ | 3.220 (5) | C9···C2$^{iv}$ | 3.524 (5) |
| C3···F4$^{ii}$ | 3.265 (6) | C12···C3$^{iv}$ | 3.442 (6) |
| C7···O1$^{iii}$ | 3.447 (5) | C14···C2$^{iv}$ | 3.524 (6) |
| C8···O2$^{iii}$ | 3.513 (5) | | |

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|
| C1—H1*A*···F1$^{i}$ | 2.47 (3) | 3.318 (5) | 148 (3) |
| C6—H6···F1$^{i}$ | 2.74 (2) | 3.281 (4) | 116 (2) |
| C3—H3···F2$^{ii}$ | 2.52 (2) | 3.449 (7) | 174 (2) |
| C7—H7···F3$^{iii}$ | 2.57 (2) | 3.462 (5) | 156 (2) |
| C2—H2···F4$^{ii}$ | 2.62 (2) | 3.203 (7) | 120 (1) |
| C3—H3···F4$^{ii}$ | 2.65 (2) | 3.265 (6) | 124 (1) |
| C1—H1*B*···F3$^{iv}$ | 2.77 (3) | 3.392 (6) | 126 (2) |
| C1—H1*C*···O1$^{v}$ | 2.53 (4) | 3.429 (6) | 151 (3) |
| C1—H1*C*···O2$^{v}$ | 2.66 (4) | 3.002 (5) | 101 (2) |

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXL*93 (Sheldrick, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1254). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C**54**, 140–142

# 4,9-Dihydroxy-4,9-dimethyl-4*H*,9*H*-1,2,5,6,6a,7,8-heptahydroimidazo[1,2,3-*i*,*j*]-[1,8]naphthyridinium Benzoate

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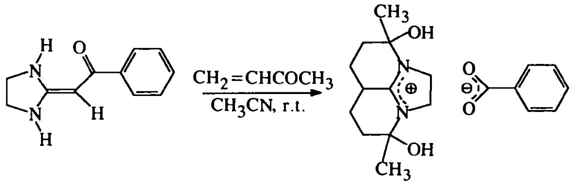
## Abstract

The crystal structure of the title compound, $C_{12}H_{21}N_2O_2^+.C_7H_5O_2^-$, consists of an imidazo[1,2,3-*i*,*j*][1,8]naphthyridinium cation and a benzoate anion, which are held together by two strong O—H···O hydrogen bonds, with O···O non-bonded contact distances of 2.642 (2) and 2.681 (2) Å. In the tricyclic cation, the imidazoline ring is almost planar, while the two six-membered rings are twisted and adopt deformed half-chair conformations. The benzoate anion is not perfectly planar, with the negative charge delocalized over the carboxylate group.

## Comment

Heterocyclic ketene aminals or cyclic 1,1-enediamines are versatile synthons for the synthesis of various heterocyclic or fused-heterocyclic compounds (Huang & Wang, 1994*a*,*b*). The reaction of benzoyl heterocyclic ketene aminal 2-benzoylmethyleneimidazolidine, (I), with methyl vinyl ketone unexpectedly afforded the title tricyclic molecule, (II). It is interesting that the ben-



(I) (II)