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(2,2′-Bipyridyl-*N*,*N*′)(bicyclo[3.3.1]nonane-C^1,C^5)-boronium trifluoromethanesulfonate

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The cations and anions in the title compound, $C_{18}H_{22}BN_2^+\cdot CF_3SO_3^-$, are connected by intermolecular C—H···O hydrogen bonds, with H···O distances between 2.34 and 2.60 Å, into layers parallel to the *bc* plane.

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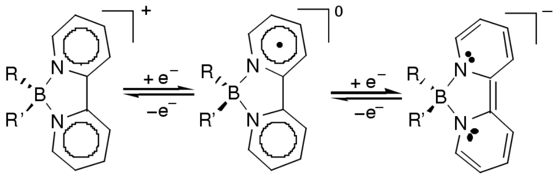
Key indicators

Single-crystal X-ray study
T = 146 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.097
Data-to-parameter ratio = 26.5

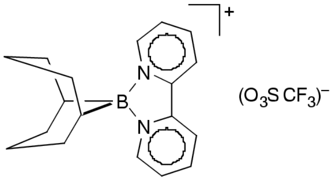
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

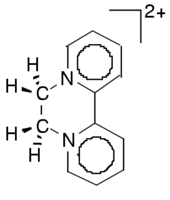
2,2′-Bipyridylboronium ions, [I]$^+$, are structurally related to the electron-acceptor diquat, which possesses an ethylene bridge instead of the B*RR*′ unit and behaves as a perfectly reversible two-step redox system (see scheme). [I]$^+$ exhibits a similar electrochemical behavior to diquat. The degree of reversibility of the two reduction processes, however, depends on the solvent employed, as well as on the nature of the substituents *R* and *R*′ (Hünig & Wehner, 1989). Currently, we are exploring the potential of 2,2′-bipyridylboronium cations as acceptor units in electron transfer salts and as redox catalysts (Fabrizi de Biani *et al.*, 1997; Ding, Ma, Fabrizi de Biani *et al.*, 2001; Ding, Ma, Bolte *et al.*, 2001). In contrast to diquat, [I]$^+$ is convenient to derivatize and can easily be incorporated into a wide variety of molecular aggregates. To generate electrochemically stable acceptor molecules possessing high solubility in organic solvents, we are currently investigating 2,2′-bipyridylboronium salts with bulky organic substituents at the boron center. In this context, the title derivative, [II], appeared to be particularly well suited. The corresponding hexafluorophosphate salt has already been shown to possess the desired electrochemical properties (Hünig & Wehner, 1989). Structural information about this molecule, however, is lacking. We report here the results of an X-ray crystal structure analysis of the trifluoromethanesulfonate salt, [II] (Fig. 1).



[I]$^+$ [I]^0 [I]$^-$



[II]



Diquat

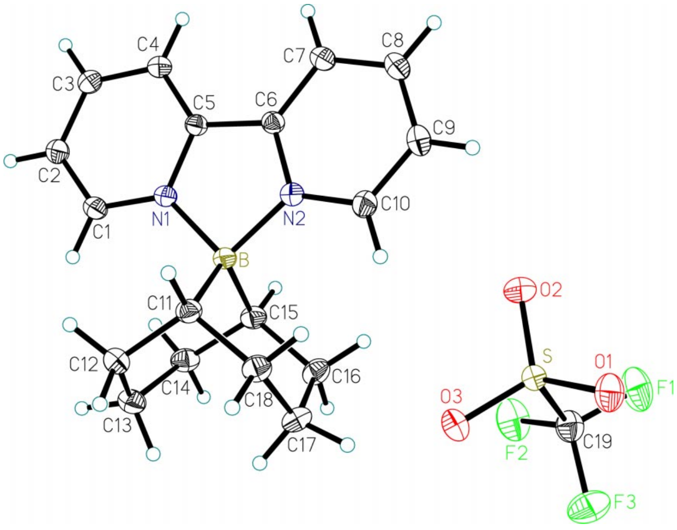


Figure 1
The structure of [II] with 50% probability displacement ellipsoids.

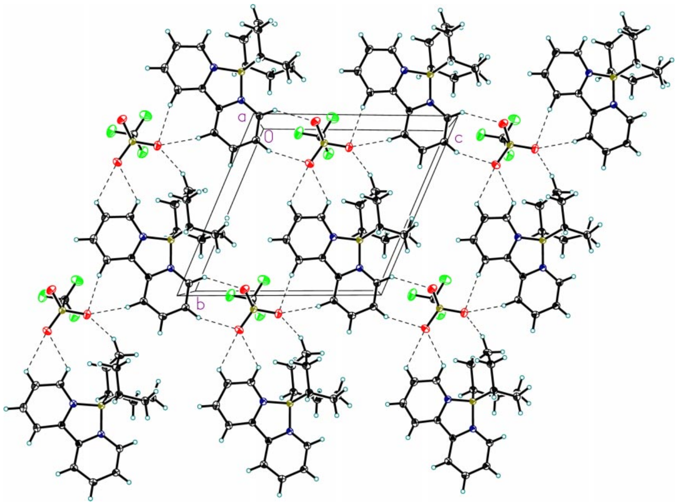


Figure 2
A layer of [II] with $0 < x < 0.5$ viewed down *a*. Intermolecular C—H···O interactions are shown as dotted lines.

The dimensions of the 9-borabicyclo[3.3.1]nonane group are comparable to those found in related structures (Brock *et al.*, 1992; Fraenk *et al.*, 1999; Yalpani *et al.*, 1990; Wrackmeyer *et al.*, 1995). The B—C bond lengths are 1.6150 (16) and 1.6188 (16) Å. The B—N bond lengths are 1.6125 (14) and 1.6136 (14) Å. The angle between the two pyridyl planes is 2.88 (5)°. The bipyridyl group is slightly tilted with respect to the 9-borabicyclo[3.3.1]nonane group; the angle between the plane through N1/C5/C6/N2 and the plane bisecting C11—B—C15 is 8.5 (1)°. This tilting may result from crystal-packing effects. The B atom lies 0.114 (2) Å outside the plane through N1/C5/C6/N2. The molecule shows three short intramolecular H···H contacts: H1···H12*A* 2.02 Å, H10···H18*A* 2.03 Å and H13A···H17*A* 2.04 Å. The crystal packing shows seven intermolecular C—H···O contacts with H···O distances between 2.34 and 2.60 Å. Each cation is connected by these C—H···O contacts to three neighbouring anions and, in a similar way, each anion is connected to three neighbouring cations, resulting in hydrogen-bonded layers of cations and anions parallel to the *bc* plane (Fig. 2). These layers are connected in the *a* direction by two very long intermolecular C—H···F contacts with H···F distances of 2.73 and 2.80 Å. These contacts are very weak. As a result, the crystals can easily be split along [100].

Experimental

A toluene solution of 2,2′-bipyridine (3.90 g, 25.0 mmol) was added dropwise with stirring at 195 K to a solution of 9-boroniumbicyclo[3.3.1]nonane trifluoromethanesulfonate (6.74 g, 25.0 mmol) in 50 ml of hexane. The white precipitate gradually formed upon warming to ambient temperature and the resulting slurry was stirred for another 2 h. The white solid material was collected on a frit, extracted three times with toluene (10 ml) and dried *in vacuo*. The yield was 9.69 g (91%) of [II], melting point 503 K. Colourless crystals suitable for the X-ray measurements were obtained by slow evaporation of a solution in acetonitrile at ambient temperature.

Crystal data

$C_{18}H_{22}BN_2^{+}\cdot CF_3O_3S^{-}$
$M_r = 426.26$
Triclinic, $P\overline{1}$
$a = 9.2198$ (19) Å
$b = 10.3158$ (14) Å
$c = 10.7956$ (11) Å
$\alpha = 112.511$ (9)°
$\beta = 96.598$ (10)°
$\gamma = 93.007$ (10)°
$V = 937.0$ (3) Å^3
$Z = 2$
$D_x = 1.511$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 211 reflections
$\theta = 3$–23°
$\mu = 0.23$ mm^{-1}
$T = 146$ (2) K
Rod, colorless
0.50 × 0.28 × 0.27 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1996)
$T_{min} = 0.907$, $T_{max} = 0.946$
21 094 measured reflections
6966 independent reflections
5659 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 34.0°$
$h = -13 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$
277 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 1.09$
6966 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.30P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0050 (16)

The H atoms were refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$] using a riding model with fixed distances: H—C(primary) = 1.00 Å, H—C(secondary) = 0.99 Å and H—C(aromatic) = 0.95 Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL*97.

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