# 3,6-Dimethyl-4,5-dihydro-3a,5a-diazapyrene ditriflate

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The crystal structure of the title compound, $C_{16}H_{16}N_2{}^{2+} \cdot 2CF_3O_3S^-$, is the first structure to be reported for a diquaternized derivative of 2,9-dimethyl-1,10-phenanthroline.

Comment

The compound 6,7-dihydrodipyrido[1,2-a:2′,1′-c]pyrazine-]pyrazinediiium dibromide (diquat dibromide) is a potent herbicide (Brian *et al.*, 1958), and related salts derived from 2,2′-bipyridyl and other α-diimines have also generated considerable interest (Summers, 1981). In recent years, the attractive redox properties of diquats have led to other uses as electron acceptors in light-harvesting chromophore-quencher systems (Ryu *et al.*, 1992; Klumpp *et al.*, 1999; Kim *et al.*, 2003, 2005) and in ion-pair charge-transfer complexes (Nunn *et al.*, 1994; Hofbauer *et al.*, 1996; Unamuno *et al.*, 1998; Vitoria *et al.*, 2002). Our studies directed at using diquats in novel metal-based chromophore-quencher arrays have afforded an unusually facile method for the synthesis of such compounds, including salts (I) and (II) (Coe, Curati & Fitzgerald, 2006). The structure of salt (II), 1,2,7,8-tetramethyl-4,5-dihydro-3a,5a-diazapyrene ditriflate, is presented in the following paper (Coe, Fitzgerald & Raftery, 2006).

(I)

(II)
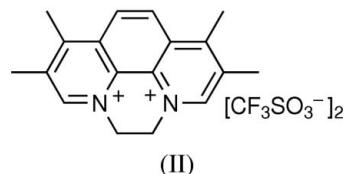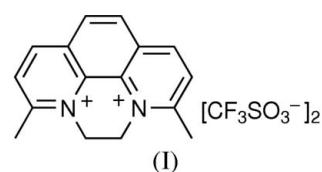
The molecular structures of the salts (I) (Fig. 1) and (II) are as indicated by ^{1}H NMR spectroscopy and, to our knowledge, the first to be reported containing these particular methyl-substituted cations. The geometrical parameters of the diquat units are as expected (Table 1), and largely identical for the two compounds. The C atoms of the ethylene bridge have normal tetrahedral geometries, with N1—C13—C14—N2 torsion angles of -58.2 (3)° for (I) and -58.83 (19)° for (II). Comparisons with previously published structures for other diquat compounds derived from 1,10-phenanthroline reveal generally similar bond lengths and angles, although the ethylene torsion angles are somewhat smaller at *ca* 53–55° (Hofbauer *et al.*, 1996; Unamuno *et al.*, 1998; Vitoria *et al.*,
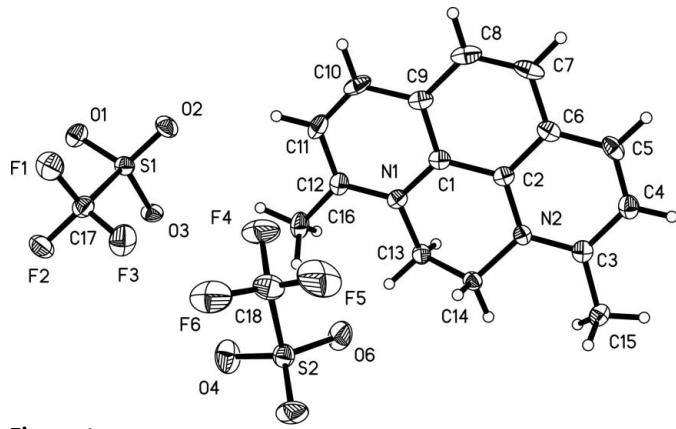
Figure 1
The asymmetric unit of salt (I), showing 50% probability displacement ellipsoids.

2002). In both compounds, the presence of the ethylene bridge imparts a small twist to the 3a,5a-diazapyrene unit, with dihedral angles between the two aromatic outer rings of 8.85 (7)° for (I) and 11.26 (5)° for (II). The crystal packing structures of both (I) and (II) reveal extensive C—H···O interactions between the diquat cations and the trifluoromethanesulfonate counter-anions.

Experimental

Salts (I) and (II) were synthesized as reported previously (Coe, Curati & Fitzgerald, 2006). Crystals suitable for single-crystal X-ray diffraction measurements were obtained by slow diffusion of diethyl ether vapour into acetone solutions at 295 K.

Crystal data

$C_{16}H_{16}N_2^{2+}\cdot 2CF_3O_3S^-$	$Z = 4$
$M_r = 534.45$	$D_x = 1.713$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.976$ (1) Å	$\mu = 0.35$ mm^{-1}
$b = 12.653$ (1) Å	$T = 100$ (2) K
$c = 16.559$ (2) Å	Block, white
$\beta = 97.426$ (2)°	$0.10 \times 0.10 \times 0.05$ mm
$V = 2072.7$ (3) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4947 independent reflections
φ and ω scans	2354 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.083$
17755 measured reflections	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.72$	$(\Delta/\sigma)_{max} < 0.001$
4947 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
309 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.379 (3)	C5—C6	1.402 (3)
C1—C9	1.397 (3)	C6—C7	1.416 (3)
C1—C2	1.427 (3)	C7—C8	1.348 (3)
C3—N2	1.344 (3)	C10—C11	1.352 (3)
C3—C4	1.397 (3)	C11—C12	1.403 (3)
C3—C15	1.486 (3)	C13—N1	1.481 (3)
C4—C5	1.360 (3)	C13—C14	1.498 (3)
N1—C1—C2	121.3 (2)	N2—C14—C13	110.2 (2)
N2—C2—C1	120.8 (2)	C1—N1—C13	116.6 (2)
N1—C13—C14	109.9 (2)	C2—N2—C14	115.4 (2)
N1—C13—C14—N2	−58.2 (3)		

All H atoms were included in calculated positions, with C—H = 0.95 (CH), 0.99 (CH$_2$) and 0.98 Å (CH$_3$). U_{iso}(H) values were fixed at $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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