

ω -2 θ scans $h = -1 \rightarrow 16$
 Absorption correction: none $k = -4 \rightarrow 6$
 3731 measured reflections $l = -32 \rightarrow 31$
 3533 independent reflections 3 standard reflections
 1403 reflections with frequency: 120 min
 $I > 2\sigma(I)$ intensity decay: <5%

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.047$ $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.143$ $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
 $S = 0.971$ Extinction correction: none
 3533 reflections Scattering factors from
 289 parameters *International Tables for*
 H atoms constrained *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

For (1), the direction of the polar axis could not be determined reliably as the heaviest atom in the structure was oxygen. For structure (3), the presence of a pseudo-*b*-glide plane (perpendicular to **a**) was noted, but no alternative cell could be identified.

For all compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *SET4* in *CAD-4 Software*; data reduction: *Xtal3.2* (Hall *et al.*, 1992); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1264). Services for accessing these data are described at the back of the journal.

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4,4'-Bipyridinium diperchlorate

SEIK WENG NG

Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: hInswen@umcsd.um.edu.my

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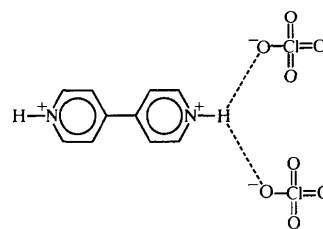
Abstract

In 4,4'-bipyridinium diperchlorate, $\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{ClO}_4^-$, the centrosymmetric dication and the anions are linked by three $\text{N} \cdots \text{O}$ hydrogen bonds [$\text{N} \cdots \text{O} = 2.893(3)$, $2.915(3)$ and $2.972(3)$ Å] into a two-dimensional network.

Comment

The two pyridyl moieties of the 4,4'-bipyridinium dication are coplanar in the diiodide (Iyere *et al.*, 1998) and in the monoclinic modification of the dinitrate (Weakley, 1987), but are twisted by 39° in the orthorhombic modification of the dinitrate (Barker *et al.*, 1990). For the dinitrate, the cation lies on a centre-of-inversion in the orthorhombic modification and on a twofold axis in the monoclinic modifications; both modifications display only one $\text{N} \cdots \text{O}$ hydrogen bond [2.77(1) Å (Weakley, 1987); 2.674 Å (Barker *et al.*, 1990)]. However, $\text{C}-\text{H} \cdots \text{X}$ interactions [3.163(6)–3.239(4) Å] are present in the two modifications as well as in the centrosymmetric diiodide [$\text{C}-\text{H} \cdots \text{I} = 3.740(5)$ – $3.818(5)$ Å] (Iyere *et al.*, 1998).

The two rings in the diperchlorate, (I) (Fig. 1), are also exactly coplanar, a feature that is predicted



(I)

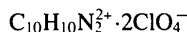
from its Raman spectrum (Barker *et al.*, 1990). The pyridinium-N atom forms hydrogen bonds to the O atoms of three anions [$N \cdots O = 2.893(3), 2.915(3), 2.972(3) \text{ \AA}$], so forming a continuous two-dimensional network (Fig. 2). Weak $C-H \cdots O$ interactions are also present (Table 2) whose angular characteristics compare reasonably well with values that are accepted as weak $C-H \cdots O$ interactions. Such interactions are better regarded as electrostatic interactions rather than as van der Waals interactions (Iyere *et al.*, 1990). Unfortunately, direct comparisons cannot be made with the pyridinium perchlorate homologue, which packed as sheets, as both the cation and the anion are disordered (Czarniecki *et al.*, 1997).

al., 1991). Some of these salts have been examined as their perchlorates (Polishchuk *et al.*, 1996; Sakai *et al.*, 1997). The colourless unsubstituted 4,4'-bipyridinium salts have been less studied, and the dinitrate, diiodide and diperchlorate represent the only structural examples of the simple salts. The unsubstituted dication has been clathrated in a $11.13 \times 11.16 \text{ \AA}$ [$Cu_4(4,4'-C_{10}H_{10}N_2)_4$] grid (Tong *et al.*, 1998) and also in the crown ether, bis-*p*-phenylene-34-crown-10 (Ashton *et al.*, 1991).

Experimental

4,4'-Bipyridinium diperchlorate can be synthesized by adding perchloric acid to 4,4'-bipyridine dissolved in ethanol (Barker *et al.*, 1990). The specimen for the study was obtained as a side-product in the synthesis of a cadmium diperchlorate-4,4'-bipyridine complex (Tong *et al.*, 1998).

Crystal data



$M_r = 357.10$

Monoclinic

$P2_1/n$

$a = 5.0210(2) \text{ \AA}$

$b = 11.3959(6) \text{ \AA}$

$c = 11.9972(6) \text{ \AA}$

$\beta = 97.323(5)^\circ$

$V = 680.87(6) \text{ \AA}^3$

$Z = 2$

$D_x = 1.742 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 12-13^\circ$

$\mu = 0.522 \text{ mm}^{-1}$

$T = 298(2) \text{ K}$

Irregular block

$0.44 \times 0.36 \times 0.32 \text{ mm}$

Colourless

Data collection

Enraf-Nonius CAD-4

diffractometer

ω scans

Absorption correction:

ψ scan (North *et al.*,

1968) in *WinGX* (Farrugia,

1998)

$T_{\min} = 0.860, T_{\max} = 0.886$

3386 measured reflections

1973 independent reflections

1565 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 29.96^\circ$

$h = -7 \rightarrow 7$

$k = 0 \rightarrow 16$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 60 min

intensity decay: 3%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.136$

$S = 1.055$

1973 reflections

120 parameters

H atoms were refined

$w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 0.0206P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.91 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

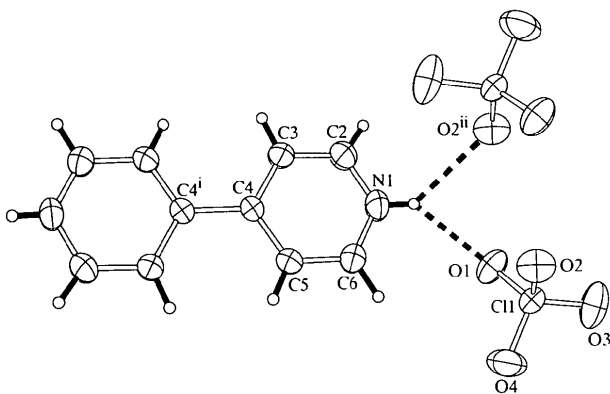


Fig. 1. ORTEP (Johnson, 1976) plot of (I) with the ellipsoids at the 50% probability level. H atoms are drawn as spheres of an arbitrary radius. Hydrogen bonds: $N1 \cdots O1$ 2.893(3), $N1 \cdots O2^{ii}$ 2.972(3) \AA ; symmetry transformations: (i) $-x - 1, 2 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.

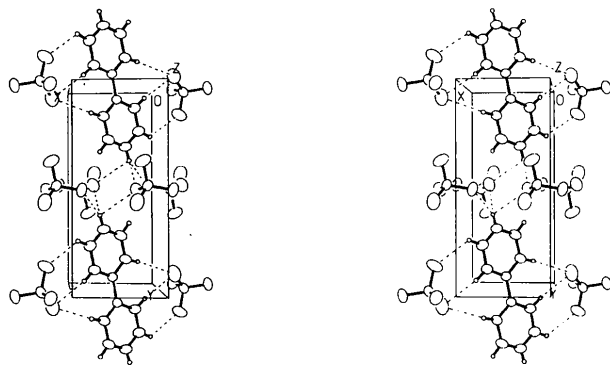


Fig. 2. Stereoview of the packing in (I). Dashed lines indicate the $NH \cdots O$ hydrogen bonds and the weak $C-H \cdots O$ interactions.

Diquarternary 4,4'-bipyridinium salts command interest owing to their interesting charge-transfer properties and their ability to undergo reversible one-electron reduction to form coloured radical cations (Wang *et al.*

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

$Cl1-O1$	1.439(2)	$Cl1-O4$	1.427(2)
$Cl1-O2$	1.429(2)	$N1-C2$	1.333(3)
$Cl1-O3$	1.423(2)		

O1—C11—O2	109.6 (1)	O2—C11—O4	109.4 (1)
O1—C11—O3	109.9 (1)	O3—C11—O4	109.7 (1)
O1—C11—O4	109.2 (1)	C6—N1—C2	122.5 (2)
O2—C11—O3	109.1 (1)		

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1	0.81 (5)	2.22 (4)	2.893 (3)	140 (3)
N1—H1...O2 ⁱ	0.81 (5)	2.54 (4)	2.915 (3)	110 (3)
N1—H1...O2 ⁱⁱ	0.81 (5)	2.36 (4)	2.972 (3)	132 (3)
C3—H3...O4 ⁱⁱⁱ	0.94 (3)	2.57 (3)	3.483 (3)	165 (2)
C5—H5...O4 ^{iv}	0.91 (4)	2.44 (4)	3.343 (3)	172 (3)
C6—H6...O3 ^v	0.97 (3)	2.52 (3)	3.227 (3)	130 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, 1-z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{3}{2}$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Data collection: CAD-4/PC (Kretschmar, 1994). Cell refinement: CELDIM (Enraf–Nonius, 1988). Data reduction: XCAD4 (Harms, 1997). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1048). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2107–2109

3,3,6,6-Tetramethyl-1-trimethylsilyl-3,6-diaza-1,4,5-tricarbaheptaborane(10)†

CHONG ZHENG AND NARAYAN S. HOSMANE

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA. E-mail: zheng@cz2.chem.niu.edu

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Abstract

The title compound, C₁₀H₃₀B₂N₂Si, was synthesized in 98% yield. It has a zwitterionic heterocyclic carborane ring in which an *N,N,N',N'*-tetramethylethylenediamine (TMEDA) unit is coordinated *via* two donor N atoms to two BH₂ units that are separated by a CH(SiMe₃) moiety to form a novel seven-membered ring. The bond distances (Å) within the ring are B—C 1.613 (3) and 1.618 (3), B—N 1.652 (3) and 1.659 (3), C—N 1.483 (3) and 1.505 (3), and C—C 1.510 (3).

Comment

The dominant structural patterns found in alkyl and aromatic hydrocarbons are reflections of the structures of elemental carbon (diamond or graphite), where an added H atom at the end of C—C bonds gives 'electron-precise carbon hydrides' (Williams, 1998). In a similar way, the structures of boron hydrides are reflections of the icosahedral units found in elemental boron and the replacement of a BH unit by a CH or CR unit gives the corresponding 'electron-deficient' carborane derivatives (Lipscomb, 1963; Muetterties & Knoth, 1968; Parry, 1998). Although our recent communication (Hosmane *et al.*, 1996) reported the first example of a polyhedral cluster that consisted of both electron-precise atoms and an electron-deficient carborane unit in a single cage framework, there has been no report on the conversion of an electron-deficient carborane cage essentially into an electron-precise heterocyclic ring. As part of an exploration of new methodologies in this area, the title compound, 3,6-dimethyl-1-trimethylsilyl-3,6-diaza-1,4,5-tricarbaheptaborane(10), (2), was synthesized. We report here the results of this investigation where

† Alternative name: 1,1,5,5-tetramethyl-3-trimethylsilyl-1,5-diazonia-2,4-diboroniacycloheptane.