

## organic compounds

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## 4,4'-Dimethyl-2,2'-bipyridinium dichloride

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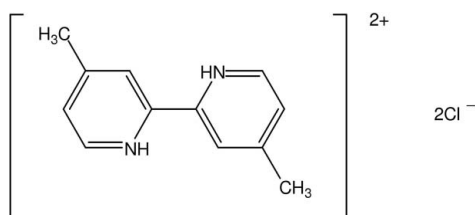
Received 10 July 2008; accepted 18 August 2008

Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.080; data-to-parameter ratio = 14.7.

In the title compound,  $\text{C}_{12}\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{Cl}^-$ , the 4,4'-dimethyl-2,2'-bipyridinium cation is essentially planar (r.m.s. deviation for all non-H atoms = 0.004 Å) and is located on a crystallographic inversion centre. The cations and chloride anions lie in planes parallel to (111) and are connected by  $\text{N}-\text{H} \cdots \text{Cl}$  and  $\text{C}-\text{H} \cdots \text{Cl}$  hydrogen bonds.

## Related literature

For related literature, see: Eckensberger (2006); Scheibitz *et al.* (2005). For structures containing the 4,4'-dimethyl-2,2'-bipyridinium cation, see: Linden *et al.* (1999); Willett *et al.* (2001).



## Experimental

## Crystal data

 $\text{C}_{12}\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{Cl}^-$   
 $M_r = 257.15$ 

 Triclinic,  $P\bar{1}$   
 $a = 5.1999$  (10) Å

 $b = 7.2705$  (13) Å  
 $c = 8.4785$  (15) Å  
 $\alpha = 93.877$  (15)°  
 $\beta = 102.349$  (15)°  
 $\gamma = 97.759$  (15)°  
 $V = 308.71$  (10) Å<sup>3</sup>
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.50$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 $0.21 \times 0.21 \times 0.14$  mm

## Data collection

 Stoe IPDSII two-circle diffractometer  
 Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)  
 $T_{\min} = 0.902$ ,  $T_{\max} = 0.933$ 

 3382 measured reflections  
 1147 independent reflections  
 926 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.058$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.079$   
 $S = 0.97$   
 1147 reflections  
 78 parameters

 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{Cl1}$	0.86 (3)	2.17 (3)	3.009 (2)	165 (3)
$\text{C2}-\text{H2} \cdots \text{Cl1}^{\text{i}}$	0.95	2.75	3.496 (2)	136
$\text{C5}-\text{H5} \cdots \text{Cl1}^{\text{ii}}$	0.95	2.62	3.554 (2)	169

Symmetry codes: (i)  $-x + 2, -y, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: B12297).

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**supplementary materials**

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## 4,4'-Dimethyl-2,2'-bipyridinium dichloride

U. D. Eckensberger, H.-W. Lerner and M. Bolte

### Comment

Recently, we have synthesized the dimeric diferrocenylboryl cation **I** (see Scheme) (Scheibitz *et al.*, 2005). Now we are interested to prepare the cationic dinuclear complex with a pentamethylcyclopentadienyl ring **III**. In an attempt to synthesize **III** from **II** (Eckensberger, 2006) and 4,4'-dimethyl-2,2'-bipyridine, we obtained the title compound as a by-product. X-ray quality crystals were grown from CD<sub>3</sub>CN in an NMR tube at ambient temperature.

The title compound crystallizes with one formula unit in the unit cell. The cation is located on a crystallographic inversion centre. It is essentially planar (r.m.s. deviation for all non-H atoms 0.004 Å). The chloride anions deviate by just 0.072 (3) Å from this plane. These planes are parallel to the (111) plane. In a plane, cations and anions are connected by N—H···Cl and C—H···Cl hydrogen bonds (Fig. 2).

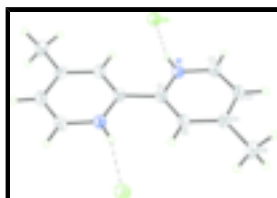
### Experimental

In an attempt to synthesize complex **III** (Eckensberger, 2006) from **II** (0.156 g, 0.32 mmol) with 4,4'-dimethyl-2,2'-bipyridine (0.065 g, 0.35 mmol) in 5 ml acetonitrile, the title compound was obtained as a by-product. X-ray quality crystals were grown from CD<sub>3</sub>CN in an NMR tube at ambient temperature after several days.

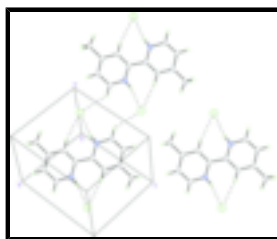
### Refinement

H atoms were geometrically positioned with  $C_{\text{aromatic}}\text{—H} = 0.95$  Å and  $C_{\text{methyl}}\text{—H} = 0.98$  Å, and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  or  $1.5 U_{\text{eq}}(\text{C}_{\text{methyl}})$ . The methyl group was allowed to rotate about its local threefold axis. The H atom bonded to N was freely refined.

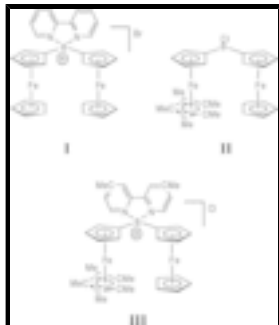
### Figures



Perspective view of the title compound with the atom numbering scheme; displacement ellipsoids are at the 50% probability level; H atoms are drawn as small spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. Symmetry operator for generating equivalent atoms:  $1 - x, 1 - y, 1 - z$ .



Packing diagram of the title compound viewed perpendicular to the (1 1 1) plane. Hydrogen bonds are indicated as dashed lines.



## 4,4'-Dimethyl-2,2'-bipyridinium dichloride

### Crystal data

$C_{12}H_{14}N_2^{2+} \cdot 2(Cl^-)$

$M_r = 257.15$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 5.1999$  (10) Å

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$\alpha = 93.877$  (15)°

$\beta = 102.349$  (15)°

$\gamma = 97.759$  (15)°

$V = 308.71$  (10) Å<sup>3</sup>

$Z = 1$

$F_{000} = 134$

$D_x = 1.383$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 3157 reflections

$\theta = 3.6$ – $25.8$ °

$\mu = 0.50$  mm<sup>-1</sup>

$T = 173$  (2) K

Block, colourless

$0.21 \times 0.21 \times 0.14$  mm

### Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ (2) K

$\omega$  scans

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

$T_{\min} = 0.902$ ,  $T_{\max} = 0.933$

3382 measured reflections

1147 independent reflections

926 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 25.6$ °

$\theta_{\min} = 3.6$ °

$h = -6 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -10 \rightarrow 9$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2]$
$S = 0.97$	where $P = (F_o^2 + 2F_c^2)/3$
1147 reflections	$(\Delta/\sigma)_{\max} < 0.001$
78 parameters	$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.97517 (12)	0.22553 (7)	0.26756 (7)	0.02679 (18)
N1	0.6763 (4)	0.3002 (2)	0.5264 (2)	0.0219 (4)
H1	0.749 (6)	0.296 (4)	0.444 (4)	0.047 (8)*
C1	0.5194 (4)	0.4274 (2)	0.5570 (2)	0.0195 (4)
C2	0.7255 (5)	0.1636 (3)	0.6223 (3)	0.0254 (5)
H2	0.8362	0.0774	0.5967	0.031*
C3	0.6195 (5)	0.1455 (3)	0.7564 (3)	0.0273 (5)
H3	0.6568	0.0483	0.8232	0.033*
C4	0.4553 (4)	0.2725 (3)	0.7936 (3)	0.0223 (5)
C5	0.4078 (4)	0.4121 (3)	0.6904 (2)	0.0210 (5)
H5	0.2957	0.4988	0.7125	0.025*
C6	0.3345 (5)	0.2555 (3)	0.9383 (3)	0.0287 (5)
H6A	0.2337	0.3585	0.9488	0.043*
H6B	0.4761	0.2605	1.0362	0.043*
H6C	0.2147	0.1365	0.9244	0.043*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0285 (3)	0.0269 (3)	0.0288 (3)	0.00927 (19)	0.0113 (2)	0.00399 (18)
N1	0.0236 (10)	0.0228 (8)	0.0223 (10)	0.0070 (7)	0.0082 (8)	0.0064 (7)
C1	0.0204 (11)	0.0195 (9)	0.0181 (10)	0.0029 (8)	0.0031 (8)	0.0028 (8)
C2	0.0262 (12)	0.0238 (9)	0.0293 (12)	0.0086 (8)	0.0081 (10)	0.0084 (8)
C3	0.0284 (13)	0.0244 (10)	0.0295 (12)	0.0066 (9)	0.0032 (10)	0.0110 (9)
C4	0.0231 (11)	0.0217 (9)	0.0204 (10)	-0.0012 (8)	0.0035 (9)	0.0039 (8)

## supplementary materials

C5	0.0243 (12)	0.0196 (9)	0.0200 (10)	0.0061 (8)	0.0043 (9)	0.0049 (8)
C6	0.0350 (14)	0.0301 (11)	0.0218 (11)	0.0040 (10)	0.0076 (10)	0.0075 (9)

### Geometric parameters (Å, °)

N1—C2	1.342 (3)	C3—H3	0.950
N1—C1	1.360 (2)	C4—C5	1.397 (3)
N1—H1	0.86 (3)	C4—C6	1.498 (3)
C1—C5	1.382 (3)	C5—H5	0.950
C1—C1 <sup>i</sup>	1.484 (4)	C6—H6A	0.980
C2—C3	1.372 (3)	C6—H6B	0.980
C2—H2	0.950	C6—H6C	0.980
C3—C4	1.404 (3)		
C2—N1—C1	121.9 (2)	C5—C4—C3	117.6 (2)
C2—N1—H1	113.5 (19)	C5—C4—C6	121.92 (17)
C1—N1—H1	124.6 (19)	C3—C4—C6	120.46 (19)
N1—C1—C5	118.08 (18)	C1—C5—C4	121.78 (17)
N1—C1—C1 <sup>i</sup>	117.0 (2)	C1—C5—H5	119.1
C5—C1—C1 <sup>i</sup>	124.9 (2)	C4—C5—H5	119.1
N1—C2—C3	121.46 (17)	C4—C6—H6A	109.5
N1—C2—H2	119.3	C4—C6—H6B	109.5
C3—C2—H2	119.3	H6A—C6—H6B	109.5
C2—C3—C4	119.17 (19)	C4—C6—H6C	109.5
C2—C3—H3	120.4	H6A—C6—H6C	109.5
C4—C3—H3	120.4	H6B—C6—H6C	109.5
C2—N1—C1—C5	-0.5 (3)	C2—C3—C4—C6	179.4 (2)
C2—N1—C1—C1 <sup>i</sup>	179.7 (2)	N1—C1—C5—C4	0.9 (3)
C1—N1—C2—C3	0.0 (3)	C1 <sup>i</sup> —C1—C5—C4	-179.3 (2)
N1—C2—C3—C4	0.2 (3)	C3—C4—C5—C1	-0.7 (3)
C2—C3—C4—C5	0.1 (3)	C6—C4—C5—C1	-180.0 (2)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ .

### Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ C11	0.86 (3)	2.17 (3)	3.009 (2)	165 (3)
C2—H2 $\cdots$ C11 <sup>ii</sup>	0.95	2.75	3.496 (2)	136
C5—H5 $\cdots$ C11 <sup>i</sup>	0.95	2.62	3.554 (2)	169

Symmetry codes: (ii)  $-x+2, -y, -z+1$ ; (i)  $-x+1, -y+1, -z+1$ .

Fig. 1

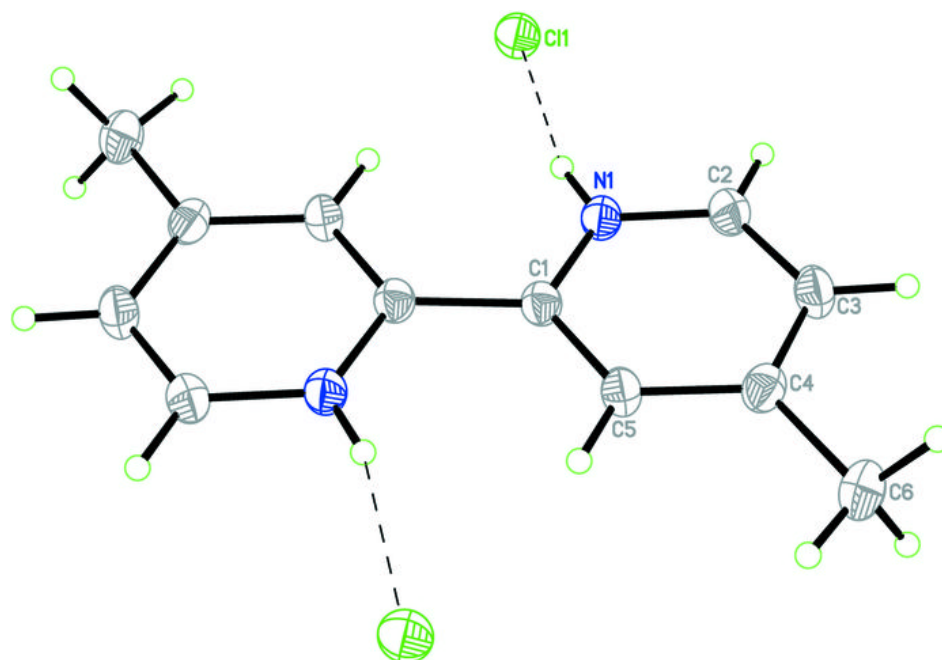


Fig. 2

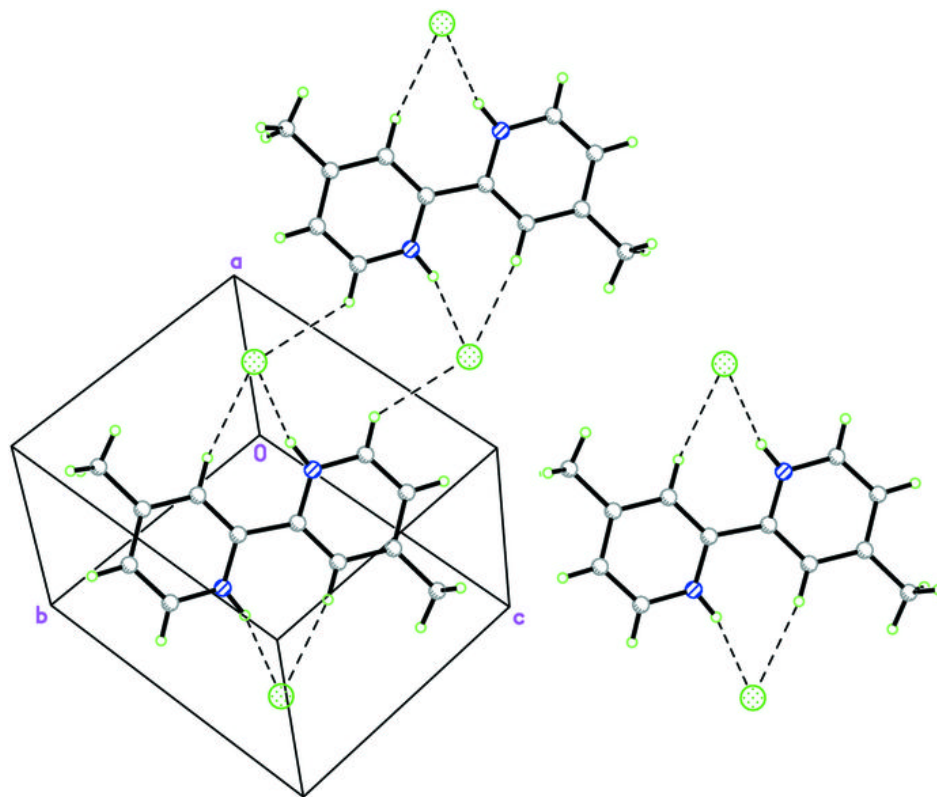




Fig. 3

