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#### Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
 Mean  $\sigma(C-C) = 0.005$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.076  
 Data-to-parameter ratio = 27.5

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

## Bis(2,6-dimethylpyridyl)iodonium dibromiodate

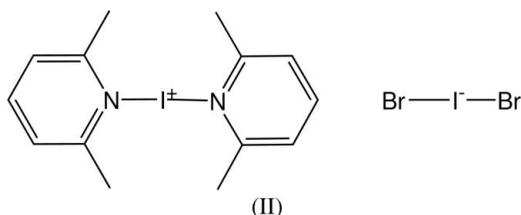
The crystal structure of the title compound,  $C_{14}H_{18}IN_2^+ \cdot Br_2I^-$ , isostructural with the  $Cl_2I$  analogue, comprises discrete centrosymmetric cations and anions, both with linear coordination of the I atoms.

Received 27 January 2006

Accepted 30 January 2006

#### Comment

Electropositive sources of iodine are useful reagents for the iododeboronation of alkenylboronate derivatives (Brown *et al.*, 1973). Iodine monochloride is an important representative of such reagents (Stewart & Whiting, 1995; Lightfoot *et al.*, 2004), but its shortcomings concerning reactivity, stereo-control and chemoselectivity necessitated the development of adjusted reagents involving amine- $ICl$  complexes (Batsanov *et al.*, 2005). In the course of the latter work, we obtained bis(2,6-dimethylpyridyl)iodonium dichloriodate (I), the crystal structure of which unexpectedly comprised discrete  $I(NC_7H_9)_2^+$  and  $ICl_2^-$  ions rather than neutral  $Cl-I-NC_7H_9$  molecules (Batsanov *et al.*, 2005), but which also proved to be active in iododeboronation. Continuing these studies, we have prepared the bromide analogue of compound (I), *viz.*  $I(NC_7H_9)_2^+ \cdot IBr_2^-$  (II), which proved not to be superior to (I) as an iododeboronation agent.



The crystals of (II) are isomorphous with those of (I), with an increase of the volume per molecule by  $14 \text{ \AA}^3$ , or *ca* 3%. The structure comprises discrete bis(2,6-dimethylpyridyl)iodonium cations and  $IBr_2^-$  anions (Fig. 1). In both ions, the central I atoms occupy special positions at inversion centres, hence the  $N-I-N'$  and  $Br-I-Br'$  angles exactly equal  $180^\circ$ .

Atom I1 is tilted out of the pyridine ring plane by  $0.190$  (5) Å, whereas atoms C1 and C7 deviate on the opposite side of the plane by  $0.026$  (6) and  $0.080$  (6) Å, respectively. Thus, the two rings of the cation are parallel but not coplanar, with an interplanar separation of  $0.38$  Å, *cf.*  $0.60$  Å in (I). The  $I1-N$  bond distance of  $2.294$  (3) Å agrees with  $2.300$  (1) Å in (I),  $2.259$  (3) Å in bis(pyridine)iodonium (Álvarez-Rúa *et al.*, 2002) and  $2.29$  (1) Å in bis(2,4,6-collidine)iodonium (Brayer & James, 1982). All these distances are much longer than the single  $Nsp^2-I$  bonds in *N*-iodosuccinimide [ $2.059$  (4) Å; Padmanabhan *et al.*, 1990] or diiodoformamide [mean

2.07 (3) Å; Pritzkow, 1974] and can be regarded as hypervalent bonds. Likewise, the I2—Br bond length of 2.6962 (4) Å is normal for IBr<sub>2</sub><sup>−</sup> anions in the solid state, cf. 2.710 (1) Å in [Me<sub>3</sub>S][IBr<sub>2</sub>] (Svensson & Kloo, 2000), 2.709 (2) Å in [H<sub>2</sub>(pc)][IBr<sub>2</sub>] or 2.6986 (4) Å in [H<sub>2</sub>(pc)]<sub>2</sub>[IBr<sub>2</sub>]Br (pc is phthalocyanine; Gardberg *et al.*, 2002). However, these bonds also are much weaker than a single bond, as observed in the IBr molecule in the gas phase (2.469 Å; Huber & Herzberg, 1979).

## Experimental

A 1.0 M solution of IBr in dichloromethane (DCM; 30 mmol, 30 ml) was cooled to 273 K with stirring under argon prior to the dropwise addition of 2,6-lutidine (30 mmol, 3.50 ml). After 30 min, the reaction was allowed to warm to room temperature before the addition of hexane (40 ml) to induce precipitation of the product. Filtration, drying (MgSO<sub>4</sub>) and evaporation gave the product as an orange solid (7.37 g, 78%). IR  $\nu_{\max}$ , cm<sup>−1</sup>: 2978, 1601, 1466, 1377, 1161 and 792. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 2.78 (6H, *s*, 2 × Me), 7.13 (2H, *d*, *J* = 7.6 Hz, Ar—H) and 7.62 (1H, *t*, *J* = 7.6 Hz, Ar—H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 28.1 (Me), 123.0 (Ar), 139.2 (Ar) and 157.6 (Ar). (C<sub>7</sub>H<sub>9</sub>NIBr)<sub>2</sub> requires: C 26.76, H 2.89, N 4.46%; found: C 26.22, H 2.88, N 4.28%. Single crystals of X-ray quality were obtained by slow evaporation of a solution in DCM–hexane (1:1). To test the deboronation properties of (II), it has been reacted with 4,4,5,5-tetramethyl-2-non-1-enyl-1,3,2-dioxaborolane and 4,4,6-trimethyl-2-non-1-enyl-1,3,2-dioxaborinane in DCM, yielding BrCH=CHC<sub>7</sub>H<sub>15</sub> as the sole product and with complete selectivity for the *Z*-alkene in both cases. However, the maximum conversions achieved (47 and 52%, respectively) were low.

### Crystal data

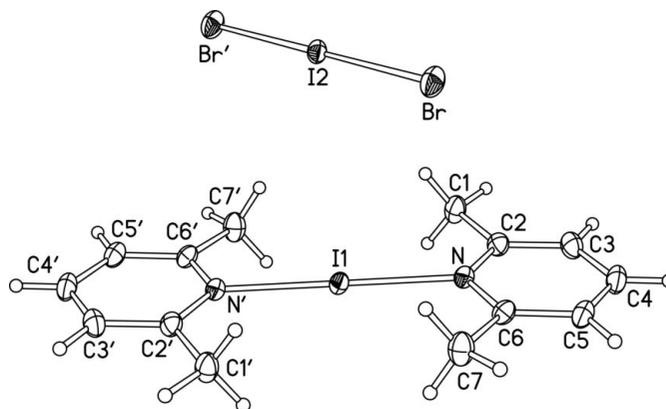
C <sub>14</sub> H <sub>18</sub> IN <sub>2</sub> <sup>+</sup> ·Br <sub>2</sub> I <sup>−</sup>	<i>Z</i> = 1
<i>M<sub>r</sub></i> = 627.92	<i>D<sub>x</sub></i> = 2.254 Mg m <sup>−3</sup>
Triclinic, P $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 7.5777 (7) Å	Cell parameters from 3235 reflections
<i>b</i> = 8.2610 (7) Å	$\theta$ = 2.5–30.0°
<i>c</i> = 8.5800 (7) Å	$\mu$ = 7.71 mm <sup>−1</sup>
$\alpha$ = 99.09 (1)°	<i>T</i> = 120 (2) K
$\beta$ = 101.45 (1)°	Block, orange
$\gamma$ = 114.20 (1)°	0.10 × 0.08 × 0.02 mm
<i>V</i> = 462.6 (1) Å <sup>3</sup>	

### Data collection

Bruker SMART 6K CCD area-detector diffractometer	2693 independent reflections
$\omega$ scans	2309 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Bruker, 2003)	<i>R</i> <sub>int</sub> = 0.037
<i>T</i> <sub>min</sub> = 0.637, <i>T</i> <sub>max</sub> = 0.861	$\theta_{\max}$ = 30.0°
6548 measured reflections	<i>h</i> = −10 → 10
	<i>k</i> = −11 → 11
	<i>l</i> = −12 → 12

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2]$
$wR(F^2) = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.99	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
2693 reflections	$\Delta\rho_{\max} = 2.54 \text{ e \AA}^{-3}$
98 parameters	$\Delta\rho_{\min} = -1.41 \text{ e \AA}^{-3}$



**Figure 1**

The cation and anion in (II). Atomic displacement ellipsoids are drawn at the 50% probability level. Br' is generated by the symmetry operator ( $-x, -y, 1 - z$ ), and the other primed atoms are generated by the symmetry operator ( $1 - x, 1 - y, 1 - z$ ).

Methyl groups were treated as rigid bodies (C—H = 0.98 Å) rotating around the C—C bonds, with a common refined *U*<sub>iso</sub> value for three H atoms. Aromatic H atoms were treated as riding on the C atoms [C—H = 0.95 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)]. The five strongest maxima and minima of the final difference map are located at distances of 0.8–0.9 Å from atoms I1 and I2.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors are grateful to the EPSRC for a DTA award to SJRT and to GlaxoSmithKline Pharmaceuticals for a CASE studentship.

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## supporting information

*Acta Cryst.* (2006). E62, o901–o902 [https://doi.org/10.1107/S1600536806003680]

## Bis(2,6-dimethylpyridyl)iodonium dibromiodate

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## Bis(2,6-dimethylpyridyl)iodinium dibromiodate

*Crystal data*

$C_{14}H_{18}IN_2^+Br_2I^-$

$M_r = 627.92$

Triclinic,  $P\bar{1}$

$a = 7.5777$  (7) Å

$b = 8.2610$  (7) Å

$c = 8.5800$  (7) Å

$\alpha = 99.09$  (1)°

$\beta = 101.45$  (1)°

$\gamma = 114.20$  (1)°

$V = 462.6$  (1) Å<sup>3</sup>

$Z = 1$

$F(000) = 292$

$D_x = 2.254$  Mg m<sup>-3</sup>

Melting point: 383(1) K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3235 reflections

$\theta = 2.5$ – $30.0$ °

$\mu = 7.71$  mm<sup>-1</sup>

$T = 120$  K

Block, orange

$0.10 \times 0.08 \times 0.02$  mm

*Data collection*

Bruker SMART 6K CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 5.6 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2003)

$T_{\min} = 0.637$ ,  $T_{\max} = 0.861$

6548 measured reflections

2693 independent reflections

2309 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.076$

$S = 0.99$

2693 reflections

98 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2]$

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

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

$\Delta\rho_{\max} = 2.54$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.41$  e Å<sup>-3</sup>

*Special details*

**Experimental.** The data collection nominally covered full sphere of reciprocal space, by a combination of 3 sets of  $\omega$  scans; each set at different  $\phi$  angles and each scan (20 s exposure) covering 0.3° in  $\omega$ . Crystal to detector distance 4.85 cm.

**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.

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.5000	0.5000	0.5000	0.01576 (9)
I2	0.0000	0.0000	0.5000	0.01764 (9)
Br	-0.12080 (6)	0.18586 (6)	0.30774 (5)	0.02574 (10)
N	0.3548 (4)	0.4793 (4)	0.2315 (3)	0.0157 (5)
C1	0.3316 (6)	0.1696 (5)	0.1580 (5)	0.0237 (8)
H11	0.4749	0.2085	0.2109	0.028 (7)*
H12	0.2822	0.0684	0.0584	0.028 (7)*
H13	0.2535	0.1279	0.2347	0.028 (7)*
C2	0.3060 (5)	0.3288 (5)	0.1115 (4)	0.0186 (7)
C3	0.2344 (5)	0.3203 (5)	-0.0527 (4)	0.0225 (7)
H3	0.2021	0.2140	-0.1366	0.027*
C4	0.2092 (6)	0.4668 (6)	-0.0944 (4)	0.0230 (7)
H4	0.1604	0.4626	-0.2066	0.028*
C5	0.2572 (5)	0.6189 (5)	0.0308 (4)	0.0210 (7)
H5	0.2416	0.7207	0.0046	0.025*
C6	0.3291 (5)	0.6239 (5)	0.1946 (4)	0.0173 (6)
C7	0.3721 (6)	0.7836 (6)	0.3326 (5)	0.0256 (8)
H71	0.2964	0.7385	0.4099	0.033 (7)*
H72	0.3305	0.8685	0.2873	0.033 (7)*
H73	0.5173	0.8483	0.3908	0.033 (7)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.01858 (15)	0.01675 (16)	0.01325 (15)	0.00838 (12)	0.00566 (11)	0.00521 (11)
I2	0.01924 (16)	0.02170 (17)	0.01317 (15)	0.01004 (13)	0.00530 (11)	0.00509 (12)
Br	0.0292 (2)	0.0335 (2)	0.02382 (19)	0.01926 (17)	0.01002 (15)	0.01507 (16)
N	0.0171 (13)	0.0173 (14)	0.0139 (13)	0.0083 (11)	0.0056 (10)	0.0051 (11)
C1	0.036 (2)	0.0186 (18)	0.0163 (17)	0.0139 (16)	0.0061 (15)	0.0035 (14)
C2	0.0186 (16)	0.0225 (18)	0.0160 (16)	0.0097 (14)	0.0073 (13)	0.0051 (13)
C3	0.0237 (18)	0.026 (2)	0.0155 (16)	0.0114 (15)	0.0044 (13)	0.0023 (14)
C4	0.0255 (18)	0.031 (2)	0.0155 (16)	0.0143 (16)	0.0065 (14)	0.0100 (15)
C5	0.0235 (17)	0.0264 (19)	0.0196 (17)	0.0141 (15)	0.0087 (14)	0.0123 (15)
C6	0.0201 (16)	0.0201 (17)	0.0163 (16)	0.0107 (14)	0.0101 (13)	0.0065 (13)
C7	0.033 (2)	0.028 (2)	0.0201 (18)	0.0191 (17)	0.0072 (15)	0.0059 (15)

## Geometric parameters (Å, °)

I1—N <sup>i</sup>	2.294 (3)	C3—C4	1.389 (5)
I1—N	2.294 (3)	C3—H3	0.9500
I2—Br	2.6962 (4)	C4—C5	1.382 (5)
I2—Br <sup>ii</sup>	2.6962 (4)	C4—H4	0.9500
N—C2	1.345 (5)	C5—C6	1.390 (5)
N—C6	1.361 (4)	C5—H5	0.9500
C1—C2	1.507 (5)	C6—C7	1.500 (5)
C1—H11	0.9801	C7—H71	0.9800
C1—H12	0.9800	C7—H72	0.9800
C1—H13	0.9800	C7—H73	0.9801
C2—C3	1.385 (5)		
N <sup>i</sup> —I1—N	180.0	C4—C3—H3	120.1
Br—I2—Br <sup>ii</sup>	179.999 (12)	C5—C4—C3	118.6 (3)
C2—N—C6	120.8 (3)	C5—C4—H4	120.8
C2—N—I1	119.8 (2)	C3—C4—H4	120.7
C6—N—I1	119.4 (2)	C4—C5—C6	120.3 (3)
C2—C1—H11	109.7	C4—C5—H5	119.7
C2—C1—H12	109.3	C6—C5—H5	120.0
H11—C1—H12	109.5	N—C6—C5	119.8 (3)
C2—C1—H13	109.4	N—C6—C7	119.1 (3)
H11—C1—H13	109.5	C5—C6—C7	121.1 (3)
H12—C1—H13	109.5	C6—C7—H71	109.5
N—C2—C3	120.7 (3)	C6—C7—H72	109.4
N—C2—C1	119.0 (3)	H71—C7—H72	109.5
C3—C2—C1	120.3 (3)	C6—C7—H73	109.6
C2—C3—C4	119.9 (3)	H71—C7—H73	109.5
C2—C3—H3	120.0	H72—C7—H73	109.5

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