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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.005$ 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

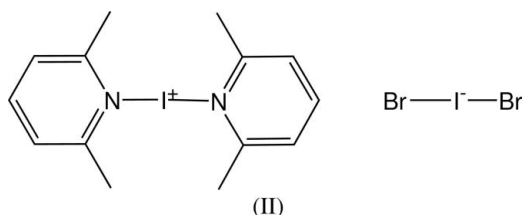
The crystal structure of the title compound, $\text{C}_{14}\text{H}_{18}\text{IN}_2^+ \cdot \text{Br}_2\text{I}^-$, isostructural with the Cl_2I analogue, comprises discrete centrosymmetric cations and anions, both with linear coordination of the I atoms.

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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 $\text{I}(\text{NC}_7\text{H}_9)_2^+$ and ICl_2^- ions rather than neutral $\text{Cl}-\text{I}-\text{NC}_7\text{H}_9$ 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.* $\text{I}(\text{NC}_7\text{H}_9)_2^+ \cdot \text{IBr}_2^-$ (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 \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 $\text{N}-\text{I}-\text{N}'$ and $\text{Br}-\text{I}-\text{Br}'$ angles exactly equal 180° .

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 $\text{I1}-\text{N}$ 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 IBr₂[−] anions in the solid state, cf. 2.710 (1) Å in [Me₃S][IBr₂] (Svensson & Kloo, 2000), 2.709 (2) Å in [H₂(pc)][IBr₂] or 2.6986 (4) Å in [H₂(pc)]₂[IBr₂]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 (MgSO₄) and evaporation gave the product as an orange solid (7.37 g, 78%). IR ν_{\max} , cm^{−1}: 2978, 1601, 1466, 1377, 1161 and 792. ¹H NMR (400 MHz, CDCl₃, δ , 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). ¹³C NMR (100 MHz, CDCl₃, δ , p.p.m.): 28.1 (Me), 123.0 (Ar), 139.2 (Ar) and 157.6 (Ar). (C₇H₉NIBr)₂ 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=CHC₇H₁₅ 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 ₁₄ H ₁₈ IN ₂ ⁺ ·Br ₂ I [−]	<i>Z</i> = 1
<i>M_r</i> = 627.92	<i>D_x</i> = 2.254 Mg m ^{−3}
Triclinic, P $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.5777 (7) Å	Cell parameters from 3235 reflections
<i>b</i> = 8.2610 (7) Å	θ = 2.5–30.0°
<i>c</i> = 8.5800 (7) Å	μ = 7.71 mm ^{−1}
α = 99.09 (1)°	<i>T</i> = 120 (2) K
β = 101.45 (1)°	Block, orange
γ = 114.20 (1)°	0.10 × 0.08 × 0.02 mm
<i>V</i> = 462.6 (1) Å ³	

Data collection

Bruker SMART 6K CCD area-detector diffractometer	2693 independent reflections
ω scans	2309 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 2003)	<i>R</i> _{int} = 0.037
<i>T</i> _{min} = 0.637, <i>T</i> _{max} = 0.861	θ_{\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> ²	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	(Δ/σ) _{max} < 0.001
2693 reflections	$\Delta\rho_{\max} = 2.54 \text{ e } \text{Å}^{-3}$
98 parameters	$\Delta\rho_{\min} = -1.41 \text{ e } \text{Å}^{-3}$

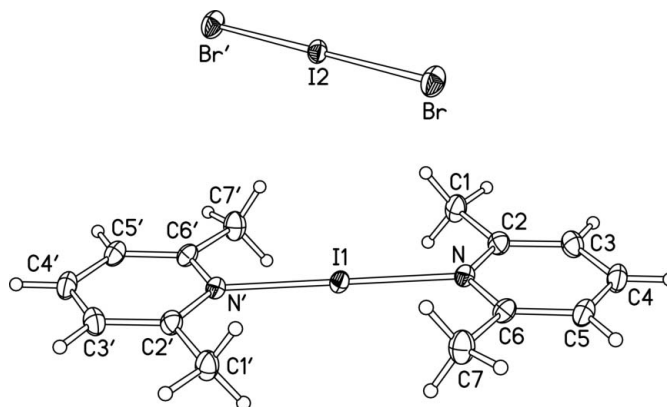


Figure 1

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*_{iso} value for three H atoms. Aromatic H atoms were treated as riding on the C atoms [C—H = 0.95 Å and *U*_{iso}(H) = 1.2*U*_{eq}(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.

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