organic compounds

2-Bromo-5-iodo-1,3-dimethylbenzene

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In the molecule of the title compound, C_8H_6BrI, the H atoms of methyl groups are disordered; site-occupation factors were fixed at 0.50. The non-H atoms all lie on a crystallographic mirror plane. Weak intramolecular C—H···Br hydrogen bonds result in the formation of two non-planar five-membered rings.

Related literature

For bond-length data, see: Allen *et al.* (1987).
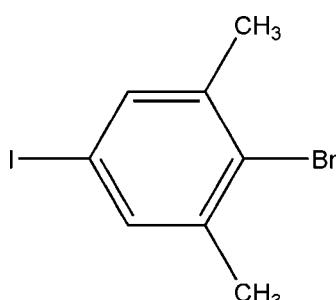
Experimental

Crystal data

C_8H_8BrI	a = 16.686 (3) Å
M_r = 310.94	b = 7.0640 (14) Å
Orthorhombic, $Pnma$	c = 8.2130 (16) Å
V = 968.1 (3) Å^3	μ = 7.37 mm^{-1}
Z = 4	T = 294 (2) K
Mo $K\alpha$ radiation	$0.40 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1030 independent reflections
Absorption correction: ψ scan (North *et al.*, 1968)	659 reflections with $I > 2\sigma(I)$
T_{min} = 0.157, T_{max} = 0.479	3 standard reflections frequency: 120 min intensity decay: none
1030 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056	63 parameters
$wR(F^2)$ = 0.137	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.62 e Å^{-3}
1030 reflections	$\Delta\rho_{min}$ = −0.85 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7C···Br2	0.96	2.74	3.156 (6)	107
C8—H8C···Br2	0.96	2.77	3.115 (5)	102

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2261).

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supporting information

2-Bromo-5-iodo-1,3-dimethylbenzene

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S1. Comment

The title compound, (I), is a fine organic intermediate, which can be utilized to construct practical functional molecules. We herein report its crystal structure.

In the molecule of (I), (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). When the crystal structure was solved, H atoms of methyl groups were found to be disordered.

The atoms Br2, I1, C7 and C8 lie in the benzene ring plane. The weak intra- molecular C—H···Br hydrogen bonds (Table 1) result in the formations of two non-planar five-membered rings; B (Br2/C1/C6/C7/H7C) and C (Br2/C1/C2/C8/H8C). Ring A (C1—C6) is, of course, planar.

As can be seen from the packing diagram, (Fig. 2), the molecules are stacked along the *b* axis.

S2. Experimental

For the preparation of the title compound, 4-iodo-2,6-dimethylaniline (5.0 g, 20 mmol), concentrated sulfuric acid (40 mmol, 2.23 ml) and water (100 ml) were stirred in an ice bath. When the temperature was below 278 K, the solution of sodium nitrite (1.44 g, 21 mmol) in water (100 ml) was added dropwise. Then, the mixture was added to a solution of CuBr (2.86 g, 20 mmol) and hydrobromic acid (20 mmol, 2.71 ml) with stirring. The solid residue was extracted with boiling hexane (40 ml) and hexane was distilled off. Crystals suitable for X-ray analysis were obtained by slow evaporation of ethanol at room temperature for about 20 d.

S3. Refinement

When the crystal structure was solved, the H atoms of methyl groups were found to be disordered over two mirror image sites of the symmetry plane passing through the benzene ring. The occupancies of disordered H atoms were kept fixed as 0.50. H atoms were positioned geometrically, with C—H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for aromatic H, and $x = 1.5$ for methyl H atoms.
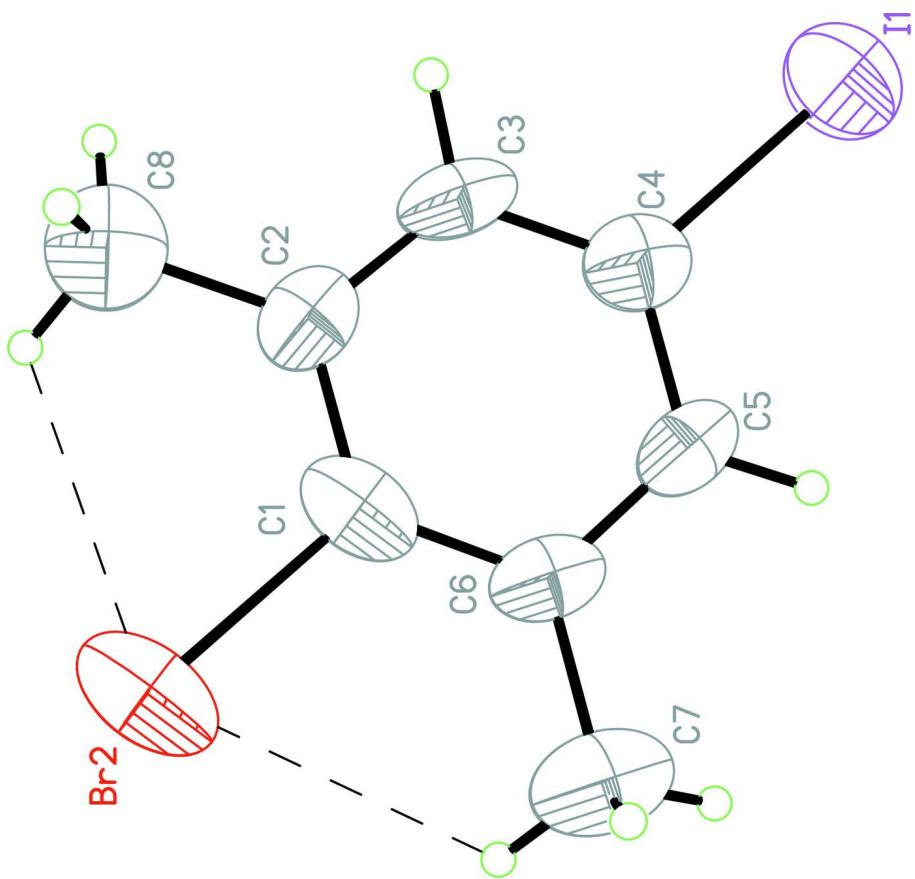
Figure 1

The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
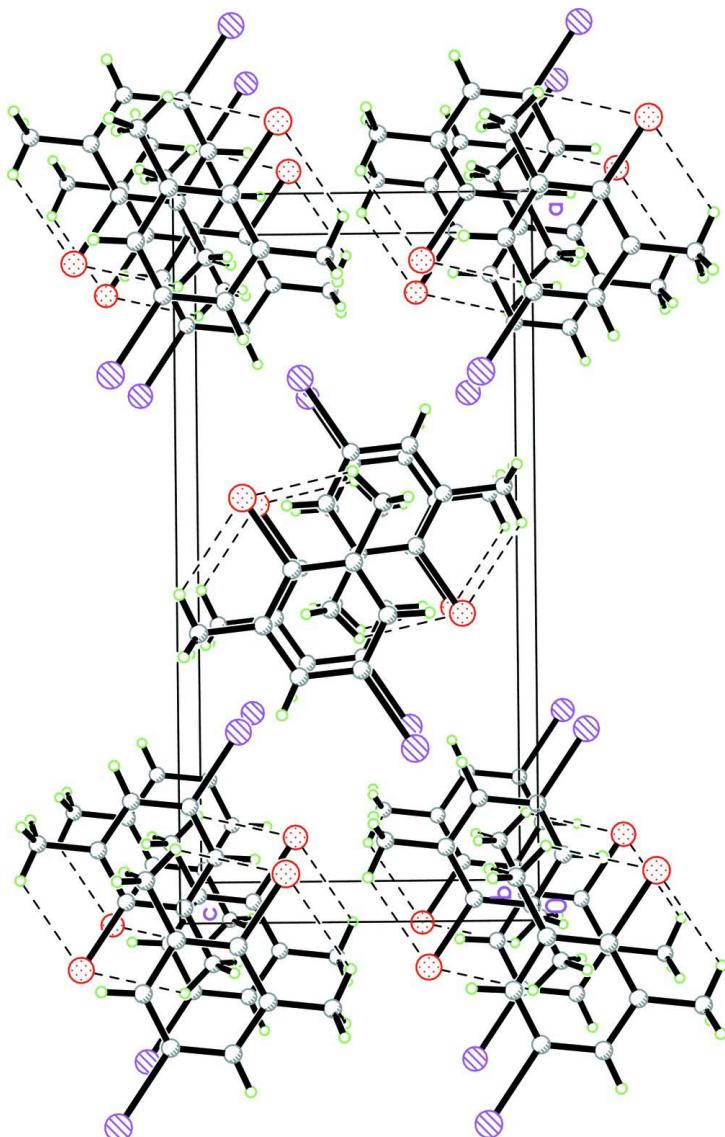
Figure 2

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

2-Bromo-5-iodo-1,3-dimethylbenzene

Crystal data

C_8H_8BrI	$D_x = 2.133$ Mg m^{-3}
$M_r = 310.94$	Melting point: 307 K
Orthorhombic, *Pnma*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 25 reflections
$a = 16.686$ (3) Å	$\theta = 10$–13°
$b = 7.0640$ (14) Å	$\mu = 7.37$ mm^{-1}
$c = 8.2130$ (16) Å	$T = 294$ K
$V = 968.1$ (3) Å^3	Needle, colorless
$Z = 4$	$0.40 \times 0.20 \times 0.10$ mm
$F(000) = 576.0$	

Data collection

Enraf–Nonius CAD-4 diffractometer	1030 independent reflections
Radiation source: fine-focus sealed tube	659 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.000$
$\omega/2\theta$ scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.4°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 20$
	$k = 0 \rightarrow 8$
	$l = 0 \rightarrow 10$
$T_{min} = 0.157$, $T_{max} = 0.479$	3 standard reflections every 120 min
1030 measured reflections	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.056$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.137$	
$S = 1.10$	H-atom parameters constrained
1030 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 1.4567P]$ where $P = (F_o^2 + 2F_c^2)/3$
63 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.62$ e Å^{-3}
	$\Delta\rho_{min} = -0.85$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
I1	0.25441 (7)	0.2500	1.15579 (9)	0.0902 (5)	
Br2	−0.08058 (5)	0.2500	0.69651 (7)	0.0800 (5)	
C1	0.0160 (4)	0.2500	0.8282 (5)	0.055 (3)	
C2	0.0066 (4)	0.2500	0.9955 (6)	0.051 (3)	
C3	0.0768 (4)	0.2500	1.0850 (6)	0.054 (3)	
H3	0.0740	0.2500	1.1981	0.065*	
C4	0.1500 (5)	0.2500	1.0117 (6)	0.057 (3)	
C5	0.1580 (5)	0.2500	0.8449 (5)	0.055 (3)	
H5	0.2085	0.2500	0.7972	0.066*	
C6	0.0897 (4)	0.2500	0.7489 (5)	0.050 (3)	
C7	0.0984 (4)	0.2500	0.5721 (4)	0.093 (5)	
H7A	0.0947	0.1226	0.5322	0.139*	0.50
H7B	0.1496	0.3022	0.5434	0.139*	0.50
H7C	0.0567	0.3252	0.5244	0.139*	0.50
C8	−0.0730 (4)	0.2500	1.0755 (6)	0.077 (4)	

H8A	−0.0672	0.2878	1.1871	0.116*	0.50
H8B	−0.0955	0.1251	1.0709	0.116*	0.50
H8C	−0.1078	0.3371	1.0203	0.116*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0675 (6)	0.1300 (10)	0.0731 (6)	0.000	−0.0170 (5)	0.000
Br2	0.0850 (9)	0.0714 (8)	0.0837 (9)	0.000	−0.0394 (8)	0.000
C1	0.065 (7)	0.038 (6)	0.063 (8)	0.000	−0.022 (6)	0.000
C6	0.074 (7)	0.049 (5)	0.047 (6)	0.000	0.006 (5)	0.000
C4	0.068 (7)	0.057 (7)	0.046 (7)	0.000	0.002 (6)	0.000
C3	0.079 (8)	0.053 (6)	0.031 (5)	0.000	0.012 (6)	0.000
C2	0.054 (5)	0.046 (6)	0.052 (7)	0.000	0.010 (5)	0.000
C5	0.060 (6)	0.059 (7)	0.045 (6)	0.000	0.017 (5)	0.000
C7	0.108 (13)	0.098 (10)	0.083 (6)	0.000	0.012 (7)	0.000
C8	0.071 (8)	0.079 (8)	0.082 (9)	0.000	0.003 (7)	0.000

Geometric parameters (Å, º)

I1—C4	2.105 (7)	C3—H3	0.9300
Br2—C1	1.941 (6)	C2—C8	1.481 (6)
C1—C2	1.383 (6)	C5—H5	0.9300
C1—C6	1.392 (6)	C7—H7A	0.9600
C6—C5	1.385 (6)	C7—H7B	0.9600
C6—C7	1.460 (5)	C7—H7C	0.9600
C4—C3	1.362 (6)	C8—H8A	0.9600
C4—C5	1.377 (6)	C8—H8B	0.9600
C3—C2	1.384 (6)	C8—H8C	0.9600
C2—C1—C6	124.4 (5)	C4—C5—C6	119.2 (5)
C2—C1—Br2	117.4 (5)	C4—C5—H5	120.4
C6—C1—Br2	118.2 (3)	C6—C5—H5	120.4
C5—C6—C1	117.4 (4)	C6—C7—H7A	109.5
C5—C6—C7	118.9 (5)	C6—C7—H7B	109.5
C1—C6—C7	123.6 (5)	H7A—C7—H7B	109.5
C3—C4—C5	121.7 (4)	C6—C7—H7C	109.5
C3—C4—I1	119.6 (4)	H7A—C7—H7C	109.5
C5—C4—I1	118.7 (4)	H7B—C7—H7C	109.5
C4—C3—C2	121.6 (5)	C2—C8—H8A	109.5
C4—C3—H3	119.2	C2—C8—H8B	109.5
C2—C3—H3	119.2	H8A—C8—H8B	109.5
C1—C2—C3	115.6 (5)	C2—C8—H8C	109.5
C1—C2—C8	122.8 (6)	H8A—C8—H8C	109.5
C3—C2—C8	121.5 (5)	H8B—C8—H8C	109.5
C2—C1—C6—C5	0.000 (3)	C6—C1—C2—C8	180.000 (3)
Br2—C1—C6—C5	180.000 (2)	Br2—C1—C2—C8	0.000 (3)

C2—C1—C6—C7	180.000 (2)	C4—C3—C2—C1	0.000 (3)
Br2—C1—C6—C7	0.000 (2)	C4—C3—C2—C8	180.000 (3)
C5—C4—C3—C2	0.000 (3)	C3—C4—C5—C6	0.000 (3)
I1—C4—C3—C2	180.000 (3)	I1—C4—C5—C6	180.000 (2)
C6—C1—C2—C3	0.000 (3)	C1—C6—C5—C4	0.000 (3)
Br2—C1—C2—C3	180.000 (2)	C7—C6—C5—C4	180.000 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*C*···Br2	0.96	2.74	3.156 (6)	107
C8—H8*C*···Br2	0.96	2.77	3.115 (5)	102