

Template-directed growth of *p*-bromiodobenzeneRupa Hiremath,<sup>a</sup> Amy A. Sarjeant<sup>b</sup> and Jennifer A. Swift<sup>a\*</sup><sup>a</sup>Department of Chemistry, Georgetown University, Washington, DC 20057, USA, and  
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Crystals of the title compound, C<sub>6</sub>H<sub>4</sub>BrI, were obtained by growth on a two-dimensional self-assembled monolayer template. Single-crystal X-ray diffraction at 110 K revealed a centrosymmetric structure in which the center of the benzene ring lies on an inversion center and the halogen atoms are statistically disordered. The monoclinic structure reported here is isostructural with *p*-dibromobenzene but not with *p*-diiodobenzene.

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## Key indicators

Single-crystal X-ray study

T = 110 K

Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$ 

Disorder in main residue

R factor = 0.023

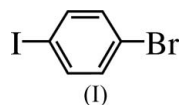
wR factor = 0.059

Data-to-parameter ratio = 19.2

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

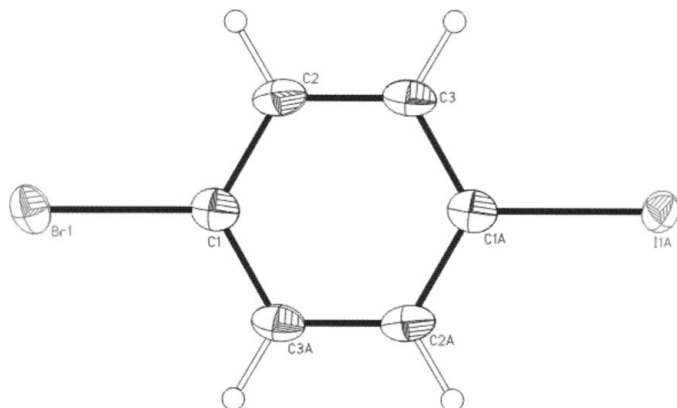
## Comment

The crystal structures of *p*-dihalobenzenes ( $X\text{-C}_6\text{H}_4\text{-Y}$ , where  $X$  and  $Y$  are Cl, Br or I) have interested crystal chemists for several decades, largely for reasons related to understanding substituent effects, solid-state miscibility and phase transformations (Klug, 1947; Prasad & Stevens, 1977). A large number of *p*-dihalobenzenes adopt isostructural  $P2_1/c$  monoclinic structures at room temperature, including the symmetrical *p*-dichlorobenzene (Estop *et al.*, 1997) and *p*-dibromobenzene. Also isostructural are the unsymmetrical dihalo compounds *p*-bromochlorobenzene (Klug, 1947) and *p*-chloriodobenzene, reported most recently by Meriles *et al.* (1999). While the latter two compounds formally lack a center of inversion, centrosymmetric packing is achieved through the superposition and statistical disorder of the halogen substituents. In contrast, *p*-diiodobenzene adopts an entirely different orthorhombic *Pbca* structure at room temperature (Alcobe *et al.*, 1994). While both *p*-dichlorobenzene and *p*-diiodobenzene are known to undergo phase transformations at higher temperatures (Housty & Clastre, 1957; Alcobe *et al.*, 1994), their structures are never identical.

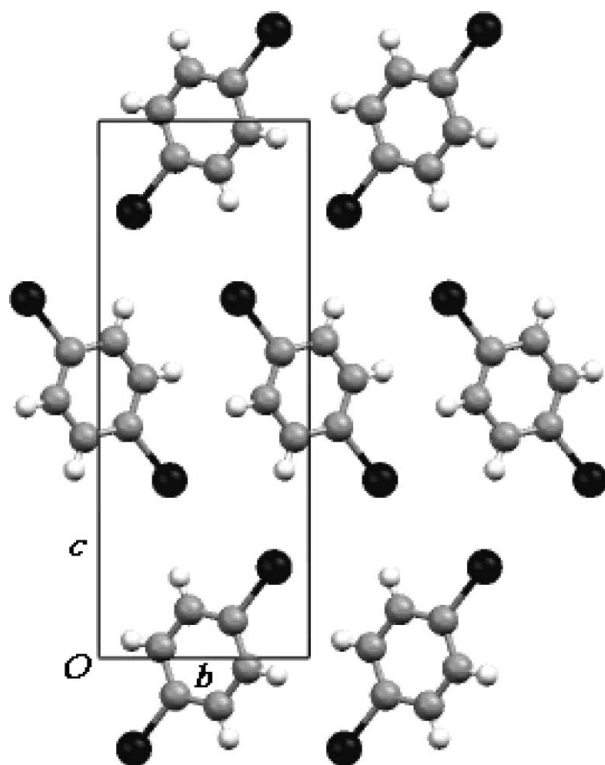


The van der Waals radii for halogen substituents increase in the order Cl (1.81 Å) < Br (1.95 Å) < I (2.16 Å) (Pauling, 1940). Given the similarity in Cl and Br substituent sizes, it is perhaps not surprising that the unsymmetrical *p*-bromochlorobenzene derivative would be isostructural with the other symmetrical monoclinic structures. It is somewhat less obvious in the case of *p*-bromiodobenzene whether the compound would adopt a monoclinic structure like *p*-dibromobenzene, an orthorhombic structure like *p*-diiodobenzene, or a different packing arrangement entirely.

A full single-crystal structure of *p*-bromiodobenzene, (I), has not previously been reported to our knowledge. Prasad & Stevens (1977) reported the unit-cell parameters for this



**Figure 1**  
A view of the molecule of (I), showing displacement ellipsoids at the 50% probability level. [Symmetry code: (A)  $1 - x, -y, 1 - x$ .



**Figure 2**  
A packing diagram of the *p*-bromiodobenzene crystal structure, viewed along the *a* axis.

compound as  $a = 14.96$ ,  $b = 5.89$  and  $c = 4.25$  Å, and  $\beta = 99.1^\circ$ , based on single-crystal X-ray precession photographs obtained at room temperature. Calvet *et al.* (1992) more recently reported its space group as  $P2_1/a$ , with  $a = 16.196$ ,  $b = 5.872$  and  $c = 4.233$  Å, and  $\beta = 113.86^\circ$ , based on room-temperature powder diffraction data. The unit-cell parameters of our structure obtained at 110 K agree more closely with those of Prasad & Stevens.

Like the other known unsymmetrical dihalobenzenes, the structure of (I) was solved in the space group  $P2_1/c$ . The halogen-atom positions are related by an inversion center and are therefore statistically disordered. The observed C—X



**Figure 3**  
A photograph of a rectangular crystal of *p*-bromiodobenzene grown on a self-assembled monolayer. Scale bar = 0.5 mm.

bond length of 2.011 Å is consistent with this, as it is longer than a typical C—Br bond (1.899 Å) but shorter than a C—I bond (2.095 Å). We note that the elongated displacement parameters of the C atoms suggest that the benzene ring in each disorder component actually lies slightly to one side of the inversion center. Attempts to model whole-molecule disorder in order to resolve this difference proved unsuccessful. While one cannot completely discount the possibility of halogen ordering within domains of a single crystal, the diffraction data alone can neither prove nor disprove this hypothesis.

Our repeated attempts to grow *p*-bromiodobenzene from a variety of conventional solvents (*e.g.* acetone, acetonitrile, benzene, cyclohexane, dimethyl sulfoxide, dioxane, ethanol, ethyl acetate, heptane, hexane, hexanes, methanol, dichloromethane, nitromethane, propan-1-ol, propan-2-ol, toluene, xylenes) typically resulted in low-quality crystals. However, crystal growth from heptane in the presence of a gold–thiol self-assembled monolayer (SAM) template of either 4'-nitro-4-mercaptobiphenyl or 4'-cyano-4-mercaptobiphenyl resulted in transparent rectangular plates that were of sufficiently high quality to allow full structure determination by single-crystal diffraction methods. The preparation of these SAM templates has been described elsewhere (Hiremath *et al.*, 2004; Ulman, 2001). Crystals grown on these templates were always observed to have the largest plate face, {001}, in contact with the SAMs (Fig. 3). We ascribe this preferred growth orientation to favorable nitro...X (Allen *et al.*, 1997) and cyano...X (Desiraju & Harlow, 1989) interactions across the SAM–crystal interface, which enable heterogeneous nucleation to occur at lower solution supersaturations. Notably, of all the low-index surfaces, {001} has the highest density of C—X bonds projecting from the surface. Application of SAM template-based growth methods may offer advantages for other small molecule organics that are difficult to grow.

## Experimental

*p*-Bromiodobenzene was purchased from Aldrich (98%) and used without further purification. Single crystals were obtained in a few days by slow room-temperature evaporation of heptane in the presence of a (5 mm × 5 mm)<sup>2</sup> self-assembled monolayer template of either 4'-nitro-4-mercaptobiphenyl or 4'-cyano-4-mercaptobiphenyl. The crystal melting point (363–364 K) was determined on a TA 2920 differential scanning calorimeter.

## Crystal data

C <sub>6</sub> H <sub>4</sub> BrI	$D_x = 2.663 \text{ Mg m}^{-3}$
$M_r = 282.90$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2165 reflections
$a = 4.1120 (6) \text{ \AA}$	$\theta = 2.8\text{--}32.6^\circ$
$b = 5.7936 (8) \text{ \AA}$	$\mu = 10.09 \text{ mm}^{-1}$
$c = 14.931 (2) \text{ \AA}$	$T = 110 \text{ K}$
$\beta = 97.301 (11)^\circ$	Plate, colorless
$V = 352.83 (9) \text{ \AA}^3$	$0.20 \times 0.10 \times 0.02 \text{ mm}$
$Z = 2$	

## Data collection

Oxford Xcalibur3 diffractometer	882 independent reflections
$\omega$ scans	772 reflections with $I > 2\sigma(I)$
Absorption correction: numerical ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2005; Clark & Reid, 1995)	$R_{\text{int}} = 0.023$
$T_{\text{min}} = 0.182$ , $T_{\text{max}} = 0.652$	$\theta_{\text{max}} = 28.3^\circ$
2583 measured reflections	$h = -5 \rightarrow 3$
	$k = -7 \rightarrow 7$
	$l = -18 \rightarrow 19$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.3465P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.11$	$\Delta\rho_{\text{max}} = 1.06 \text{ e \AA}^{-3}$
882 reflections	$\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$
46 parameters	
H-atom parameters constrained	

H atoms were positioned geometrically and refined as riding, with C–H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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