Eric C. Hosten and Richard Betz*

The crystal structure of 1-bromo-4-iodo-benzene, C_6H_4BrI

<https://doi.org/10.1515/ncrs-2020-0516>

Received October 3, 2020; accepted October 30, 2020;

published online November 13, 2020

Abstract

C_6H_4BrI , monoclinic, $P2_1/c$ (no. 14), $a = 4.1704(6)$ Å, $b = 5.8242(8)$ Å, $c = 14.929(2)$ Å, $\beta = 97.315(5)^\circ$, $V = 359.67(9)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0303$, $wR_{ref}(F^2) = 0.0982$, $T = 200$ K.

CCDC no.: 2041503

The molecular structure is shown in the Figure. Table 1 contains crystallographic data, and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Fluka). Crystals suitable for the diffraction study were obtained upon free evaporation of a solution of the compound in acetone.

*Corresponding author: Dr Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa. <https://orcid.org/0000-0003-4173-2550>

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	$0.55 \times 0.44 \times 0.18$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	9.90 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.0° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2943, 865, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 741
$N(\text{param})_{\text{refined}}$:	47
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6450 (12)	0.3659 (8)	0.5698 (4)	0.0351 (10)
C2	0.4980 (13)	0.5681 (9)	0.5891 (3)	0.0386 (11)
H2	0.496918	0.614045	0.650151	0.046*
C3	0.3519 (14)	0.7046 (9)	0.5201 (4)	0.0404 (12)
H3	0.250514	0.844592	0.533202	0.049*
I1 ^a	0.862 (2)	0.1563 (17)	0.6714 (5)	0.0347 (9)
Br1 ^a	0.843 (3)	0.184 (3)	0.6651 (8)	0.0348 (13)

^aOccupancy: 0.5.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

The two halogen atoms show orientational disorder over two positions that has been resolved by a 1:1 distribution model.

Comment

Benzene is one of the most important synthons in chemistry. Via electrophilic substitution reactions a vast variety of functionalized derivatives is readily available. The interplay between activating and deactivating substituents as well as the competition and synergism between

inductive and mesomeric effects allows for benzene's seemingly endless functionalization. The later gives rise to a large toolbox of new synthons that can be applied for the production of dyes, medications, catalysts and ligands for novel coordination compounds. At the beginning of a synthesis of a specific aromatic ligand and in continuation of our interest in the structures of halogenated derivatives of benzene [7–16], the structure of the title compound was determined. The structure of the latter has been determined previously [17]; however, the chosen technique of powder diffraction precluded the availability of 3D coordinates. Furthermore, structural information about the title compound as a ligand in a ruthenium coordination compound [18] as well as a co-crystallizate with a derivative of pyridine [19] is available.

The title structure shows the presence of a *para*-substituted derivative of benzene featuring a bromo as well as an iodo substituent. The asymmetric unit consists of half a molecule. The two halogen atoms show orientational disorder over their two positions. The carbon-halogen bond lengths of 1.879(15) Å and 2.064(11)° for bromine and iodine, respectively, are in good agreement with other bromophenyl and iodophenyl compounds whose metrical parameters have been deposited with the Cambridge Structural Database [20]. Intracyclic C–C–C angles are found in a very narrow range of 119.2(5)–120.6(5)°.

In the crystal, dispersive halogen...halogen contacts are observed whose range falls up to more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. These connect the molecules to undulated sheets along [1 0 1/2]. π -Stacking is not a prominent feature in the crystal structure of the title compound as the shortest distance between two centers of gravity was measured at 4.170(3) Å which corresponds to the length of one of the unit cell's axes.

It is pertinent to point out that the cell constants found in the present study deviate from the values obtained by means of powder diffraction [17].

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Research Foundation.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. APEX2; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, A64, 112–122.
4. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, 45, 849–854.
5. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* 2008, 41, 466–470.
6. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, D65, 148–155.
7. Betz R., McClelland C., Glover S. 2-(4-Iodophenoxy)acetamide. *Acta Crystallogr.* 2011, E67, o1928.
8. Betz R., Klüfers P. 1-Bromomethyl-2-iodobenzene. *Acta Crystallogr.* 2007, E63, o4753.
9. Betz R., Klüfers P. 2-Iodobenzaldehyde. *Acta Crystallogr.* 2007, E63, o4879.
10. Schmitt B., Gerber T., Hosten E., Betz R. 4-Bromobenzoyl 4-bromobenzoate monohydrate. *Acta Crystallogr.* 2011, E67, o1662.
11. Betz R., Klüfers P. *N*-(2-Iodophenylmethyl) hexamethylenetetraminium bromide dihydrate. *Acta Crystallogr.* 2007, E63, o4279.
12. Vijesh A. M., Isloor A. M., Gerber T., van Brecht B., Betz R. 1,5-Dibromo-2,4-dimethoxybenzene. *Acta Crystallogr.* 2012, E68, o3479.
13. Betz R., Betzler F., Klüfers P. 2-Bromobenzaldehyde cyanohydrin. *Acta Crystallogr.* 2008, E64, o55.
14. Hosten E. C., Betz R. Crystal structure of 4-bromo-4'-methoxybiphenyl, at 200 K, C₁₃H₁₁BrO. *Z. Kristallogr. NCS* 2015, 230, 29–30.
15. Nogororabanga J., Mama N., Hosten E. C., Betz R. Crystal structure of 3-iodo-4,6-dimethoxy-benzaldehyde, C₉H₉IO₃. *Z. Kristallogr. NCS* 2015, 230, 91–92.
16. Hosten E. C., Betz R. Redetermination of the crystal structure of *p*-bromophenacyl bromide at 200 K – localization of hydrogen atoms, C₈H₆Br₂O. *Z. Kristallogr. NCS* 2015, 230, 59–60.
17. Calvet M. T., Alcobe X., Tauler E., Cuevas Diarte M. A., Haget Y. Crystal data and powder diffraction data for *p*-bromiodobenzene at 293. *Powder Diffr.* 1992, 7, 42–43.
18. Bodes G., Heinemann F. W., Jobi G., Klodwig J., Neumann S., Zenneck U. Halogen atoms as reactive centers for the introduction of functional side chains into (arene)ruthenium(0) complexes. *Eur. J. Inorg. Chem.* 2003, 2003, 281–292.
19. Roper L. C., Prasang C., Whitwood A. C., Bruce D. W. A halogen-bonded complex of DMAP with 4-bromiodobenzene. *CrystEngComm* 2010, 12, 3382–3384.
20. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, B58, 380–388.