

# 7-Bromo-1*H*-indole-2,3-dione

James A. Golen and David R. Manke\*

Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA. \*Correspondence e-mail: dmanke@umassd.edu

Received 13 February 2016

Accepted 15 February 2016

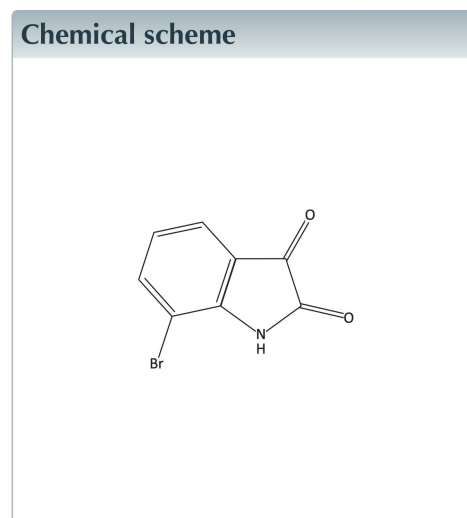
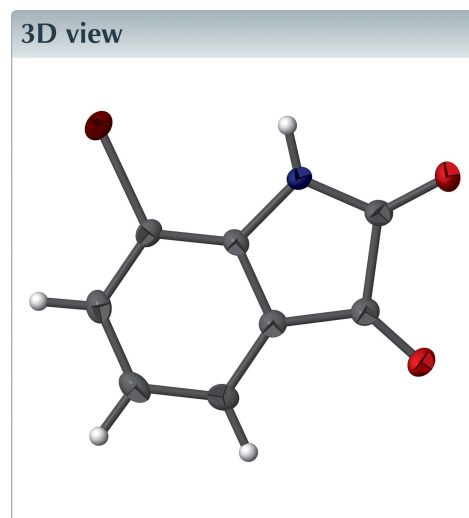
Edited by L. Van Meervelt, Katholieke Universiteit Leuven, Belgium

Keywords: crystal structure; hydrogen bonding; isatins;  $\pi$ - $\pi$  interactions; halogen-oxygen interactions.

CCDC reference: 1453500

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

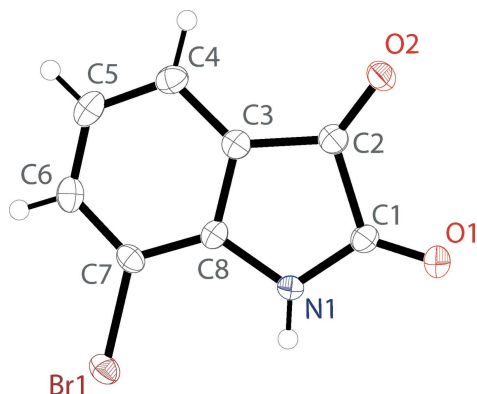
The title compound,  $C_8H_4BrNO_2$ , has a single planar molecule in the asymmetric unit with the non-H atoms possessing a mean deviation from planarity of 0.034 Å. The molecules dimerize in the solid state through N—H $\cdots$ O hydrogen bonds. These dimers are further linked by intermolecular Br $\cdots$ O close contacts of 3.085 (2) Å to yield infinite chains along [20 $\bar{1}$ ]. The nine-membered rings of the isatins stack along the *a* axis, with parallel slipped  $\pi$ - $\pi$  interactions [intercentroid distance = 3.8320 (7) Å, interplanar distance = 3.341 (2) Å and slippage = 1.876 (4) Å].



## Structure description

As part of a continuing study into the structure of halogenated isatins, we report, herein the crystal structure of 7-bromoisatin (Fig. 1). The structure exhibits a near planar molecule with the non-hydrogen atoms possessing a mean deviation from planarity of 0.034 Å, with similar bond lengths and angles as those observed in isatin (Goldschmidt *et al.*, 1950). The structure of the title compound demonstrates intermolecular Br1 $\cdots$ O2 close contacts of 3.085 (2) Å, which are also observed in the structures of 4-bromoisatin and 6-bromoisatin (Huang *et al.*, 2016; Turbitt *et al.*, 2016). No such halogen interactions were observed for 5-bromoisatin, 7-fluoroisatin or 7-chloroisatin (Gurung *et al.*, 2016; Mohamed *et al.*, 2007, 2008; Shankland *et al.*, 2007; Sun *et al.*, 2010).

In the crystals, the molecules dimerize through N1—H1 $\cdots$ O1 hydrogen bonds (Table 1). These couple with the Br $\cdots$ O interactions to form chains along [20 $\bar{1}$ ]. The nine-membered rings of the isatins stack along [100] with parallel slipped  $\pi$ - $\pi$  interactions [inter-centroid distance: 3.8320 (7) Å, inter-planar distance: 3.341 (2) Å, slippage: 1.876 (4) Å]. The packing of the title compound showing the hydrogen bonding is illustrated in Fig. 2.



**Figure 1**  
Molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

### Synthesis and crystallization

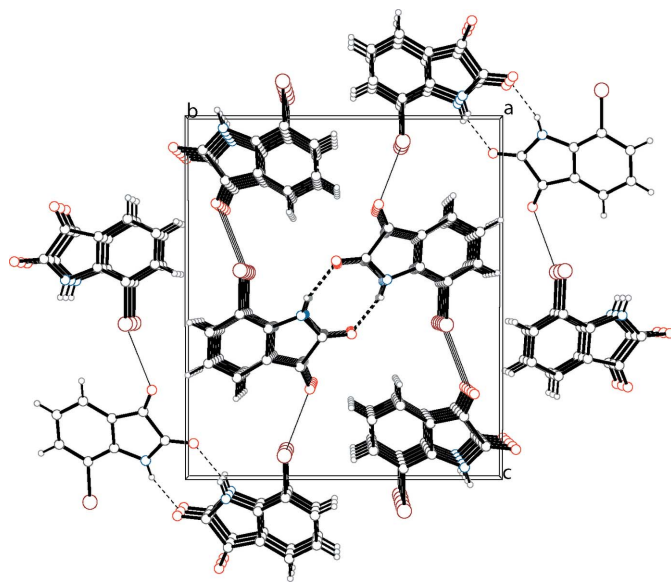
A commercial sample (Matrix Scientific) of 7-bromo-1H-indole-2,3-dione was used for the crystallization. A sample suitable for single-crystal X-ray analysis was grown from the slow evaporation of its methylene chloride solution.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

### Acknowledgements

We greatly acknowledge support from the National Science Foundation (CHE-1429086).



**Figure 2**  
Molecular packing of the title compound along the *a*-axis with hydrogen bonding shown as dashed lines and Br...O interactions shown with thin solid lines.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 <sup>i</sup>	0.85 (2)	2.07 (2)	2.878 (4)	161 (4)

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>8</sub> H <sub>4</sub> BrNO <sub>2</sub>
<i>M<sub>r</sub></i>	226.03
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.8320 (7), 13.072 (2), 15.004 (3)
β (°)	91.917 (7)
<i>V</i> (Å <sup>3</sup> )	751.1 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	5.42
Crystal size (mm)	0.18 × 0.14 × 0.08
Data collection	
Diffractometer	Bruker D8 Venture CMOS
Absorption correction	Multi-scan (SADABS; Bruker, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.178, 0.259
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	17212, 1374, 1231
<i>R<sub>int</sub></i>	0.051
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.602
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.029, 0.072, 1.19
No. of reflections	1374
No. of parameters	112
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.69, -0.37

Computer programs: APEX2 (Bruker, 2014), SAINT (Bruker, 2014), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), OLEX2 (Dolomanov *et al.*, 2009) and publCIF (Westrip, 2010).

### References

- Bruker (2014). APEX2, SAINT, and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Goldschmidt, G. H. & Llewellyn, F. J. (1950). *Acta Cryst.* **3**, 294–305.
- Gurung, S., Golen, J. A. & Manke, D. R. (2016). *IUCrData*, **1**, x160177.
- Huang, H., Golen, J. A. & Manke, D. R. (2016). *IUCrData*, **1**, x160007.
- Mohamed, S., Barnett, S. A. & Tocher, D. A. (2007). *Acta Cryst.* **E63**, o3575.
- Mohamed, S., Barnett, S. A., Tocher, D. A., Price, S. L., Shankland, K. & Leech, C. K. (2008). *CrystEngComm*, **10**, 399–404.
- Shankland, K., Leech, C. K., Mohamed, S., Barnett, S. A. & Tocher, D. A. (2007). *Acta Cryst.* **E63**, o3574.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Sun, J. & Cai, Z.-S. (2010). *Acta Cryst.* **E66**, o25.
- Turbitt, J. R., Golen, J. A. & Manke, D. R. (2016). *IUCrData*, **1**, x152434.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## full crystallographic data

*IUCrData* (2016). **1**, x160268 [https://doi.org/10.1107/S2414314616002686]

7-Bromo-1*H*-indole-2,3-dione

James A. Golen and David R. Manke

7-Bromo-1*H*-indole-2,3-dione*Crystal data*

$C_8H_4BrNO_2$

$M_r = 226.03$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 3.8320$  (7) Å

$b = 13.072$  (2) Å

$c = 15.004$  (3) Å

$\beta = 91.917$  (7)°

$V = 751.1$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 440$

$D_x = 1.999$  Mg m<sup>-3</sup>

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

Cell parameters from 7365 reflections

$\theta = 3.1$ – $25.3$ °

$\mu = 5.42$  mm<sup>-1</sup>

$T = 120$  K

BLOCK, orange

$0.18 \times 0.14 \times 0.08$  mm

*Data collection*

Bruker D8 Venture CMOS  
diffractometer

Radiation source: Mo

TRIUMPH monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2014)

$T_{\min} = 0.178$ ,  $T_{\max} = 0.259$

17212 measured reflections

1374 independent reflections

1231 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 25.3$ °,  $\theta_{\min} = 3.1$ °

$h = -4 \rightarrow 4$

$k = -15 \rightarrow 15$

$l = -18 \rightarrow 18$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.072$

$S = 1.19$

1374 reflections

112 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 1.3045P]$

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

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

$\Delta\rho_{\max} = 0.69$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.37$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.78559 (9)	0.81463 (3)	0.42774 (2)	0.02233 (14)
O1	0.2403 (7)	0.47659 (19)	0.59756 (17)	0.0310 (6)
O2	0.0200 (7)	0.6053 (2)	0.74584 (16)	0.0261 (6)
N1	0.4553 (8)	0.6310 (2)	0.54806 (19)	0.0210 (6)
H1	0.553 (9)	0.614 (3)	0.5007 (18)	0.025*
C1	0.2953 (9)	0.5674 (3)	0.6052 (2)	0.0209 (7)
C2	0.1872 (9)	0.6353 (3)	0.6853 (2)	0.0196 (7)
C3	0.3267 (8)	0.7365 (3)	0.6663 (2)	0.0176 (7)
C4	0.3144 (9)	0.8280 (3)	0.7137 (2)	0.0216 (7)
H4	0.2105	0.8314	0.7703	0.026*
C5	0.4604 (9)	0.9145 (3)	0.6752 (2)	0.0241 (8)
H5	0.4629	0.9776	0.7067	0.029*
C6	0.6015 (9)	0.9095 (3)	0.5915 (2)	0.0211 (7)
H6	0.6955	0.9697	0.5661	0.025*
C7	0.6088 (9)	0.8177 (2)	0.5437 (2)	0.0180 (7)
C8	0.4733 (8)	0.7315 (2)	0.5823 (2)	0.0165 (7)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0209 (2)	0.0246 (2)	0.0218 (2)	−0.00089 (15)	0.00512 (13)	0.00333 (14)
O1	0.0463 (17)	0.0174 (13)	0.0300 (14)	−0.0051 (12)	0.0133 (12)	−0.0004 (11)
O2	0.0329 (14)	0.0209 (13)	0.0251 (14)	0.0032 (11)	0.0116 (11)	0.0045 (10)
N1	0.0292 (16)	0.0165 (15)	0.0179 (15)	0.0000 (13)	0.0091 (12)	−0.0006 (12)
C1	0.0243 (18)	0.0176 (18)	0.0211 (17)	0.0046 (15)	0.0039 (14)	0.0002 (14)
C2	0.0164 (16)	0.0201 (18)	0.0224 (18)	0.0047 (14)	0.0023 (14)	0.0015 (14)
C3	0.0132 (16)	0.0196 (18)	0.0200 (17)	0.0035 (13)	−0.0003 (13)	0.0011 (13)
C4	0.0223 (17)	0.0226 (19)	0.0199 (17)	0.0044 (15)	−0.0006 (14)	−0.0022 (14)
C5	0.0233 (18)	0.0193 (17)	0.029 (2)	0.0017 (15)	−0.0053 (15)	−0.0053 (15)
C6	0.0159 (16)	0.0184 (17)	0.0288 (19)	−0.0015 (14)	−0.0023 (14)	0.0024 (14)
C7	0.0169 (15)	0.0209 (18)	0.0162 (16)	0.0014 (14)	−0.0002 (13)	0.0042 (13)
C8	0.0136 (15)	0.0159 (16)	0.0199 (17)	0.0019 (13)	−0.0014 (13)	−0.0011 (13)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br1—C7	1.888 (3)	C3—C8	1.399 (5)
O1—C1	1.210 (4)	C4—H4	0.9500
O2—C2	1.195 (4)	C4—C5	1.396 (5)
N1—H1	0.846 (19)	C5—H5	0.9500
N1—C1	1.356 (4)	C5—C6	1.385 (5)
N1—C8	1.411 (4)	C6—H6	0.9500
C1—C2	1.562 (5)	C6—C7	1.399 (5)
C2—C3	1.458 (5)	C7—C8	1.377 (5)
C3—C4	1.394 (5)		

C1—N1—H1	126 (3)	C5—C4—H4	121.2
C1—N1—C8	111.0 (3)	C4—C5—H5	119.6
C8—N1—H1	123 (3)	C6—C5—C4	120.8 (3)
O1—C1—N1	128.6 (3)	C6—C5—H5	119.6
O1—C1—C2	125.5 (3)	C5—C6—H6	119.3
N1—C1—C2	106.0 (3)	C5—C6—C7	121.4 (3)
O2—C2—C1	124.1 (3)	C7—C6—H6	119.3
O2—C2—C3	131.0 (3)	C6—C7—Br1	120.3 (2)
C3—C2—C1	104.9 (3)	C8—C7—Br1	121.5 (3)
C4—C3—C2	131.3 (3)	C8—C7—C6	118.2 (3)
C4—C3—C8	121.4 (3)	C3—C8—N1	110.8 (3)
C8—C3—C2	107.1 (3)	C7—C8—N1	128.6 (3)
C3—C4—H4	121.2	C7—C8—C3	120.6 (3)
C3—C4—C5	117.6 (3)		
Br1—C7—C8—N1	3.0 (5)	C2—C3—C8—N1	-3.5 (4)
Br1—C7—C8—C3	-176.6 (2)	C2—C3—C8—C7	176.1 (3)
O1—C1—C2—O2	-4.3 (6)	C3—C4—C5—C6	2.0 (5)
O1—C1—C2—C3	176.9 (4)	C4—C3—C8—N1	180.0 (3)
O2—C2—C3—C4	1.6 (6)	C4—C3—C8—C7	-0.4 (5)
O2—C2—C3—C8	-174.4 (4)	C4—C5—C6—C7	-1.2 (5)
N1—C1—C2—O2	175.1 (3)	C5—C6—C7—Br1	177.4 (3)
N1—C1—C2—C3	-3.7 (4)	C5—C6—C7—C8	-0.5 (5)
C1—N1—C8—C3	1.1 (4)	C6—C7—C8—N1	-179.1 (3)
C1—N1—C8—C7	-178.6 (3)	C6—C7—C8—C3	1.2 (5)
C1—C2—C3—C4	-179.7 (3)	C8—N1—C1—O1	-179.0 (4)
C1—C2—C3—C8	4.3 (3)	C8—N1—C1—C2	1.7 (4)
C2—C3—C4—C5	-176.8 (3)	C8—C3—C4—C5	-1.3 (5)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 <sup>i</sup>	0.85 (2)	2.07 (2)	2.878 (4)	161 (4)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .