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6-Bromo-1*H*-indole-2,3-dione hemihydrate

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Keywords: crystal structure; isatins; hydrogen bonding; π–π interactions; halogen–oxygen interactions.

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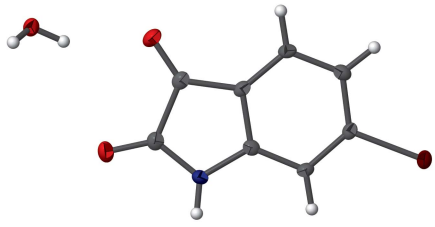
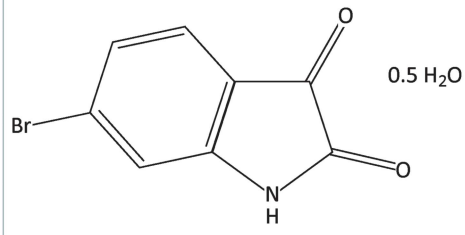
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_8H_4BrNO_2\cdot0.5H_2O$, has a single planar molecule in the asymmetric unit with the non-H atoms having a mean deviation from planarity of 0.028 Å. There is also a half of a water molecule (twofold symmetry) present in the asymmetric unit, which hydrogen bonds with the isatin molecules through O—H···O and N—H···O hydrogen bonds to form a two-dimensional framework in the *ab* plane. There are close Br···O contacts of 2.999 (2) Å to link the layers. The nine-membered rings of the isatin molecules stack along the *a* axis with parallel slipped π–π interactions [inter-centroid distances = 3.6989 (19) and 4.1227 (19) Å].

3D view



Chemical scheme



Structure description

Isatins are a class of compounds that have a wide use in organic synthesis and in pharmaceuticals. We have begun a study on the structure of halogenated isatin compounds, and herein report the crystal structure of 6-bromoisatin, Fig. 1. The structure exhibits a nearly planar molecule with the non-hydrogen atoms having a mean deviation from planarity of 0.028 Å. The bond lengths and angles observed are similar to those seen in isatin (Goldschmidt *et al.*, 1950). The structure also demonstrates an intermolecular Br1···O1 close contact of 2.999 (2) Å. A related I···O interaction is observed in the structure of 6-iodoisatin (Garden *et al.*, 2006), though no such halogen-oxygen interactions are observed for the derivatives of 6-bromoisatin (Ji *et al.*, 2009; Zhao *et al.*, 2012).

In the crystal, there is a half of a water molecule present in the asymmetric unit along with the organic molecule. The water molecule hydrogen bonds with isatin molecules through N1—H1···O3 and O3—H3···O2 hydrogen bonds, Table 1, to form a two-dimensional framework parallel to to the *ab* plane. The nine-membered rings of the isatins stack along *a* with parallel slipped π–π interactions [inter-centroid distances: 3.6989 (19) and 4.1227 (19) Å, inter-planar distances: 3.345 (2) and 3.341 (3) Å, slippage:

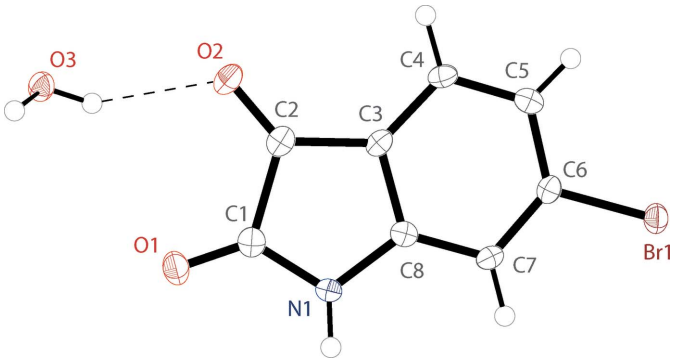


Figure 1
Molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

1.579 (4) and 2.415 (3) Å]. Halogen bonding of the type Br···O links layers along the *c* axis. The packing of the title compound indicating hydrogen bonding is shown in Fig. 2.

Synthesis and crystallization

A commercial sample (Matrix Scientific) of 6-bromo-1*H*-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 acetone solution.

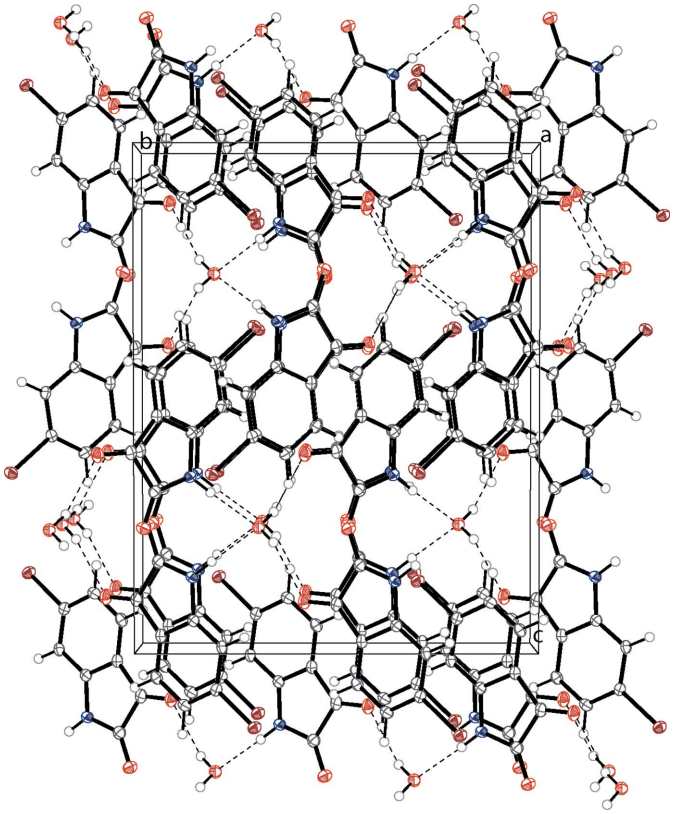


Figure 2
Molecular packing of the title compound with hydrogen bonding shown as dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.83 (2)	2.13 (3)	2.873 (3)	148 (4)
N1—H1···O3^{i}	0.86 (2)	2.02 (2)	2.876 (3)	178 (4)

Symmetry code: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Refinement

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

Acknowledgements

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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.
Garden, S. J., Pinto, A. C., Wardell, J. L., Low, J. N. & Glidewell, C. (2006). *Acta Cryst.* C**62**, o321–o323.
Goldschmidt, G. H. & Llewellyn, F. J. (1950). *Acta Cryst.* **3**, 294–305.
Ji, L., Fang, Q. & Fan, J. (2009). *Acta Cryst.* E**65**, o136.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_4BrNO_2\cdot0.5H_2O$
M_r	235.04
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	120
a, *b*, *c* (Å)	7.4556 (11), 12.9055 (19), 16.334 (2)
β (°)	95.063 (5)
V (Å^3)	1565.5 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.21
Crystal size (mm)	0.2 × 0.2 × 0.1
Data collection	
Diffractometer	Bruker D8 Venture CMOS diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014/4)
T_{min}, T_{max}	0.192, 0.259
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13613, 1429, 1253
R_{int}	0.050
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.604
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.065, 1.09
No. of reflections	1429
No. of parameters	120
No. of restraints	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, −0.39

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

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zhao, M.-X., Chen, M.-X., Tang, W.-H., Wei, D.-K., Dai, T.-L. & Shi, M. (2012). *Eur. J. Org. Chem.* pp. 3598–3606.

full crystallographic data

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6-Bromo-1*H*-indole-2,3-dione hemihydrate

Crystal data

$C_8H_4BrNO_2·0.5H_2O$
M_r = 235.04
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 7.4556 (11) Å
b = 12.9055 (19) Å
c = 16.334 (2) Å
β = 95.063 (5)°
V = 1565.5 (4) Å^3
Z = 8
F(000) = 920
D_x = 1.995 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6603 reflections
θ = 3.2–25.4°
μ = 5.21 mm^{-1}
T = 120 K
Prism, orange
0.2 × 0.2 × 0.1 mm

Data collection

Bruker D8 Venture CMOS diffractometer
Radiation source: Mo
TRIUMPH monochromator
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014/4)
T_{min} = 0.192, T_{max} = 0.259
13613 measured reflections
1429 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 25.4°, θ_{min} = 3.2°
h = −8→8
k = −15→15
l = −18→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.065
S = 1.09
1429 reflections
120 parameters
2 restraints
Hydrogen site location: mixed
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 4.3923P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.40315 (4)	0.20161 (2)	0.35694 (2)	0.01836 (12)

O1	0.7463 (3)	0.47056 (16)	0.75002 (12)	0.0226 (5)
O2	0.8623 (3)	0.57877 (16)	0.60676 (13)	0.0207 (5)
O3	1.0000	0.6924 (2)	0.7500	0.0188 (6)
H3	0.928 (4)	0.655 (2)	0.721 (2)	0.028*
N1	0.6201 (3)	0.3580 (2)	0.65031 (15)	0.0167 (5)
H1	0.586 (5)	0.309 (2)	0.6811 (19)	0.020*
C1	0.7134 (4)	0.4428 (2)	0.67950 (18)	0.0176 (6)
C2	0.7746 (4)	0.4998 (2)	0.60258 (18)	0.0161 (6)
C3	0.7031 (4)	0.4379 (2)	0.53218 (18)	0.0142 (6)
C4	0.7102 (4)	0.4495 (2)	0.44812 (18)	0.0160 (6)
H4	0.7749	0.5054	0.4269	0.019*
C5	0.6213 (4)	0.3780 (2)	0.39562 (18)	0.0172 (6)
H5	0.6249	0.3838	0.3378	0.021*
C6	0.5265 (4)	0.2975 (2)	0.42903 (18)	0.0145 (6)
C7	0.5173 (4)	0.2830 (2)	0.51294 (18)	0.0149 (6)
H7	0.4518	0.2273	0.5340	0.018*
C8	0.6093 (4)	0.3546 (2)	0.56402 (17)	0.0141 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01939 (18)	0.01899 (18)	0.01625 (18)	−0.00163 (12)	−0.00102 (11)	−0.00288 (11)
O1	0.0291 (12)	0.0215 (11)	0.0166 (12)	0.0020 (10)	−0.0014 (9)	−0.0030 (9)
O2	0.0203 (11)	0.0153 (11)	0.0259 (12)	−0.0032 (9)	−0.0017 (9)	−0.0008 (8)
O3	0.0219 (17)	0.0156 (15)	0.0180 (16)	0.000	−0.0038 (12)	0.000
N1	0.0208 (13)	0.0161 (13)	0.0136 (12)	−0.0028 (10)	0.0036 (10)	0.0013 (9)
C1	0.0167 (15)	0.0168 (15)	0.0188 (16)	0.0031 (12)	−0.0006 (12)	−0.0003 (12)
C2	0.0118 (14)	0.0142 (14)	0.0216 (16)	0.0038 (12)	−0.0015 (11)	−0.0002 (12)
C3	0.0102 (14)	0.0123 (14)	0.0197 (15)	0.0006 (11)	−0.0007 (11)	0.0003 (11)
C4	0.0132 (14)	0.0155 (14)	0.0195 (16)	−0.0019 (11)	0.0019 (11)	0.0034 (11)
C5	0.0180 (15)	0.0184 (15)	0.0153 (15)	0.0015 (12)	0.0027 (12)	0.0031 (12)
C6	0.0114 (14)	0.0139 (14)	0.0175 (15)	0.0010 (11)	−0.0017 (11)	−0.0015 (11)
C7	0.0142 (14)	0.0119 (14)	0.0187 (15)	−0.0008 (11)	0.0034 (11)	0.0008 (11)
C8	0.0126 (14)	0.0143 (14)	0.0158 (14)	0.0035 (11)	0.0029 (11)	0.0008 (11)

Geometric parameters (Å, º)

Br1—C6	1.890 (3)	C3—C4	1.387 (4)
O1—C1	1.210 (4)	C3—C8	1.406 (4)
O2—C2	1.209 (4)	C4—H4	0.9500
O3—H3	0.833 (18)	C4—C5	1.388 (4)
N1—H1	0.857 (18)	C5—H5	0.9500
N1—C1	1.361 (4)	C5—C6	1.394 (4)
N1—C8	1.405 (4)	C6—C7	1.391 (4)
C1—C2	1.559 (4)	C7—H7	0.9500
C2—C3	1.462 (4)	C7—C8	1.386 (4)
C1—N1—H1	124 (2)	C5—C4—H4	120.6

C1—N1—C8	111.0 (2)	C4—C5—H5	120.5
C8—N1—H1	125 (2)	C4—C5—C6	119.0 (3)
O1—C1—N1	128.7 (3)	C6—C5—H5	120.5
O1—C1—C2	125.3 (3)	C5—C6—Br1	118.7 (2)
N1—C1—C2	105.9 (2)	C7—C6—Br1	117.5 (2)
O2—C2—C1	123.2 (3)	C7—C6—C5	123.8 (3)
O2—C2—C3	131.5 (3)	C6—C7—H7	122.0
C3—C2—C1	105.3 (2)	C8—C7—C6	116.0 (3)
C4—C3—C2	132.5 (3)	C8—C7—H7	122.0
C4—C3—C8	120.8 (3)	N1—C8—C3	111.2 (2)
C8—C3—C2	106.6 (3)	C7—C8—N1	127.3 (3)
C3—C4—H4	120.6	C7—C8—C3	121.5 (3)
C3—C4—C5	118.8 (3)		

Br1—C6—C7—C8	180.0 (2)	C2—C3—C8—C7	177.0 (3)
O1—C1—C2—O2	−0.2 (5)	C3—C4—C5—C6	0.5 (4)
O1—C1—C2—C3	−179.9 (3)	C4—C3—C8—N1	179.9 (3)
O2—C2—C3—C4	−0.7 (6)	C4—C3—C8—C7	−1.7 (4)
O2—C2—C3—C8	−179.2 (3)	C4—C5—C6—Br1	179.2 (2)
N1—C1—C2—O2	−179.6 (3)	C4—C5—C6—C7	−1.0 (4)
N1—C1—C2—C3	0.7 (3)	C5—C6—C7—C8	0.1 (4)
C1—N1—C8—C3	2.0 (3)	C6—C7—C8—N1	179.4 (3)
C1—N1—C8—C7	−176.4 (3)	C6—C7—C8—C3	1.2 (4)
C1—C2—C3—C4	178.9 (3)	C8—N1—C1—O1	179.0 (3)
C1—C2—C3—C8	0.4 (3)	C8—N1—C1—C2	−1.6 (3)
C2—C3—C4—C5	−177.6 (3)	C8—C3—C4—C5	0.7 (4)
C2—C3—C8—N1	−1.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.83 (2)	2.13 (3)	2.873 (3)	148 (4)
N1—H1···O3^{i}	0.86 (2)	2.02 (2)	2.876 (3)	178 (4)

Symmetry code: (i) $x-1/2, y-1/2, z$.