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

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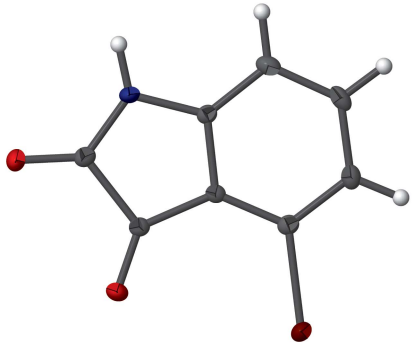
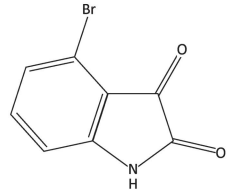
Structural data: full structural data are available from iucrdata.iucr.org

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 0.024 Å. The molecules dimerize in the solid state through N—H···O hydrogen bonds. There are intermolecular Br···O close contacts at 3.0430 (14) Å. The nine-membered rings of the isatins stack along [001] with parallel slipped π–π interactions [inter-centroid distance: 3.7173 (6) Å, inter-planar distance: 3.3110 (8) Å, slippage: 1.6898 (14) Å].

3D view



Chemical scheme



Structure description

Isatins are a class of compounds that are widely used in pharmaceuticals and organic synthesis. Herein we report the crystal structure of 4-bromoisatin as part of a study on the structure of halogenated isatin compounds. The structure exhibits a near planar molecule with the non-hydrogen atoms possessing a mean deviation from planarity of 0.024 Å (Fig. 1). The bond lengths and angles observed are similar to those seen in isatin (Goldschmidt *et al.*, 1950). The structure of the title compound demonstrates an intermolecular Br1···O2^{ii} close contact of 3.0430 (14) Å, symmetry code: (ii) $-x+2, -y, -z+1$. A similar bromo–oxygen interaction is observed in the structure of 6-bromoisatin (Turbitt *et al.* 2016), though no such halogen–oxygen interactions are observed for the derivatives of 4-chloroisatin (Hughes *et al.*, 2010; Wang *et al.*, 2012; Yu *et al.*, 2012)

In the crystal, the molecules dimerize through N1—H1···O1 hydrogen bonds (Table 1). The nine-membered rings of the isatins stack along [001] with parallel slipped π–π interactions [inter-centroid distance: 3.7173 (6) Å, inter-planar distance: 3.3110 (8) Å, slippage: 1.6898 (14) Å]. The packing of the title compound indicating hydrogen bonding is shown in Fig. 2.

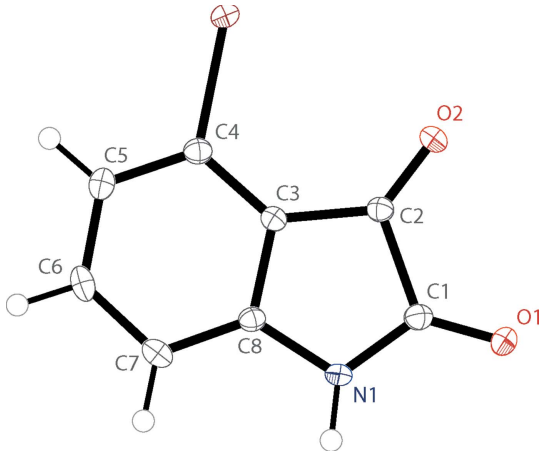


Figure 1
Molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

Synthesis and crystallization

A commercial sample (Matrix Scientific) of 4-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 an acetone/dimethylsulfoxide solution.

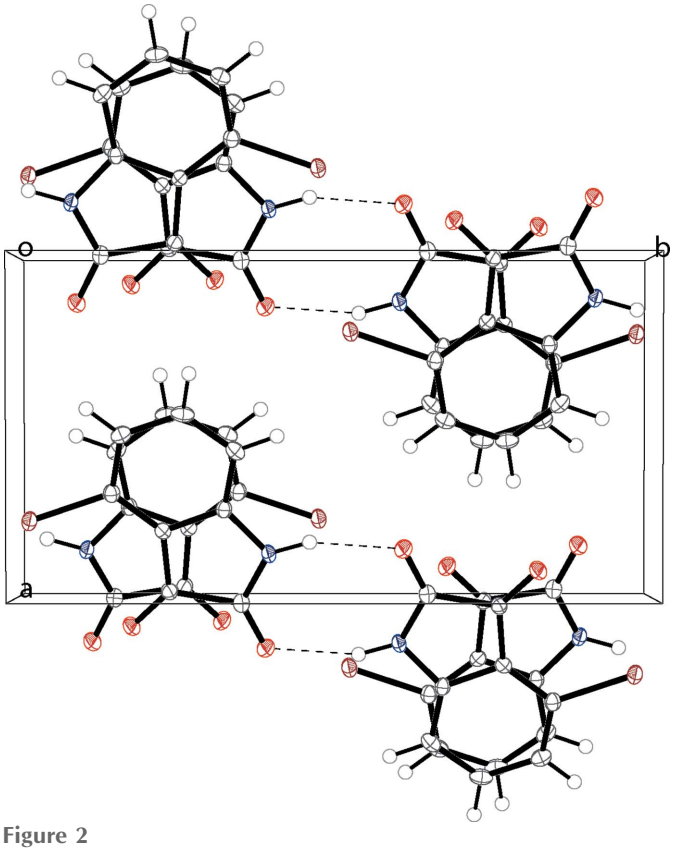


Figure 2
View of the molecular packing of the title compound along the *c* axis with hydrogen bonding shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.91 (2)	2.01 (2)	2.874 (2)	159 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_4BrNO_2$
M_r	226.03
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	7.3655 (11), 13.689 (2), 7.2866 (12)
β (°)	93.378 (5)
V (Å^3)	733.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.55
Crystal size (mm)	0.2 × 0.2 × 0.1
Data collection	
Diffractometer	Bruker D8 Venture CMOS diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.174, 0.259
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12353, 1381, 1285
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.049, 1.08
No. of reflections	1381
No. of parameters	112
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.45

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

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160007 [https://doi.org/10.1107/S2414314616000079]

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Crystal data

$C_8H_4BrNO_2$
M_r = 226.03
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 7.3655 (11) Å
b = 13.689 (2) Å
c = 7.2866 (12) Å
β = 93.378 (5)°
V = 733.4 (2) Å^3
Z = 4
$F(000)$ = 440
D_x = 2.047 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8354 reflections
θ = 3.0–25.6°
μ = 5.55 mm^{-1}
T = 120 K
BLOCK, 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)
T_{min} = 0.174, T_{max} = 0.259
12353 measured reflections
1381 independent reflections
1285 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.6°, θ_{min} = 3.0°
h = −8→8
k = −16→16
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.049
S = 1.08
1381 reflections
112 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 0.4818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.77232 (2)	0.02480 (2)	0.59115 (3)	0.01707 (9)
O1	1.14710 (19)	0.39227 (10)	0.4387 (2)	0.0203 (3)
O2	1.08320 (19)	0.18127 (10)	0.4576 (2)	0.0193 (3)
N1	0.8665 (2)	0.39792 (12)	0.5663 (2)	0.0154 (3)
H1	0.834 (3)	0.4616 (12)	0.575 (3)	0.018*
C1	1.0132 (3)	0.35425 (13)	0.4988 (2)	0.0152 (4)
C2	0.9784 (3)	0.24155 (13)	0.5103 (2)	0.0132 (4)
C3	0.8006 (2)	0.23315 (14)	0.5902 (2)	0.0121 (4)
C4	0.6908 (3)	0.15392 (14)	0.6301 (2)	0.0140 (4)
C5	0.5213 (3)	0.17041 (15)	0.6988 (3)	0.0167 (4)
H5	0.4463	0.1169	0.7285	0.020*
C6	0.4620 (3)	0.26585 (15)	0.7239 (2)	0.0170 (4)
H6	0.3457	0.2762	0.7704	0.020*
C7	0.5677 (3)	0.34683 (15)	0.6832 (3)	0.0160 (4)
H7	0.5253	0.4116	0.6999	0.019*
C8	0.7367 (3)	0.32875 (14)	0.6174 (2)	0.0126 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01757 (13)	0.01081 (13)	0.02316 (13)	−0.00138 (7)	0.00398 (8)	0.00006 (7)
O1	0.0166 (7)	0.0146 (7)	0.0303 (8)	−0.0016 (6)	0.0073 (6)	0.0022 (6)
O2	0.0169 (7)	0.0139 (7)	0.0278 (8)	0.0028 (6)	0.0075 (6)	−0.0008 (6)
N1	0.0152 (8)	0.0096 (8)	0.0217 (8)	0.0017 (6)	0.0039 (6)	−0.0004 (7)
C1	0.0167 (10)	0.0128 (9)	0.0160 (9)	0.0004 (8)	0.0009 (7)	0.0006 (8)
C2	0.0136 (9)	0.0123 (9)	0.0138 (8)	0.0009 (7)	0.0000 (7)	0.0000 (7)
C3	0.0123 (9)	0.0124 (9)	0.0114 (8)	0.0010 (7)	0.0000 (7)	−0.0007 (7)
C4	0.0160 (9)	0.0128 (9)	0.0129 (8)	0.0001 (7)	−0.0001 (7)	−0.0004 (7)
C5	0.0148 (9)	0.0194 (10)	0.0160 (9)	−0.0026 (8)	0.0023 (7)	0.0008 (8)
C6	0.0121 (9)	0.0259 (11)	0.0134 (8)	0.0016 (8)	0.0026 (7)	−0.0017 (8)
C7	0.0165 (10)	0.0171 (10)	0.0144 (9)	0.0046 (8)	0.0003 (7)	−0.0016 (7)
C8	0.0146 (9)	0.0114 (9)	0.0116 (8)	−0.0004 (7)	0.0002 (7)	−0.0007 (7)

Geometric parameters (Å, º)

Br1—C4	1.8933 (19)	C3—C8	1.409 (3)
O1—C1	1.219 (2)	C4—C5	1.391 (3)
O2—C2	1.208 (2)	C5—H5	0.9500
N1—H1	0.908 (16)	C5—C6	1.393 (3)
N1—C1	1.352 (3)	C6—H6	0.9500
N1—C8	1.411 (3)	C6—C7	1.396 (3)
C1—C2	1.567 (3)	C7—H7	0.9500
C2—C3	1.468 (3)	C7—C8	1.382 (3)
C3—C4	1.394 (3)		

C1—N1—H1	132.2 (17)	C5—C4—C3	119.55 (18)
C1—N1—C8	111.58 (16)	C4—C5—H5	120.2
C8—N1—H1	116.0 (17)	C4—C5—C6	119.62 (18)
O1—C1—N1	128.50 (17)	C6—C5—H5	120.2
O1—C1—C2	125.29 (17)	C5—C6—H6	118.9
N1—C1—C2	106.20 (15)	C5—C6—C7	122.26 (18)
O2—C2—C1	123.09 (17)	C7—C6—H6	118.9
O2—C2—C3	132.38 (18)	C6—C7—H7	121.4
C3—C2—C1	104.52 (15)	C8—C7—C6	117.14 (18)
C4—C3—C2	133.28 (18)	C8—C7—H7	121.4
C4—C3—C8	119.37 (17)	C3—C8—N1	110.39 (16)
C8—C3—C2	107.25 (16)	C7—C8—N1	127.55 (18)
C3—C4—Br1	120.15 (14)	C7—C8—C3	122.05 (18)
C5—C4—Br1	120.30 (15)		

Br1—C4—C5—C6	−178.98 (14)	C2—C3—C8—N1	−2.3 (2)
O1—C1—C2—O2	−0.8 (3)	C2—C3—C8—C7	176.91 (16)
O1—C1—C2—C3	−179.57 (18)	C3—C4—C5—C6	1.1 (3)
O2—C2—C3—C4	−1.0 (4)	C4—C3—C8—N1	−179.08 (16)
O2—C2—C3—C8	−177.2 (2)	C4—C3—C8—C7	0.1 (3)
N1—C1—C2—O2	178.72 (18)	C4—C5—C6—C7	−0.3 (3)
N1—C1—C2—C3	−0.04 (19)	C5—C6—C7—C8	−0.5 (3)
C1—N1—C8—C3	2.4 (2)	C6—C7—C8—N1	179.71 (17)
C1—N1—C8—C7	−176.77 (18)	C6—C7—C8—C3	0.6 (3)
C1—C2—C3—C4	177.55 (18)	C8—N1—C1—O1	178.14 (19)
C1—C2—C3—C8	1.40 (18)	C8—N1—C1—C2	−1.4 (2)
C2—C3—C4—Br1	3.3 (3)	C8—C3—C4—Br1	179.07 (13)
C2—C3—C4—C5	−176.79 (18)	C8—C3—C4—C5	−1.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.91 (2)	2.01 (2)	2.874 (2)	159 (2)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.