

5-Bromo-1-(4-bromophenyl)isatin

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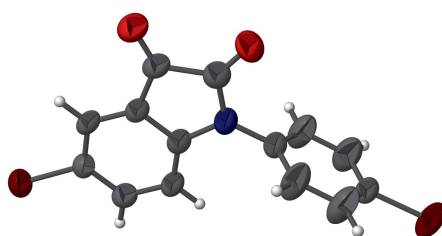
Keywords: crystal structure; isatin; hydrogen bonding.

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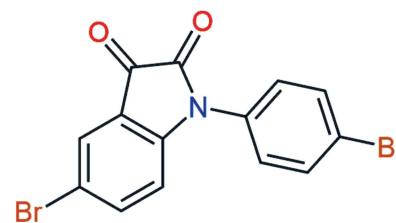
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound [systematic name: 5-bromo-1-(4-bromophenyl)-2,3-dihydro-1*H*-indole-2,3-dione], C₁₄H₇Br₂NO₂, all of the atoms except the C–H groups in the bromobenzene ring lie on a (010) crystallographic mirror plane, with the benzene ring completed by reflection. The dihedral angle between the ring systems is constrained to be 90° by symmetry. In the crystal, molecules are linked by weak C–H···Br interactions in the [001] direction and paired very weak C–H···O interactions to the same acceptor in the [100] direction, generating (010) sheets. Possible extremely weak π – π stacking occurs between the layers.

3D view



Chemical scheme



Structure description

A number of synthetic procedures have been established for obtaining isatins. These include reactions of *N'*-(2-bromoaryl)-*N,N*-dimethylureas with methyl lithium (1.1 molar equivalents) and *tert*-butyllithium (2.2 molar equivalents) at 0°C followed by treatment with carbon monoxide (Smith *et al.*, 1999, 2003), oxidative cyclization of 2'-aminoacetophenones by use of iodine and *tert*-butyl hydroperoxide (TBHP) (Ilangoan & Satish, 2014) or aqueous copper(II) acetate in dimethyl sulfoxide (DMSO) at 80°C for 4–10 h (Ilangoan & Satish, 2013), oxidative amidation of 2'-aminophenylacetylenes in the presence of I₂ in DMSO at 100°C for 5–12 h (Satish *et al.*, 2015), oxidation of indoles with I₂/TBHP in DMSO at 80°C for 24 h (Zi *et al.*, 2014), or reactions of diarylamines with oxalyl chloride (Bryant *et al.*, 1993). As part of our studies in this area, we now describe the synthesis and structure of the title compound.

All the atoms except C10 and C11 lie on a (010) crystallographic mirror plane, with the benzene ring completed by reflection (Fig. 1). The dihedral angle between the ring

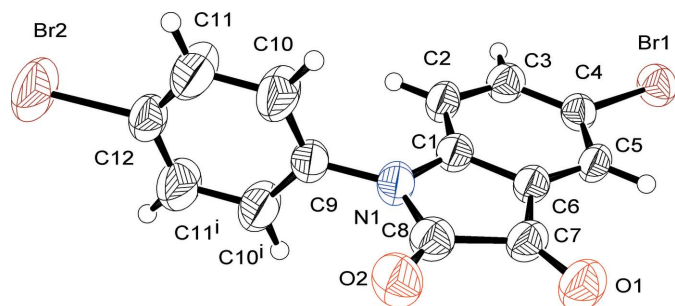


Figure 1
The molecular structure of the title compound showing 50% displacement ellipsoids.

systems is constrained to be 90° by symmetry. In the crystal, the molecules are linked by weak C—H···Br interactions (Table 1) in the [001] direction and paired C—H···O interactions to the same acceptor in the [100] direction, generating (010) sheets (Fig. 2). The layers are stacked along the *b* axis, resulting in possible extremely weak π – π overlap between neighbouring bromoisatin groups (Fig. 3). The centroid-to-centroid distance between adjacent isatin units is 4.431 (2) Å.

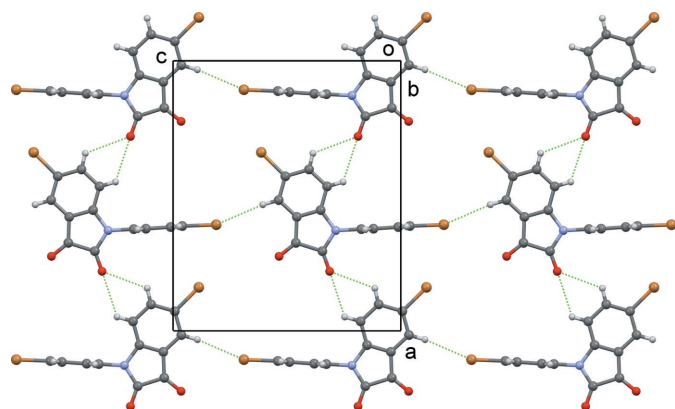


Figure 2
Intermolecular interactions (dashed lines) in a layer of the structure.

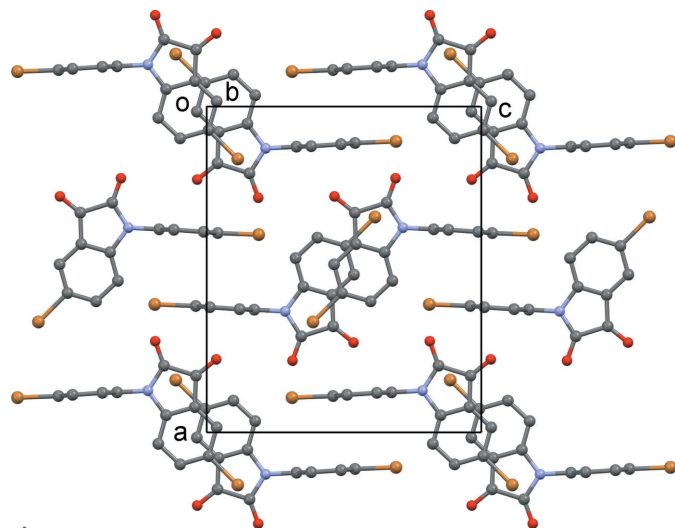


Figure 3
Crystal packing viewed along the *b* axis.

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>
C2—H2···O2 ⁱ	0.93	2.68	3.296 (6)	124
C3—H3···O2 ⁱ	0.93	2.70	3.312 (7)	124
C5—H5···Br2 ⁱⁱ	0.93	2.84	3.763 (5)	173

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $x, y, z + 1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₇ Br ₂ NO ₂
<i>M_r</i>	381.03
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.1160 (14), 6.8728 (6), 12.7492 (11)
<i>V</i> (Å ³)	1324.5 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	6.12
Crystal size (mm)	0.29 × 0.24 × 0.19
Data collection	
Diffractometer	Agilent SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.377, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5624, 1801, 1174
<i>R_{int}</i>	0.041
(sin θ/λ) _{max} (Å ⁻¹)	0.703
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.096, 1.06
No. of reflections	1801
No. of parameters	110
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.53, −0.59

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *CHEM3D Ultra* (Cambridge Soft, 2001).

Synthesis and crystallization

A solution of bis(4-bromophenyl)amine in dichloromethane (DCM) was added dropwise to a stirred, boiling solution of oxalyl chloride (2.0 mole equivalents) in DCM. The mixture was heated under reflux for 1 h and the volatiles were removed under reduced pressure. To the residue obtained, DCM and excess anhydrous aluminium chloride (2.2 molar equivalents in portions) were added and the mixture was refluxed for 1 h. Dichloromethane was removed under reduced pressure and dilute hydrochloric acid (1 *M*) was added and the mixture was stirred for 30 min. The product was extracted with DCM, dried over anhydrous magnesium sulfate and the solvent was removed under vacuum to give the essentially pure product in 91% yield. Recrystallization from acetonitrile solution gave the title compound as orange crystals (m.p. 235–236°C).

Refinement

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

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full crystallographic data

IUCrData (2018). 3, x180426 [https://doi.org/10.1107/S2414314618004261]

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5-Bromo-1-(4-bromophenyl)-2,3-dihydro-1*H*-indole-2,3-dione*Crystal data*

$C_{14}H_7Br_2NO_2$

$M_r = 381.03$

Orthorhombic, *Pnma*

$a = 15.1160$ (14) Å

$b = 6.8728$ (6) Å

$c = 12.7492$ (11) Å

$V = 1324.5$ (2) Å³

$Z = 4$

$F(000) = 736$

$D_x = 1.911$ Mg m⁻³

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

Cell parameters from 1378 reflections

$\theta = 4.3$ – 25.8°

$\mu = 6.12$ mm⁻¹

$T = 293$ K

Block, orange

$0.29 \times 0.24 \times 0.19$ mm

Data collection

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer

ω scans

Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.377$, $T_{\max} = 1.000$

5624 measured reflections

1801 independent reflections

1174 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -14 \rightarrow 20$

$k = -6 \rightarrow 9$

$l = -16 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.096$

$S = 1.06$

1801 reflections

110 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 1.353P]$

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

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

$\Delta\rho_{\max} = 0.53$ e Å⁻³

$\Delta\rho_{\min} = -0.59$ e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0052 (4)

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.

Refinement. All H atoms were placed in calculated positions and refined using a riding model. C—H bonds were fixed at 0.93 Å and $U_{\text{iso}}(\text{H})$ set to 1.2Ueq(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5530 (3)	0.250000	0.3519 (4)	0.0438 (12)
C2	0.4652 (3)	0.250000	0.3236 (4)	0.0476 (12)
H2	0.448493	0.250000	0.253441	0.057*
C3	0.4023 (4)	0.250000	0.4030 (4)	0.0501 (13)
H3	0.342467	0.250000	0.385924	0.060*
C4	0.4276 (3)	0.250000	0.5072 (4)	0.0429 (11)
C5	0.5158 (3)	0.250000	0.5361 (4)	0.0433 (12)
H5	0.532555	0.250000	0.606269	0.052*
C6	0.5780 (3)	0.250000	0.4567 (4)	0.0421 (11)
C7	0.6743 (3)	0.250000	0.4607 (4)	0.0480 (12)
C8	0.7050 (4)	0.250000	0.3443 (5)	0.0516 (13)
C9	0.6233 (3)	0.250000	0.1732 (4)	0.0469 (12)
C10	0.6218 (4)	0.0790 (6)	0.1197 (3)	0.0771 (14)
H10	0.625054	-0.038212	0.155897	0.092*
C11	0.6156 (4)	0.0789 (7)	0.0112 (4)	0.0831 (15)
H11	0.613968	-0.037843	-0.025692	0.100*
C12	0.6118 (3)	0.250000	-0.0401 (4)	0.0535 (14)
N1	0.6283 (3)	0.250000	0.2857 (3)	0.0484 (10)
O1	0.7242 (2)	0.250000	0.5347 (3)	0.0650 (11)
O2	0.7799 (3)	0.250000	0.3124 (3)	0.0666 (11)
Br1	0.33910 (4)	0.250000	0.61293 (5)	0.0564 (2)
Br2	0.60700 (6)	0.250000	-0.18928 (5)	0.0946 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.055 (3)	0.038 (2)	0.039 (3)	0.000	-0.003 (2)	0.000
C2	0.053 (3)	0.055 (3)	0.035 (3)	0.000	-0.005 (2)	0.000
C3	0.050 (3)	0.053 (3)	0.048 (3)	0.000	-0.005 (2)	0.000
C4	0.049 (3)	0.041 (3)	0.039 (3)	0.000	0.003 (2)	0.000
C5	0.058 (3)	0.040 (3)	0.032 (3)	0.000	-0.009 (2)	0.000
C6	0.051 (3)	0.038 (2)	0.037 (3)	0.000	-0.005 (2)	0.000
C7	0.052 (3)	0.047 (3)	0.045 (3)	0.000	-0.011 (2)	0.000
C8	0.055 (4)	0.048 (3)	0.052 (3)	0.000	-0.002 (3)	0.000
C9	0.050 (3)	0.052 (3)	0.039 (3)	0.000	0.001 (2)	0.000
C10	0.135 (4)	0.050 (2)	0.046 (3)	0.007 (3)	-0.007 (3)	0.002 (2)
C11	0.136 (5)	0.063 (3)	0.050 (3)	0.010 (3)	-0.013 (3)	-0.010 (2)
C12	0.049 (3)	0.074 (4)	0.037 (3)	0.000	-0.006 (2)	0.000
N1	0.054 (3)	0.053 (2)	0.038 (3)	0.000	0.001 (2)	0.000
O1	0.059 (2)	0.081 (3)	0.055 (3)	0.000	-0.013 (2)	0.000
O2	0.049 (2)	0.085 (3)	0.066 (3)	0.000	0.0106 (19)	0.000
Br1	0.0597 (4)	0.0578 (3)	0.0518 (4)	0.000	0.0100 (3)	0.000
Br2	0.1138 (7)	0.1280 (7)	0.0420 (4)	0.000	-0.0233 (4)	0.000

Geometric parameters (Å, °)

C1—C2	1.374 (7)	C7—O1	1.208 (6)
C1—C6	1.389 (7)	C7—C8	1.554 (8)
C1—N1	1.418 (6)	C8—O2	1.203 (6)
C2—C3	1.390 (7)	C8—N1	1.379 (7)
C2—H2	0.9300	C9—C10 ⁱ	1.359 (5)
C3—C4	1.382 (7)	C9—C10	1.359 (5)
C3—H3	0.9300	C9—N1	1.436 (6)
C4—C5	1.383 (7)	C10—C11	1.386 (6)
C4—Br1	1.899 (5)	C10—H10	0.9300
C5—C6	1.381 (7)	C11—C12	1.347 (5)
C5—H5	0.9300	C11—H11	0.9300
C6—C7	1.457 (7)	C12—Br2	1.904 (6)
C2—C1—C6	121.0 (5)	C6—C7—C8	105.4 (4)
C2—C1—N1	128.3 (5)	O2—C8—N1	127.4 (6)
C6—C1—N1	110.7 (4)	O2—C8—C7	127.1 (5)
C1—C2—C3	118.0 (5)	N1—C8—C7	105.5 (4)
C1—C2—H2	121.0	C10 ⁱ —C9—C10	119.7 (5)
C3—C2—H2	121.0	C10 ⁱ —C9—N1	120.2 (3)
C4—C3—C2	120.7 (5)	C10—C9—N1	120.2 (3)
C4—C3—H3	119.7	C9—C10—C11	120.2 (4)
C2—C3—H3	119.7	C9—C10—H10	119.9
C3—C4—C5	121.5 (5)	C11—C10—H10	119.9
C3—C4—Br1	119.2 (4)	C12—C11—C10	119.1 (4)
C5—C4—Br1	119.3 (4)	C12—C11—H11	120.5
C6—C5—C4	117.5 (4)	C10—C11—H11	120.5
C6—C5—H5	121.3	C11 ⁱ —C12—C11	121.7 (6)
C4—C5—H5	121.3	C11 ⁱ —C12—Br2	119.1 (3)
C5—C6—C1	121.3 (5)	C11—C12—Br2	119.1 (3)
C5—C6—C7	130.9 (5)	C8—N1—C1	110.6 (4)
C1—C6—C7	107.8 (5)	C8—N1—C9	125.9 (4)
O1—C7—C6	130.6 (5)	C1—N1—C9	123.5 (4)
O1—C7—C8	124.0 (5)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O2 ⁱⁱ	0.93	2.68	3.296 (6)	124
C3—H3 \cdots O2 ⁱⁱ	0.93	2.70	3.312 (7)	124
C5—H5 \cdots Br2 ⁱⁱⁱ	0.93	2.84	3.763 (5)	173

Symmetry codes: (ii) $x-1/2, y, -z+1/2$; (iii) $x, y, z+1$.