5,6-Dibromo-1H-indole-2,3-dione

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The title compound, $C_8H_3Br_2NO_2$, crystallizes with two near planar molecules in the asymmetric unit, with non-H atoms possessing mean deviations from planarity of 0.012 and 0.014 Å. The two molecules are connected by an N—H···O and a C—H···O hydrogen bond. In the crystal, molecules connect through a series of bifurcated N—(H,H)···O hydrogen bonds, forming chains propagating along the [1$\overline{1}\overline{1}$] direction. The molecules are further linked through intermolecular halogen interactions, including a Br···O close contact of 2.9409 (3) Å, and two C—H···Br interactions of 3.777 (3) and 3.845 (3) Å. These interactions link the chains into sheets lying parallel to the (1$\overline{2}$3) plane.

3D view
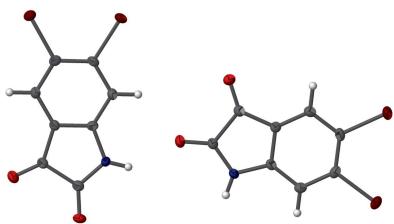
Chemical scheme
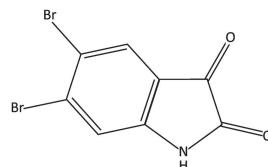
Structure description

In our continued efforts to study the interactions of halogenated isatins in the solid state, we report herein on the crystal structure of the title compound, 5,6-dibromoisatin (Fig. 1). There are two molecules in the asymmetric unit, both are nearly planar, with the non-hydrogen atoms possessing mean deviations from planarity of 0.012 and 0.014 Å. The two molecules are connected by an N—H···O and a C—H···O hydrogen bond (Table 1). The geometrical parameters of the isatin molecules are similar to those observed in the parent compound (Goldschmidt & Llewellyn, 1950). Of note in the structure are Br2···O2 close contacts of 2.9409 (3) Å, with the bromine substituted at the 6 position of the isatin ring. In previous reports, 6-bromoisatin (Turbitt et al., 2016) was found to have a similar interaction, which was also observed in 4-bromoisatin (Huang et al., 2016) and 7-bromoisatin (Golen & Manke, 2016a). Interestingly, Br1, which is at the 5-position of the isatin is not involved in a Br···O interaction. This was also not present in the solid state structure of 5-bromoisatin (Gurung et al., 2016). For comparison, I···O close contacts were observed for both 5-iodoisatin (Garden et al., 2006) and 6-iodoisatin (Golen & Manke, 2016b).
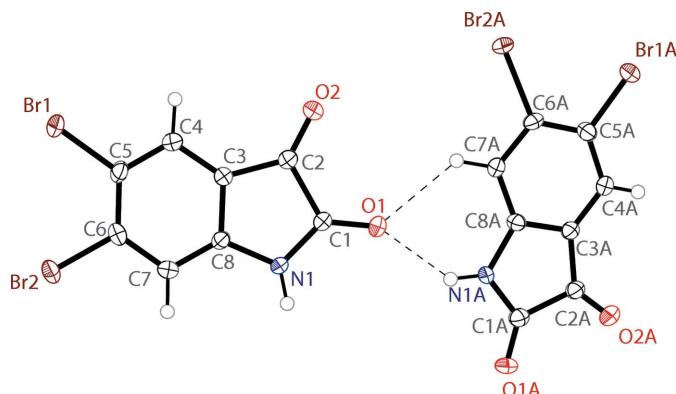
Figure 1
The molecular structure of the two independent molecules of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines (see Table 1).

In the crystal, molecules combine through bifurcated N—(H,H)···O hydrogen bonds (Table 1), resulting in infinite chains along [1$\bar{1}\bar{1}$]. The molecules are further linked through a C—H···O hydrogen bond, two C—H···Br interactions and the aforementioned Br···O interaction, to yield infinite sheets lying parallel to (1$\bar{2}$3); see Table 1 and Fig. 2.

Synthesis and crystallization

A commercial sample (AK Scientific) of 5,6-dibromo-1H-indole-2,3-dione was used for crystallization. Orange block-
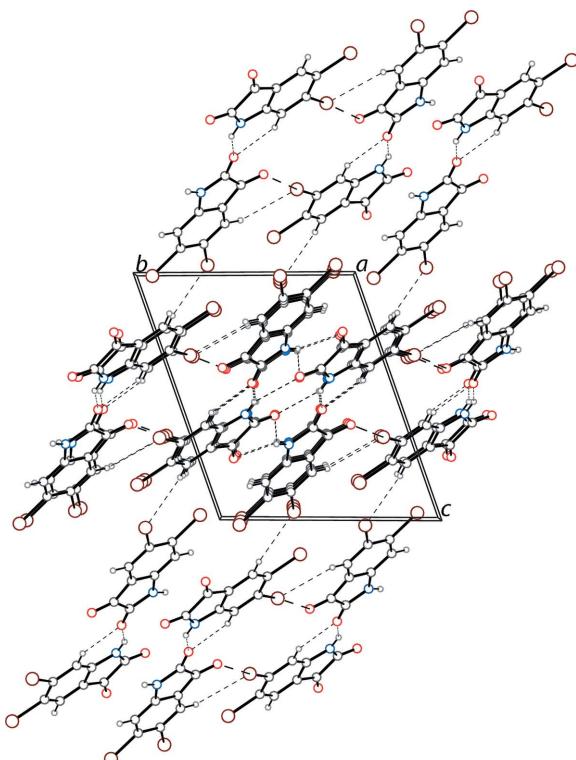
Figure 2
The crystal packing of the title compound, viewed along the a axis. The N—H···O and C—H···Br hydrogen bonds and O···Br interactions are shown as dashed lines (see Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1A^{i}	0.86 (2)	2.34 (3)	2.979 (3)	132 (3)
N1—H1···O2A^{i}	0.86 (2)	2.40 (2)	3.191 (3)	153 (3)
N1A—H1A···O1A^{i}	0.86 (2)	2.40 (2)	3.109 (3)	140 (3)
N1A—H1A···O1	0.86 (2)	2.13 (2)	2.835 (3)	140 (3)
C7A—H7A···O1	0.95	2.31	3.039 (3)	133
C4—H4···Br2A^{ii}	0.95	3.03	3.845 (3)	145
C4A—H4A···Br1^{iii}	0.95	2.94	3.777 (3)	147

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_3Br_2NO_2$
M_r	304.93
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	200
a, b, c (Å)	7.1044 (10), 10.5317 (15), 12.2598 (17)
α, β, γ (°)	108.078 (4), 93.481 (5), 101.484 (4)
V (Å^3)	847.1 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.53
Crystal size (mm)	0.18 × 0.07 × 0.05
Data collection	
Diffractometer	Bruker D8 Venture CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.147, 0.259
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23591, 3116, 2728
R_{int}	0.037
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.047, 1.04
No. of reflections	3116
No. of parameters	241
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.38, −0.59

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

like crystals were grown by slow evaporation of a solution in tetrahydrofuran.

Refinement

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

Funding information

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full crystallographic data

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5,6-Dibromo-1*H*-indole-2,3-dione

Crystal data

$C_8H_3Br_2NO_2$	$Z = 4$
$M_r = 304.93$	$F(000) = 576$
Triclinic, $P\bar{1}$	$D_x = 2.391$ Mg m^{-3}
$a = 7.1044 (10)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.5317 (15)$ Å	Cell parameters from 9890 reflections
$c = 12.2598 (17)$ Å	$\theta = 3.2$–$25.4°$
$\alpha = 108.078 (4)°$	$\mu = 9.53$ mm^{-1}
$\beta = 93.481 (5)°$	$T = 200$ K
$\gamma = 101.484 (4)°$	Block, orange
$V = 847.1 (2)$ Å^3	$0.18 \times 0.07 \times 0.05$ mm

Data collection

Bruker D8 Venture CMOS diffractometer	3116 independent reflections
	2728 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.037$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$\theta_{max} = 25.4°$, $\theta_{min} = 3.0°$
$T_{min} = 0.147$, $T_{max} = 0.259$	$h = -8 \rightarrow 8$
23591 measured reflections	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.020$	Hydrogen site location: mixed
$wR(F^2) = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.04$	
3116 reflections	$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.9509P]$
241 parameters	where $P = (F_o^2 + 2F_c^2)/3$
2 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.38$ e Å^{-3}
	$\Delta\rho_{min} = -0.59$ 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*	$U_{iso}*/U_{eq}$
Br1A	0.47270 (4)	−0.30752 (3)	0.14714 (2)	0.02479 (8)
Br2A	0.22006 (4)	−0.12973 (3)	0.33501 (2)	0.02340 (8)
O1A	1.1378 (3)	0.4127 (2)	0.42202 (19)	0.0299 (5)
O2A	1.1634 (3)	0.1601 (2)	0.24850 (18)	0.0280 (5)
N1A	0.8347 (3)	0.2843 (2)	0.4282 (2)	0.0203 (5)
H1A	0.790 (4)	0.344 (3)	0.478 (2)	0.024*
C1A	1.0112 (4)	0.3079 (3)	0.3919 (2)	0.0207 (6)
C2A	1.0237 (4)	0.1715 (3)	0.2994 (2)	0.0191 (6)
C3A	0.8391 (4)	0.0758 (3)	0.2929 (2)	0.0181 (6)
C4A	0.7644 (4)	−0.0600 (3)	0.2257 (2)	0.0198 (6)
H4A	0.8380	−0.1092	0.1729	0.024*
C5A	0.5791 (4)	−0.1220 (3)	0.2376 (2)	0.0201 (6)
C6A	0.4717 (4)	−0.0480 (3)	0.3155 (2)	0.0187 (6)
C7A	0.5464 (4)	0.0886 (3)	0.3829 (2)	0.0196 (6)
H7A	0.4728	0.1384	0.4354	0.023*
C8A	0.7306 (4)	0.1485 (3)	0.3706 (2)	0.0176 (6)
Br1	−0.16323 (4)	0.65214 (3)	0.96887 (3)	0.03334 (9)
Br2	0.21559 (4)	0.91557 (3)	1.01670 (3)	0.02740 (8)
O1	0.5314 (3)	0.3653 (2)	0.55313 (19)	0.0328 (5)
O2	0.1546 (3)	0.2594 (2)	0.61325 (18)	0.0280 (5)
N1	0.5037 (3)	0.5666 (2)	0.6916 (2)	0.0225 (5)
H1	0.609 (3)	0.621 (3)	0.690 (3)	0.027*
C1	0.4470 (4)	0.4324 (3)	0.6242 (2)	0.0219 (6)
C2	0.2460 (4)	0.3766 (3)	0.6564 (2)	0.0205 (6)
C3	0.2055 (4)	0.4942 (3)	0.7454 (2)	0.0197 (6)
C4	0.0484 (4)	0.5079 (3)	0.8054 (2)	0.0218 (6)
H4	−0.0593	0.4326	0.7917	0.026*
C5	0.0522 (4)	0.6344 (3)	0.8861 (2)	0.0225 (6)
C6	0.2115 (4)	0.7443 (3)	0.9055 (2)	0.0205 (6)
C7	0.3705 (4)	0.7315 (3)	0.8445 (2)	0.0209 (6)
H7	0.4782	0.8066	0.8576	0.025*
C8	0.3639 (4)	0.6048 (3)	0.7644 (2)	0.0184 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1A	0.02325 (15)	0.01670 (14)	0.02779 (16)	0.00039 (11)	0.00439 (11)	0.00042 (12)
Br2A	0.01509 (14)	0.02296 (15)	0.02782 (16)	−0.00174 (11)	0.00595 (11)	0.00550 (12)
O1A	0.0210 (10)	0.0198 (11)	0.0399 (13)	−0.0048 (9)	0.0090 (9)	0.0023 (10)
O2A	0.0210 (10)	0.0254 (11)	0.0353 (12)	0.0038 (8)	0.0126 (9)	0.0060 (9)
N1A	0.0179 (11)	0.0143 (11)	0.0233 (12)	0.0014 (9)	0.0079 (9)	−0.0007 (10)
C1A	0.0167 (13)	0.0196 (14)	0.0247 (15)	0.0027 (11)	0.0032 (11)	0.0065 (12)
C2A	0.0164 (13)	0.0180 (14)	0.0235 (14)	0.0041 (11)	0.0050 (11)	0.0074 (12)
C3A	0.0158 (13)	0.0171 (13)	0.0215 (14)	0.0040 (10)	0.0048 (11)	0.0060 (11)
C4A	0.0186 (13)	0.0195 (14)	0.0203 (14)	0.0049 (11)	0.0063 (11)	0.0041 (12)

C5A	0.0214 (14)	0.0161 (13)	0.0203 (14)	0.0021 (11)	0.0017 (11)	0.0040 (11)
C6A	0.0129 (13)	0.0216 (14)	0.0209 (14)	0.0010 (10)	0.0027 (10)	0.0080 (12)
C7A	0.0176 (13)	0.0201 (14)	0.0199 (14)	0.0048 (11)	0.0057 (11)	0.0042 (12)
C8A	0.0165 (13)	0.0161 (13)	0.0178 (13)	0.0010 (10)	0.0010 (10)	0.0043 (11)
Br1	0.02592 (16)	0.02957 (17)	0.03630 (18)	0.00441 (12)	0.01712 (13)	−0.00192 (14)
Br2	0.02990 (16)	0.01911 (15)	0.02697 (16)	0.00648 (12)	0.00552 (12)	−0.00201 (12)
O1	0.0263 (11)	0.0239 (11)	0.0409 (13)	0.0033 (9)	0.0188 (10)	−0.0007 (10)
O2	0.0247 (11)	0.0195 (11)	0.0319 (12)	−0.0005 (8)	0.0086 (9)	−0.0001 (9)
N1	0.0173 (12)	0.0180 (12)	0.0272 (13)	0.0000 (9)	0.0101 (10)	0.0015 (10)
C1	0.0186 (14)	0.0200 (14)	0.0249 (15)	0.0029 (11)	0.0081 (12)	0.0042 (12)
C2	0.0177 (13)	0.0213 (15)	0.0212 (14)	0.0032 (11)	0.0044 (11)	0.0055 (12)
C3	0.0195 (14)	0.0169 (14)	0.0210 (14)	0.0031 (11)	0.0049 (11)	0.0041 (12)
C4	0.0182 (14)	0.0212 (14)	0.0235 (15)	0.0009 (11)	0.0044 (11)	0.0059 (12)
C5	0.0182 (14)	0.0260 (15)	0.0226 (14)	0.0078 (11)	0.0072 (11)	0.0046 (12)
C6	0.0243 (14)	0.0181 (13)	0.0173 (13)	0.0070 (11)	0.0009 (11)	0.0024 (11)
C7	0.0198 (14)	0.0176 (14)	0.0233 (14)	0.0009 (11)	0.0026 (11)	0.0061 (12)
C8	0.0160 (13)	0.0204 (14)	0.0185 (14)	0.0034 (11)	0.0046 (11)	0.0061 (12)

Geometric parameters (Å, º)

Br1A—C5A	1.893 (3)	Br1—C5	1.895 (3)
Br2A—C6A	1.887 (3)	Br2—C6	1.887 (3)
O1A—C1A	1.214 (3)	O1—C1	1.212 (3)
O2A—C2A	1.210 (3)	O2—C2	1.208 (3)
N1A—H1A	0.855 (17)	N1—H1	0.858 (18)
N1A—C1A	1.358 (3)	N1—C1	1.360 (4)
N1A—C8A	1.407 (3)	N1—C8	1.411 (3)
C1A—C2A	1.553 (4)	C1—C2	1.555 (4)
C2A—C3A	1.467 (4)	C2—C3	1.465 (4)
C3A—C4A	1.385 (4)	C3—C4	1.380 (4)
C3A—C8A	1.400 (4)	C3—C8	1.398 (4)
C4A—H4A	0.9500	C4—H4	0.9500
C4A—C5A	1.386 (4)	C4—C5	1.386 (4)
C5A—C6A	1.402 (4)	C5—C6	1.397 (4)
C6A—C7A	1.392 (4)	C6—C7	1.398 (4)
C7A—H7A	0.9500	C7—H7	0.9500
C7A—C8A	1.374 (4)	C7—C8	1.379 (4)
C1A—N1A—H1A	125 (2)	C1—N1—H1	125 (2)
C1A—N1A—C8A	111.0 (2)	C1—N1—C8	111.0 (2)
C8A—N1A—H1A	124 (2)	C8—N1—H1	124 (2)
O1A—C1A—N1A	129.0 (3)	O1—C1—N1	128.9 (3)
O1A—C1A—C2A	124.7 (2)	O1—C1—C2	124.9 (2)
N1A—C1A—C2A	106.3 (2)	N1—C1—C2	106.2 (2)
O2A—C2A—C1A	122.3 (2)	O2—C2—C1	123.6 (2)
O2A—C2A—C3A	132.8 (3)	O2—C2—C3	131.6 (3)
C3A—C2A—C1A	104.9 (2)	C3—C2—C1	104.8 (2)
C4A—C3A—C2A	132.1 (2)	C4—C3—C2	131.5 (3)

C4A—C3A—C8A	121.0 (2)	C4—C3—C8	121.2 (2)
C8A—C3A—C2A	106.9 (2)	C8—C3—C2	107.3 (2)
C3A—C4A—H4A	120.9	C3—C4—H4	120.9
C3A—C4A—C5A	118.1 (2)	C3—C4—C5	118.1 (3)
C5A—C4A—H4A	120.9	C5—C4—H4	120.9
C4A—C5A—Br1A	119.2 (2)	C4—C5—Br1	117.9 (2)
C4A—C5A—C6A	120.3 (2)	C4—C5—C6	120.4 (3)
C6A—C5A—Br1A	120.5 (2)	C6—C5—Br1	121.7 (2)
C5A—C6A—Br2A	121.4 (2)	C5—C6—Br2	119.9 (2)
C7A—C6A—Br2A	116.9 (2)	C5—C6—C7	121.8 (2)
C7A—C6A—C5A	121.6 (2)	C7—C6—Br2	118.3 (2)
C6A—C7A—H7A	121.3	C6—C7—H7	121.5
C8A—C7A—C6A	117.4 (2)	C8—C7—C6	117.0 (2)
C8A—C7A—H7A	121.3	C8—C7—H7	121.5
C3A—C8A—N1A	110.9 (2)	C3—C8—N1	110.7 (2)
C7A—C8A—N1A	127.6 (2)	C7—C8—N1	127.8 (2)
C7A—C8A—C3A	121.5 (2)	C7—C8—C3	121.5 (2)
Br1A—C5A—C6A—Br2A	0.9 (3)	Br1—C5—C6—Br2	0.1 (4)
Br1A—C5A—C6A—C7A	−179.9 (2)	Br1—C5—C6—C7	−180.0 (2)
Br2A—C6A—C7A—C8A	179.1 (2)	Br2—C6—C7—C8	179.6 (2)
O1A—C1A—C2A—O2A	−0.8 (5)	O1—C1—C2—O2	0.3 (5)
O1A—C1A—C2A—C3A	179.9 (3)	O1—C1—C2—C3	179.8 (3)
O2A—C2A—C3A—C4A	0.0 (6)	O2—C2—C3—C4	−1.7 (6)
O2A—C2A—C3A—C8A	−178.1 (3)	O2—C2—C3—C8	178.7 (3)
N1A—C1A—C2A—O2A	178.5 (3)	N1—C1—C2—O2	−179.1 (3)
N1A—C1A—C2A—C3A	−0.8 (3)	N1—C1—C2—C3	0.3 (3)
C1A—N1A—C8A—C3A	0.5 (3)	C1—N1—C8—C3	−0.7 (3)
C1A—N1A—C8A—C7A	−178.6 (3)	C1—N1—C8—C7	179.8 (3)
C1A—C2A—C3A—C4A	179.2 (3)	C1—C2—C3—C4	179.0 (3)
C1A—C2A—C3A—C8A	1.0 (3)	C1—C2—C3—C8	−0.7 (3)
C2A—C3A—C4A—C5A	−178.0 (3)	C2—C3—C4—C5	179.8 (3)
C2A—C3A—C8A—N1A	−1.0 (3)	C2—C3—C8—N1	0.9 (3)
C2A—C3A—C8A—C7A	178.1 (3)	C2—C3—C8—C7	−179.6 (3)
C3A—C4A—C5A—Br1A	−180.0 (2)	C3—C4—C5—Br1	−179.6 (2)
C3A—C4A—C5A—C6A	0.3 (4)	C3—C4—C5—C6	0.0 (4)
C4A—C3A—C8A—N1A	−179.4 (3)	C4—C3—C8—N1	−178.8 (3)
C4A—C3A—C8A—C7A	−0.3 (4)	C4—C3—C8—C7	0.7 (4)
C4A—C5A—C6A—Br2A	−179.4 (2)	C4—C5—C6—Br2	−179.4 (2)
C4A—C5A—C6A—C7A	−0.2 (4)	C4—C5—C6—C7	0.5 (5)
C5A—C6A—C7A—C8A	−0.2 (4)	C5—C6—C7—C8	−0.4 (4)
C6A—C7A—C8A—N1A	179.3 (3)	C6—C7—C8—N1	179.2 (3)
C6A—C7A—C8A—C3A	0.4 (4)	C6—C7—C8—C3	−0.2 (4)
C8A—N1A—C1A—O1A	179.5 (3)	C8—N1—C1—O1	−179.2 (3)
C8A—N1A—C1A—C2A	0.2 (3)	C8—N1—C1—C2	0.2 (3)
C8A—C3A—C4A—C5A	−0.1 (4)	C8—C3—C4—C5	−0.6 (4)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1*A*ⁱ	0.86 (2)	2.34 (3)	2.979 (3)	132 (3)
N1—H1⋯O2*A*ⁱ	0.86 (2)	2.40 (2)	3.191 (3)	153 (3)
N1*A*—H1*A*⋯O1*A*ⁱ	0.86 (2)	2.40 (2)	3.109 (3)	140 (3)
N1*A*—H1*A*⋯O1	0.86 (2)	2.13 (2)	2.835 (3)	140 (3)
C7*A*—H7*A*⋯O1	0.95	2.31	3.039 (3)	133
C4—H4⋯Br2*A*ⁱⁱ	0.95	3.03	3.845 (3)	145
C4*A*—H4*A*⋯Br1ⁱⁱⁱ	0.95	2.94	3.777 (3)	147

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*+1; (iii) *x*+1, *y*−1, *z*−1.