

## 4,5-Dibromophthalimide forms two centrosymmetric dimers, one linked by C—H···O hydrogen bonds and one by N—H···O hydrogen bonds

Craig Williamson and William T. A. Harrison\*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland  
Correspondence e-mail: w.harrison@abdn.ac.uk

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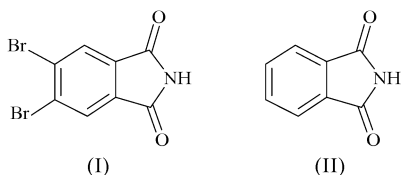
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In the title compound [also called 5,6-dibromoisindole-1,3(2*H*)-dione],  $C_8H_3Br_2NO_2$ , there are two planar molecules in the asymmetric unit. They both form inversion dimers, one *via* N—H···O links and one *via* short near-linear C—H···O links. The dimers are then linked into chains by further N—H···O hydrogen bonds.

### Comment

The title compound, (I), was prepared as an intermediate *en route* to potential novel chromophores. This compound was first reported by Hanack & Stihler (2000).



All the geometrical parameters for (I) (Fig. 1) lie within their expected ranges (Allen *et al.*, 1995). There are two molecules in the asymmetric unit of (I); both are essentially flat, with an r.m.s. deviation from the mean plane of 0.017 Å for the molecule containing C1 and 0.012 Å for the molecule containing C9. The dihedral angle between the two molecules is 7.96 (16)°. The geometries of the six- and five-membered rings in (I) are not significantly different from those in phthalimide, (II) (Zakaria *et al.*, 2002), with the exception of the C1—C2 and C9—C10 bonds [mean = 1.414 (9) Å], which are slightly longer than the equivalent bond of 1.387 (2) Å in (II), perhaps due to steric repulsion between the *ortho* Br atoms.

The crystal packing (Fig. 2) for (I) results in hydrogen-bonded inversion dimers for both molecules (Table 1). For the molecule containing C1, two strong near-linear C6—H6···O2<sup>i</sup> (see Table 1 for symmetry codes) interactions are the linking bonds. The H···O separation of 2.36 Å implies a strong

interaction (Taylor & Kennard, 1982; Desiraju & Steiner, 1999). An  $R_2^2(10)$  supramolecular ring motif (Bernstein *et al.*, 1995) arises. For the C9 species, two more conventional, 'hard', N—H···O bonds fuse the dimeric pair of molecules together. The supramolecular motif that results is an  $R_2^2(8)$  loop. Adjacent C1 and C9 dimers are then linked by the N1—H1···O4 bond, resulting in molecular tapes propagating in [210].

A PLATON (Spek, 2003) analysis of (I) identified two short Br···O interactions, compared with the Bondi (1964) van der Waals separation of 3.37 Å for these atoms. The close Br1···O3<sup>iii</sup> separation of 3.209 (6) Å probably correlates with the N1—H1···O4 hydrogen bond linking the molecules into chains (see Fig. 2). The significance of the second short contact, Br3···O1<sup>iv</sup> [symmetry code: (iv)  $-x, 1-y, -z$ ] of 3.117 (6) Å, which occurs between adjacent [110] chains, is less obvious. A short Br4···Br2<sup>iv</sup> contact of 3.59017 (14) Å (the contact radius is 3.7 Å) is also apparent. Any  $\pi$ — $\pi$  stacking

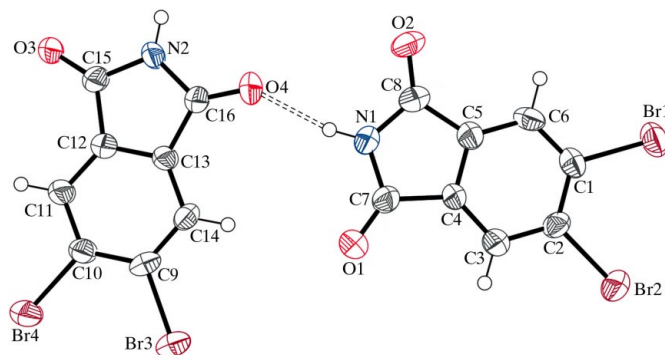


Figure 1

A view of (I), showing 50% probability displacement ellipsoids (H atoms are drawn as small spheres of arbitrary radii). The N—H···O hydrogen bond is shown as a double-dashed line. The C14—H14 group appears to be well aligned to form a C—H···O interaction to O1 (C—H···O = 174°), but the H···O separation of 2.80 Å is longer than the Bondi (1964) contact distance of 2.72 Å, suggesting that, at best, this is a very weak interaction.

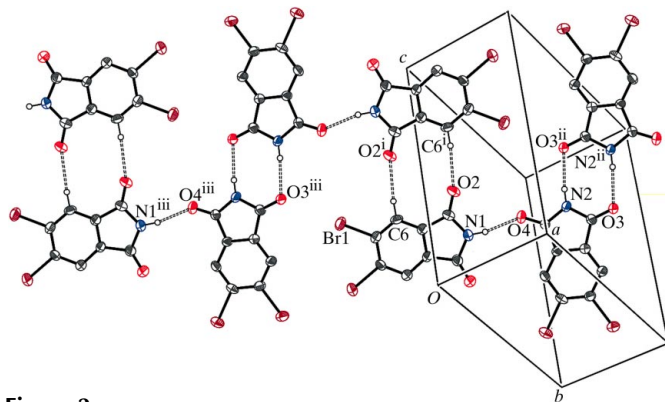


Figure 2

Detail of the packing of (I), showing part of a [110] tape of dimers linked by C—H···O and N—H···O hydrogen bonds (40% probability displacement ellipsoids; H atoms involved in hydrogen bonding are drawn as small spheres of arbitrary radii and other H atoms have been omitted). The hydrogen bonds are shown as double-dashed lines. The short Br1···O3<sup>iii</sup> separation of 3.209 (6) Å is discussed in the *Comment*. [Symmetry codes as in Table 1; additionally (iii)  $x-2, y-1, z$ ]

effects in (I) must be exceedingly weak, with a minimum ring-centroid separation of 4.12 Å.

The crystal structure of (II) with one asymmetric molecule (Zakaria *et al.*, 2002) also shows chains of molecules linked by N—H...O and C—H...O intermolecular interactions, but the C—H...O bonds in (II) (mean H...O = 2.55 Å) are much weaker than those in (I). Although inversion-generated loops featuring C—H...O and N—H...O interactions are present, the chain and overall structures of (I) and (II) are quite different.

### Experimental

Rather than the published method of Hanack & Stihler (2000), a modified Wohrle (Wohrle *et al.*, 1993) synthesis was used to prepare (I). Dibromophthalic anhydride and excess formamide were heated with stirring, at 413 K, without solvent for 5 h. The solution was cooled and filtered, and the residue was washed with cold water. The crude product was recrystallized (50:50 *v/v*, EtOH—H<sub>2</sub>O) and dried overnight in a desiccator (P<sub>2</sub>O<sub>5</sub>). Slow crystallization from dichloromethane yielded colourless blocks of (I) (yield 66%; m.p. 508–513 K). Analysis found: C 31.4, H 0.9, N 4.4, Br 52.1%; C<sub>8</sub>H<sub>3</sub>Br<sub>2</sub>NO<sub>2</sub> requires: C 31.5, H 1.0, N 4.6, Br 52.4%

#### Crystal data

C <sub>8</sub> H <sub>3</sub> Br <sub>2</sub> NO <sub>2</sub>	$V = 899.08 (14) \text{ \AA}^3$
$M_r = 304.94$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 2.253 \text{ Mg m}^{-3}$
$a = 6.7725 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.0759 (10) \text{ \AA}$	$\mu = 8.98 \text{ mm}^{-1}$
$c = 12.3543 (10) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 101.734 (2)^\circ$	Block, colourless
$\beta = 91.725 (2)^\circ$	$0.34 \times 0.29 \times 0.11 \text{ mm}$
$\gamma = 97.031 (2)^\circ$	

#### Data collection

Bruker SMART1000 CCD diffractometer	5395 measured reflections
$\omega$ scans	3154 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	1994 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.076$ , $T_{\max} = 0.373$	$R_{\text{int}} = 0.034$
	$\theta_{\max} = 25.1^\circ$

#### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\max} < 0.001$
3154 reflections	$\Delta\rho_{\max} = 0.96 \text{ e \AA}^{-3}$
235 parameters	$\Delta\rho_{\min} = -0.68 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6...O2 <sup>i</sup>	0.93	2.36	3.274 (9)	167
N1—H1...O4	0.86	1.95	2.793 (8)	167
N2—H2...O3 <sup>ii</sup>	0.86	2.04	2.902 (8)	175

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

All H atoms were placed in calculated positions, with C—H distances of 0.93 Å and N—H distances of 0.86 Å, and refined as riding, with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{carrier})$ .

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3087). Services for accessing these data are described at the back of the journal.

### References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, Vol. C, Section 9.5, pp. 685–706. Dordrecht: Kluwer.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bruker (1999). SMART (Version 5.624), SAINT (Version 6.02A) and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, p. 38. Oxford University Press.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hanack, M. & Stihler, P. (2000). *Eur. J. Org. Chem.* pp. 303–311.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Wohrle, D., Eskes, M., Shigehara, K. & Yamada, A. (1993). *Synthesis (Stuttgart)*, pp. 194–196.
- Zakaria, C. M., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* **C58**, o9–o10.