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

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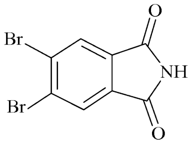
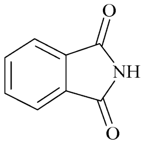
In the title compound [also called 5,6-dibromoisoindole-1,3(2*H*)-dione], $C_8H_3Br_2NO_2$, there are two planar molecules in the asymmetric unit. They both form inversion dimers, one *via* N—H···O links and one *via* short near-linear C—H···O links. The dimers are then linked into chains by further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



(I)



(II)

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^{i} (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^{iii} 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^{iv} [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^{iv} contact of 3.59017 (14) Å (the contact radius is 3.7 Å) is also apparent. Any π–π stacking

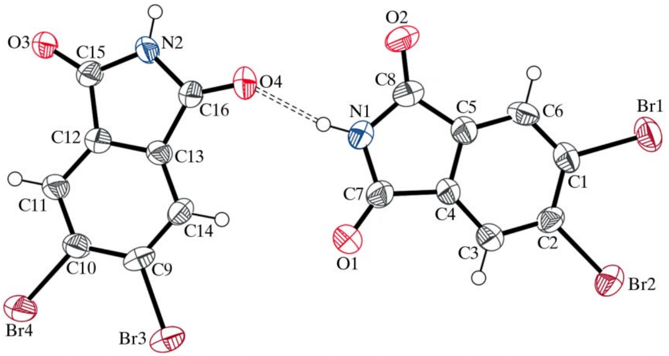


Figure 1
A view of (I), showing 50% probability displacement ellipsoids (H atoms are drawn as small spheres of arbitrary radii). The N—H···O hydrogen bond is shown as a double-dashed line. The C14—H14 group appears to be well aligned to form a C—H···O interaction to O1 (C—H···O = 174°), but the H···O 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.

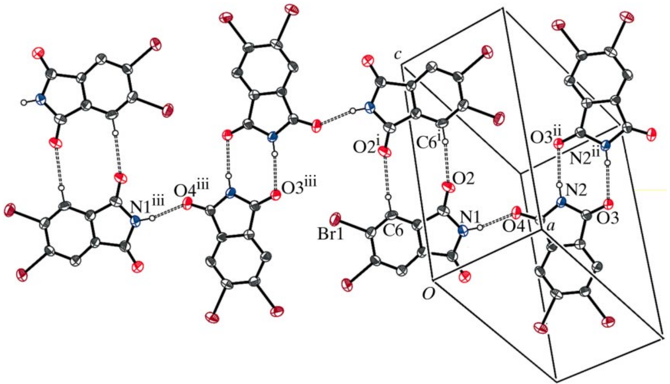


Figure 2
Detail of the packing of (I), showing part of a [110] tape of dimers linked by C—H···O and N—H···O hydrogen bonds (40% probability displacement ellipsoids; H atoms involved in hydrogen bonding are drawn as small spheres of arbitrary radii and other H atoms have been omitted). The hydrogen bonds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

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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_2O) and dried overnight in a desiccator (P_2O_5). 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%; $C_8H_3Br_2NO_2$ requires: C 31.5, H 1.0, N 4.6, Br 52.4%

Crystal data

$C_8H_3Br_2NO_2$
M_r = 304.94
Triclinic, $P\overline{1}$
a = 6.7725 (6) Å
b = 11.0759 (10) Å
c = 12.3543 (10) Å
α = 101.734 (2)°
β = 91.725 (2)°
γ = 97.031 (2)°
V = 899.08 (14) $Å^3$
Z = 4
D_x = 2.253 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 8.98 mm^{-1}
T = 293 (2) K
Block, colourless
0.34 × 0.29 × 0.11 mm

Data collection

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

Refinement

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O2^{i}	0.93	2.36	3.274 (9)	167
N1—H1···O4	0.86	1.95	2.793 (8)	167
N2—H2···O3^{ii}	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_{iso}(H) values of $1.2U_{eq}$(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.

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