# Chains of edge-fused hydrogen-bonded $R_3^3(12)$ rings in N-phenyl-4-nitrophthalimide

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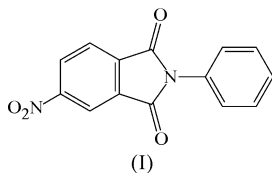
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Molecules of the title compound [systematic name: 5-nitro-1H-isoindole-1,3(2H)-dione], $C_{14}H_8N_2O_4$, adopt a conformation in the solid state which renders them chiral, and they are linked by three distinct types of direction-specific inter-molecular interaction. The molecules are linked by two C—H···O hydrogen bonds [H···O = 2.50 and 2.52 Å, C···O = 3.118 (7) and 3.294 (7) Å, and C—H···O = 123 and 139°] into chains of edge-fused $R_3^3(12)$ rings, which are themselves weakly linked into sheets by a combination of an aromatic π–π stacking interaction and a sheared-parallel carbonyl–carbonyl interaction.

## Comment

As part of a study of the supramolecular arrangements in N-arylnitrophthalimides, the title compound, (I) (Fig. 1), has been prepared and its structure determined. The small and rather simple molecules of (I) are involved in three distinct types of direction-specific intermolecular interaction.

(I)

The dihedral angle in (I) between the C11–C16 aryl ring and the heterocyclic ring is 36.2 (2)°. Associated with this inter-ring twist are two fairly short intramolecular C—H···O contacts (Table 1), which are probably weakly attractive, in view of the likely positive polarization of the aryl H atoms and the negative polarization of the carbonyl O atoms. In addition, the nitro group is not quite coplanar with the adjacent C3–C8 aromatic ring; the dihedral angle between this ring and the C5/N5/O51/O52 plane is 6.4 (3)°. Accordingly, the molecules have no internal symmetry and are chiral. Thus, in space group

$P2_12_12_1$, only one enantiomorph will be present in each crystal, providing that inversion twinning is absent. The bond lengths and angles present no unusual features.

Molecules of (I) are linked into chains by the co-operative action of two C—H···O hydrogen bonds, each individually of only modest strength and each having a nitro O atom as acceptor, as opposed to the more usual carbonyl O atom. Aryl atom C7 in the molecule at $(x, y, z)$ acts as hydrogen-bond donor to nitro atom O51 in the molecule at $(x, -1 + y, z)$, so generating by translation a $C(6)$ (Bernstein et al., 1995) chain running parallel to the [010] direction (Fig. 2). There are four chains of this type passing through each unit cell and they are linked in pairs by the second hydrogen bond. Aryl atom C6 at $(x, y, z)$ acts as donor towards nitro atom O52 in the molecule at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, so forming a second chain running parallel to [010], this time of $C(5)$ type generated by the $2_1$ screw axis along $(\frac{1}{2}, y, \frac{3}{4})$. The combination of these two simple chain motifs generates a chain of edge-fused $R_3^3(12)$ rings (Fig. 2).

The chains of rings are weakly linked into sheets by a combination of an aromatic π–π stacking interaction and a dipolar interaction between carbonyl groups. The C3–C8 and
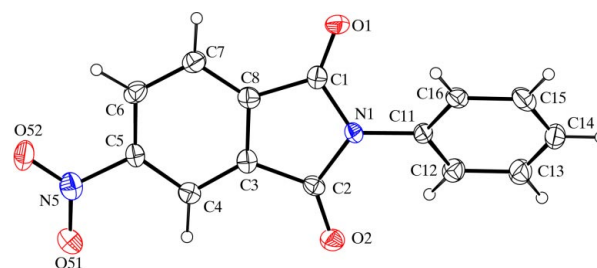


**Figure 1**
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
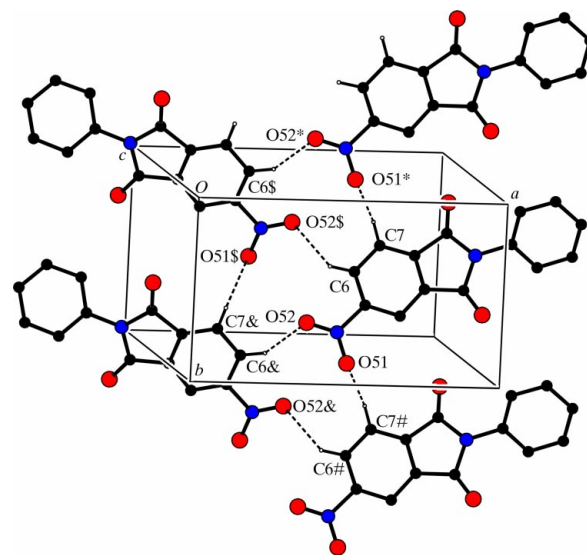


**Figure 2**
Part of the crystal structure of (I), showing the formation of a chain of $R_3^3(12)$ rings along [010]. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, -1 + y, z)$, $(x, 1 + y, z)$, $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

C11–C16 rings in the molecules at $(x, y, z)$ and $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively, are components of the chains of rings generated by the $2_1$ screw axes along $(\frac{1}{2}, y, \frac{3}{4})$ and $(\frac{3}{2}, y, \frac{3}{4})$. These two rings make a dihedral angle of 12.7 (2)°, but their ring-centroid separation of 3.770 (3) Å and interplanar separation of ca 3.6 Å suggest a structurally significant interaction, the effect of which is to link [010] chains into (001) sheets. This linking of [010] chains is reinforced by an attractive dipolar interaction involving the two carbonyl groups. The C1—O1 carbonyl group in the molecule at $(x, y, z)$, which forms part of the chain along $(\frac{1}{2}, y, \frac{3}{4})$, forms a type III sheared-parallel interaction (Allen *et al.*, 1998) with the C2—O2 carbonyl group in the molecule at $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, part of the chain along $(\frac{3}{2}, y, \frac{3}{4})$. The $O1 \cdots C2^i$ distance is 2.957 (5) Å, and the $C1—O1 \cdots C2^i$ and $O1 \cdots C2^i—O2^i$ angles are 118.5 (3) and 107.0 (2)°, respectively [symmetry code: (i) $2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$]. It may be noted here that, although the carbonyl O atoms participate in both of the short intramolecular contacts and in the intermolecular dipolar interactions, they play no part at all in the intermolecular hydrogen bonding.

Two (010) sheets pass through each unit cell, generated by $2_1$ screw axes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, but there are no direction-specific interactions between adjacent sheets.

It is of interest to compare briefly the supramolecular structure of (I) with those of isomeric compounds having the nitro substituent in the *N*-phenyl ring. In *N*-(2-nitrophenyl)phthalimide (Voliotis *et al.*, 1984), pairs of molecules are linked by a single C—H···O hydrogen bond into $R_2^2(14)$ dimers, which are themselves linked into $\pi$-stacked chains, while in *N*-(3-nitrophenyl)phthalimide (Glidewell *et al.*, 2004), the molecules are linked into a three-dimensional framework utilizing four independent C—H···O hydrogen bonds.

## Experimental

A well ground mixture of $PhNH_2$ (0.19 g, 2 mmol) and 4-nitrophthalic anhydride (0.38 g, 2 mmol) was carefully heated at 473 K until effervescence (water evolution) ceased. To the cooled solid residue was added chloroform (10 ml) and activated charcoal. The resulting mixture was heated to reflux, filtered, and the filtrate evaporated. The residue was recrystallized from ethanol to provide compound (I).

*Crystal data*

| | |
|---|---|
| $C_{14}H_8N_2O_4$ | Mo $K\alpha$ radiation |
| $M_r = 268.22$ | Cell parameters from 1554 |
| Orthorhombic, $P2_12_12_1$ | reflections |
| $a = 11.9288$ (6) Å | $\theta = 2.9–27.6°$ |
| $b = 7.0604$ (2) Å | $\mu = 0.12$ mm$^{-1}$ |
| $c = 13.8337$ (7) Å | $T = 120$ (2) K |
| $V = 1165.10$ (9) Å$^3$ | Needle, yellow |
| $Z = 4$ | $0.12 \times 0.04 \times 0.03$ mm |
| $D_x = 1.529$ Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | 1554 independent reflections |
| | 1318 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans | $R_{int} = 0.070$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003) | $\theta_{max} = 27.6°$ |
| $T_{min} = 0.963, T_{max} = 0.997$ | $h = -15 \rightarrow 13$ |
| | $k = -9 \rightarrow 9$ |
| 13 798 measured reflections | $l = -17 \rightarrow 17$ |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C6—H6···O52$^i$ | 0.95 | 2.52 | 3.294 (6) | 139 |
| C7—H7···O51$^{ii}$ | 0.95 | 2.50 | 3.118 (7) | 123 |

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, y - 1, z$.

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0641P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.068$ | $+ 1.6397P]$ |
| $wR(F^2) = 0.171$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.09$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1554 reflections | $\Delta\rho_{max} = 0.39$ e Å$^{-3}$ |
| 181 parameters | $\Delta\rho_{min} = -0.25$ e Å$^{-3}$ |
| H-atom parameters constrained | |

All H atoms were located from difference maps and then treated as riding atoms [C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. In the absence of significant anomalous dispersion, the Flack parameter (Flack, 1983) was inconclusive (Flack & Bernardinelli, 2000). Hence, the Friedel-equivalent reflections were merged prior to the final refinement and it was not possible to determine the absolute configuration of the molecules in the crystal used for the data collection. However, this configuration has no chemical significance.

Data collection: *COLLECT* (Hooft, 1999); cell refinement and data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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