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A three-dimensional hydrogen-bonded framework in *N*-(3-nitrophenyl)phthalimide, and hydrogen-bonded chains of rings in *N*-(3,5-dinitrophenyl)phthalimide, linked into sheets by dipolar interactions

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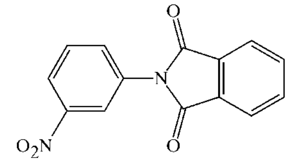
Molecules of *N*-(3-nitrophenyl)phthalimide, $C_{14}H_8N_2O_4$, are linked into a three-dimensional framework by four distinct C—H$\cdots$O hydrogen bonds [H$\cdots$O = 2.35–2.58 Å, C$\cdots$O = 3.105 (5)–3.432 (5) Å and C—H$\cdots$O = 128–167°]. Molecules of *N*-(3,5-dinitrophenyl)phthalimide, $C_{14}H_7N_3O_6$, lie across twofold rotation axes in space group *P*2/*n* and are linked by a single C—H$\cdots$O hydrogen bond [H$\cdots$O = 2.58 Å, C$\cdots$O = 3.410 (2) Å and C—H$\cdots$O = 147°] into chains of rings. These chains are weakly linked into sheets by intermolecular interactions involving short dipolar O$\cdots$N and O$\cdots$C contacts.

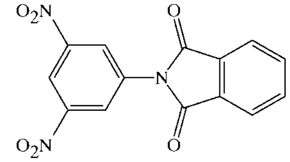
Comment

We recently described (Low *et al.*, 2000) the supramolecular structure of *N*-(2-nitrophenylthio)phthalimide, basing our analysis on the structure determination of Iwasaki & Masuko (1986). In the present paper, we report the molecular and supramolecular structure of two related compounds, *viz*. *N*-(3-nitrophenyl)phthalimide, (I), and *N*-(3,5-dinitrophenyl)phthalimide, (II).

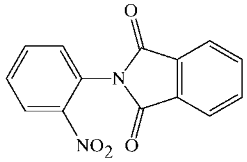
The molecules of (I) (Fig. 1) are linked by a series of C—H$\cdots$O hydrogen bonds (Table 1), thus forming a continuous three-dimensional framework. However, C—H$\cdots\pi$(arene) hydrogen bonds and aromatic π–π stacking interactions are both absent. The framework formation is most readily analysed in terms of the simple one-dimensional substructures generated by the individual hydrogen bonds. The imide O atoms are more active as hydrogen-bond acceptors than the nitro O atoms.



(I)



(II)



(III)

Atom C16 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to imide atom O1 in the molecule at (1 + *x*, *y*, *z*), so generating by translation a *C*(6) chain running parallel to the [100] direction. Atom C7 in the molecule at (*x*, *y*, *z*) acts as a donor to nitro atom O132 in the molecule at ($\frac{1}{2}$ + *x*, 1 − *y*, $\frac{1}{2}$ + *z*), so producing a *C*(10) chain running parallel to [101] and generated by the glide plane at *y* = $\frac{1}{2}$. The combination of the [100] and [101] chains generates a sheet parallel to (010), built from a single type of $R_4^4(29)$ ring (Fig. 2). At the same time, atom C4 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to imide atom O2 in the molecule at (−1 + *x*, 1 + *y*, *z*), so generating by translation a second *C*(6) chain, this time running parallel to the [$1\bar{1}0$] direction (Fig. 3), and these [$1\bar{1}0$] chains suffice to link together all of the (010) sheets. The linking of the sheets is reinforced by the final, rather weak, C—H$\cdots$O hydrogen bond, in which atom C12 at (*x*, *y*, *z*) acts as a donor to imide atom O1 in the molecule at (*x*, −1 + *y*, *z*), producing, again by translation, yet another *C*(6) chain, this time running parallel to [010].

Molecules of (II) (Fig. 4) lie across twofold rotation axes in space group *P*2/*n*. A single C—H$\cdots$O hydrogen bond (Table 2)

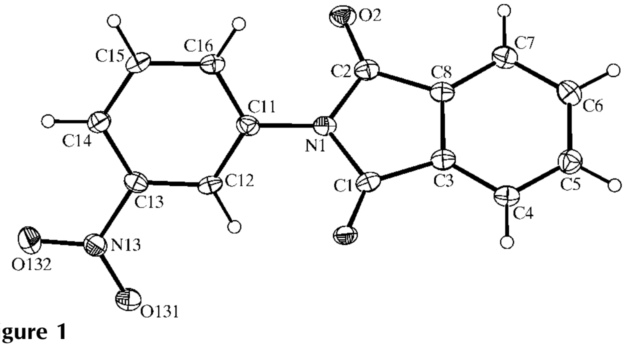


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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links the molecules into a rather elegant chain of rings. C—H$\cdots\pi$(arene) hydrogen bonds are absent, as are aromatic π–π stacking interactions, so the hydrogen-bonded structure of (II) is only one-dimensional.

Atom C12 at (x, y, z) is part of the molecule lying across the twofold axis along ($\frac{1}{4}, y, \frac{3}{4}$). This atom acts as a hydrogen-bond donor to imide atom O1 at ($-\frac{1}{2} - x, y, \frac{3}{2} - z$), which is part of the molecule lying across the twofold axis along ($-\frac{3}{4}, y, \frac{3}{4}$). In turn, atom C12 at ($-\frac{1}{2} - x, y, \frac{3}{2} - z$) acts as a donor to atom O1 at ($\frac{1}{2} - x, y, \frac{3}{2} - z$), which is part of the reference molecule along ($\frac{1}{4}, y, \frac{3}{4}$). In this way, an $R_2^2(12)$ ring is formed, lying across the twofold rotation axis along ($-\frac{1}{4}, y, \frac{3}{4}$), and propagation of this single hydrogen bond by the twofold axes serves to generate a $C(6)[R_2^2(12)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to [100] (Fig. 5). Two such chains, related to one another by the *n*-glide plane, pass through each unit cell.

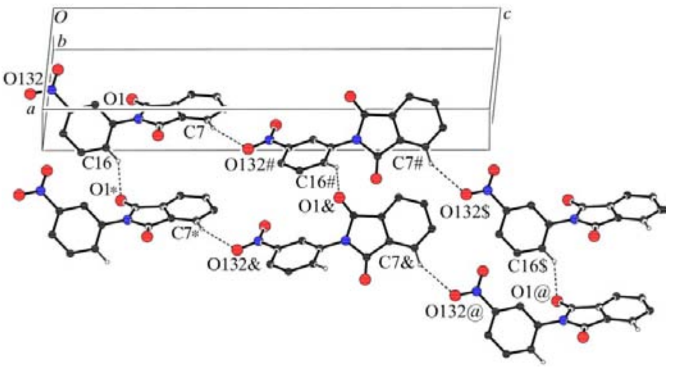

Figure 2

Part of the crystal structure of (I), showing the intersection of the [100] and [101] chains to form a sheet of $R_4^4(29)$ rings. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($), an ampersand (&) or an 'at' sign (@) are at the symmetry positions ($1 + x, y, z$), ($\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$), ($1 + x, y, 1 + z$), ($\frac{3}{2} + x, 1 - y, \frac{1}{2} + z$) and ($2 + x, y, 1 + z$), respectively.

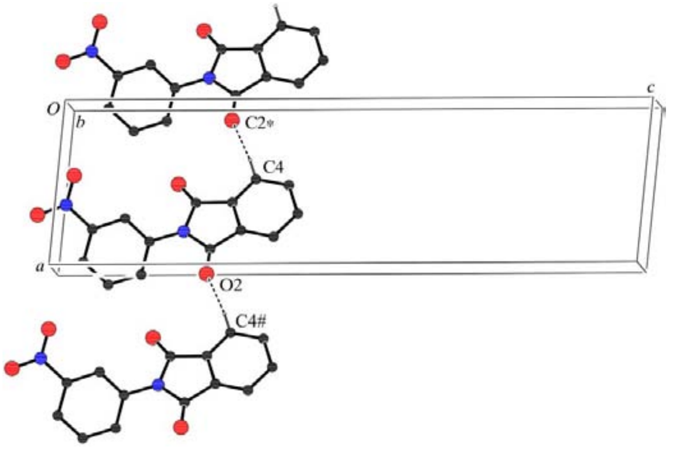

Figure 3

Part of the crystal structure of (I), showing the formation of a $C(6)$ chain along [1$\overline{1}$0]. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($-1 + x, 1 + y, z$) and ($1 + x, -1 + y, z$), respectively.

There are two short intermolecular contacts other than the hydrogen bond, both of which involve a negatively polarized O atom and either a positively polarized nitro N or a positively polarized carbonyl C atom. The non-bonded contact distances are significantly less than the sum of the van der Waals radii for C and N atoms (3.20 Å) or for C and O atoms (3.15 Å; Bondi, 1964), and hence both interactions must be regarded as attractive. Their geometry (Fig. 6) resembles that of the perpendicular interaction between pairs of carbonyl groups (Allen *et al.*, 1998). Imide atom O1 at (x, y, z), which lies in the reference molecule along ($\frac{1}{4}, y, \frac{3}{4}$), is only 2.810 (3) Å from nitro atom N13 at ($-\frac{1}{2} + x, 1 - y, -\frac{1}{2} + z$), which lies in a molecule across the twofold axis along ($-\frac{1}{4}, -y, \frac{1}{4}$); the other imide O atom in the reference molecule, at ($\frac{1}{2} - x, y, \frac{3}{2} - z$), forms a close contact with atom N13 at ($1 - x, 1 - y, 2 - z$), which lies in the molecule across the twofold axis along ($\frac{3}{4}, -y, \frac{5}{4}$), so producing a chain of edge-fused $R_2^2(14)$ rings (Starbuck *et al.*, 1999) along [101]. Nitro atom O31 at (x, y, z) is 2.868 (3) Å from carbonyl atom C1 at ($-\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$), which lies in the molecule across the twofold axis along ($-\frac{1}{4}, -y, \frac{5}{4}$), while atom O131 at ($\frac{1}{2} - x, y, \frac{3}{2} - z$) forms a close contact with atom C1 at ($1 - x, 1 - y, 1 - z$), which lies in the molecule across the twofold axis along ($\frac{3}{4}, -y, \frac{1}{4}$), so producing another chain of edge-fused $R_2^2(14)$ rings, this time along [10$\overline{1}$]. The combined effect of the [101] and [10$\overline{1}$] chains is to link the hydrogen-bonded [100] chains (Fig. 5) into a (010) sheet.

The intramolecular distances in (I) and (II) show no unusual features. The conformations of both molecules are dominated by the twist around the central C—N bond

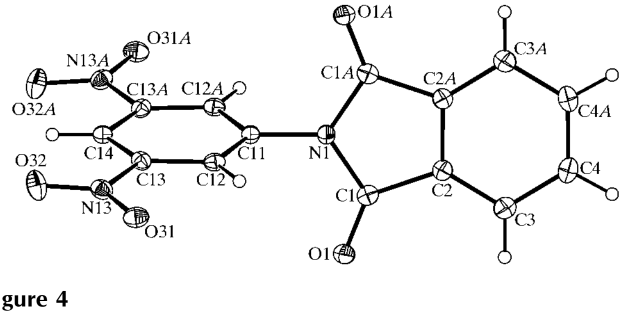

Figure 4

The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms with the suffix '*A*' are at the symmetry position ($\frac{1}{2} - x, y, \frac{3}{2} - z$).

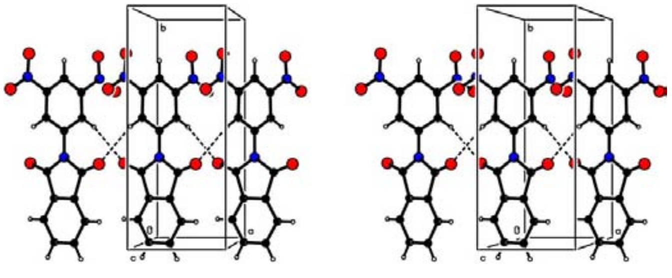

Figure 5

A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded chain of rings parallel to [100].

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between the phthalimide unit and the nitrated aryl ring. The dihedral angles between the heterocyclic ring and the nitrated ring are 45.5 (2)° in (I) and 77.3 (2)° in (II). The molecular symmetries of (I) and (II) are therefore C_1 and C_2, respectively, so that, in each compound, the molecules are chiral, although the crystals of each compound contain equal numbers of the two enantiomorphs. The non-planar conformation of (I) is unexpected in view of the very short *b* axis of the unit cell, while the C—H···O hydrogen bonding in (II) is dependent on the near orthogonality of the rings involved.

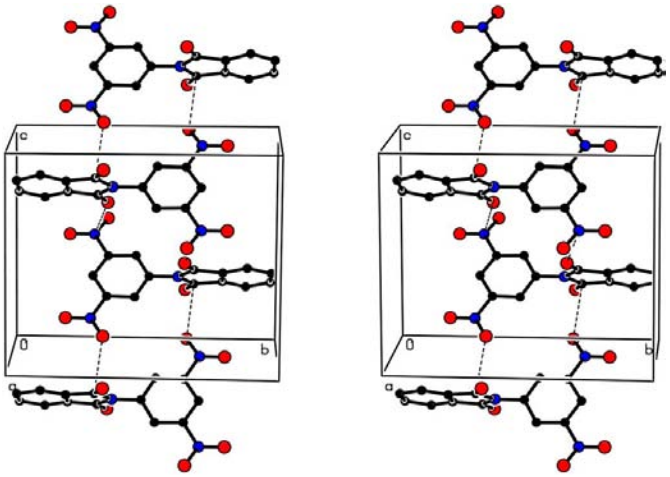

Figure 6
A stereoview of part of the crystal structure of (II), showing the weak non-bonded C···N and C···O interactions (dashed lines) that link the [100] chains.

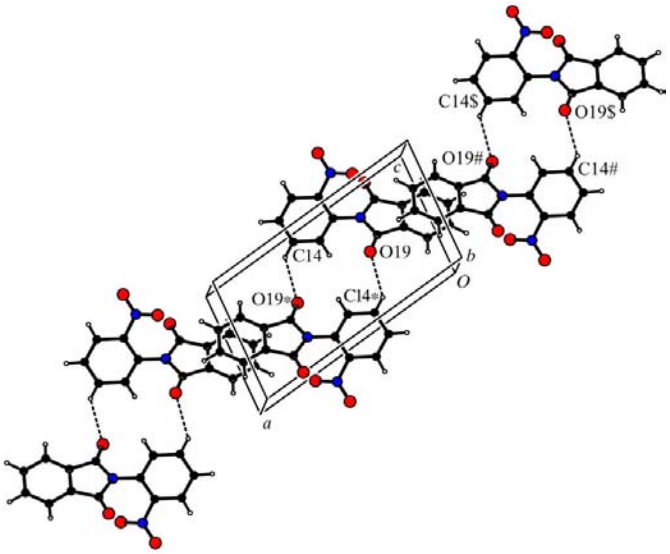

Figure 7
Part of the crystal structure of COMGUG (Voliotis *et al.*, 1984), showing the linking of hydrogen-bonded $R_2^2(14)$ dimers into a π-stacked chain along [100]; the coordinates and the atom labels are those used in the original report. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-x, 1 - y, 1 - z)$ and $(-1 + x, y, z)$, respectively.

It is of interest to compare the supramolecular aggregation in (I) and (II) with that in *N*-(2-nitrophenyl)phthalimide, (III) [Cambridge Structural Database (CSD; Allen, 2002) refcode COMGUG (Voliotis *et al.*, 1984)]. In (III), pairs of molecules are linked by a single C—H···O hydrogen bond into centrosymmetric $R_2^2(14)$ dimers, and these in turn are linked into [100] chains by an aromatic π–π stacking interaction between pairs of aryl rings related by a centre of inversion (Fig. 7). On the other hand, there are no C—H···O hydrogen bonds in the unsubstituted *N*-phenylphthalimide (CSD refcode ZZZAWJ-10; Magomedova *et al.*, 1981).

Experimental

Equimolar quantities of phthalic anhydride and the appropriate nitroaniline were mixed and then heated on a hotplate, in the absence of solvent, until evolution of water ceased. After the mixtures had been cooled to ambient temperature, crystallization of the resulting solids from ethanol solutions gave crystals of (I) and (II) suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

$C_{14}H_8N_2O_4$
M_r = 268.22
Monoclinic, *Pn*
a = 6.6650 (5) Å
b = 3.6962 (3) Å
c = 23.639 (2) Å
β = 95.208 (3)°
V = 579.95 (8) Å^3
Z = 2

D_x = 1.536 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1286 reflections
θ = 3.1–27.4°
μ = 0.12 mm^{-1}
T = 120 (2) K
Plate, colourless
0.20 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.972, T_{max} = 0.997
4904 measured reflections

1286 independent reflections
871 reflections with $I > 2\sigma(I)$
R_{int} = 0.096
θ_{max} = 27.4°
h = −8 → 8
k = −4 → 4
l = −30 → 30

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.116
S = 0.88
1286 reflections
181 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O2^{i}	0.95	2.46	3.393 (5)	167
C7—H7···O132^{ii}	0.95	2.58	3.432 (5)	150
C12—H12···O1^{iii}	0.95	2.55	3.221 (5)	128
C16—H16···O1^{iv}	0.95	2.35	3.105 (5)	136

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

Compound (II)

Crystal data

$C_{14}H_7N_3O_6$
$M_r = 313.23$
Monoclinic, $P2/n$
$a = 5.0936$ (7) Å
$b = 12.6297$ (18) Å
$c = 10.366$ (2) Å
$\beta = 101.335$ (6)°
$V = 653.84$ (18) Å^3
$Z = 2$

$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1470 reflections
$\theta = 3.2$–27.5°
$\mu = 0.13$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.50 × 0.10 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.933$, $T_{\max} = 0.995$
6913 measured reflections

1470 independent reflections
914 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.078$
$\theta_{\max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -16 \rightarrow 16$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.128$
$S = 1.00$
1470 reflections
106 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O1$^{\rm v}$	0.95	2.58	3.410 (2)	147

Symmetry codes: (v) $-\frac{1}{2} - x, y, \frac{3}{2} - z$.

Compounds (I) and (II) are both monoclinic, and the systematic absences permitted *Pn* and *P*2/*n* as possible space groups for each compound. The unit-cell volumes for both were consistent with $Z = 2$, and hence the space group *Pn* (with $Z' = 1$) was selected for (I) and *P*2/*n* (with $Z' = 0.5$) was selected for (II). These choices were confirmed by the subsequent analyses. All H atoms were treated as riding, with C—H distances of 0.95 Å. In the absence of significant anomalous scattering, the Flack (1983) parameter for (I) [value = 1 (2)] was inconclusive (Flack & Bernardinelli, 2000) and the Friedel equivalents were therefore merged prior to the final refinement; the orientation of the structure with respect to the polar axes could not be established.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1199). Services for accessing these data are described at the back of the journal.

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