

N-(4-Nitrobenzoyl)-*N'*-phenylhydrazine: a three-dimensional hydrogen-bonded framework

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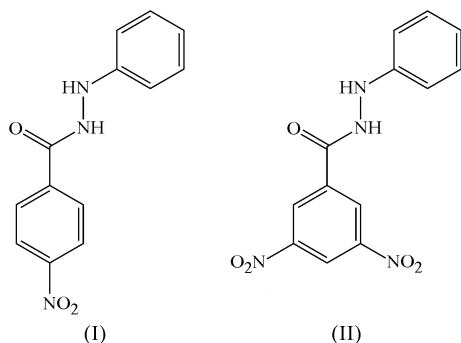
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In the title compound (systematic name: *N*-anilino-4-nitrobenzamide), C₁₃H₁₁N₃O₃, the molecules are linked into a complex three-dimensional framework structure by a combination of two-centre N—H···O and C—H···O hydrogen bonds and a three-centre N—H···(O,N) hydrogen bond.

Comment

As part of our continuing investigation of the supramolecular structures of acylhydrazines and acylhydrazones, we report here the structure of the title compound, (I) (Fig. 1), whose supramolecular structure we compare with that of the related compound *N*-(3,5-dinitrobenzoyl)-*N'*-phenylhydrazine, (II) (Wardell *et al.*, 2006).



The configuration at each of atoms N1 and N2 of (I) is almost coplanar. The central C—C(=O)—N—N unit adopts an almost planar *trans* conformation and the remainder of the molecular conformation can be defined in terms of just four further torsion angles (Table 1). The large C7—N1—N2—C21 torsion angle reflects the tendency of the lone-pair orbitals on N1 and N2 to be nearly orthogonal in order to minimize the corresponding overlap and resonance integrals. The molecules have no internal symmetry in the solid state and are thus

conformationally chiral. The achiral space group ensures that each crystal contains only a single enantiomeric form.

The molecules of compound (I) are linked into a complex three-dimensional framework structure by a combination of one two-centre N—H···O hydrogen bond, one rather asymmetric three-centre N—H···(O,N) hydrogen bond and two independent two-centre C—H···O hydrogen bonds (Table 2). The formation of the sheet is readily analysed in terms of simple substructures.

In the first substructure, amide atom N1 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to amide atom O7 in the molecule at (−1 + *x*, *y*, *z*), so generating by translation a *C*(4) (Bernstein *et al.*, 1995) chain running parallel to the [100] direction (Fig. 2). In addition, atoms N2 and C26 in the molecule at (*x*, *y*, *z*) both act as hydrogen-bond donors to atom O7 in the molecule at (−½ + *x*, ½ − *y*, 1 − *z*), so forming a *C*(5)*C*(7)[*R*₂¹(6)] chain of rings running parallel to the [100] direction and generated by the 2₁ screw axis along (*x*, ¼, ½) (Fig. 3). Atom N2 at (*x*, *y*, *z*) also forms a rather long and probably fairly weak interaction with atom N2 at (−½ + *x*, ½ − *y*,

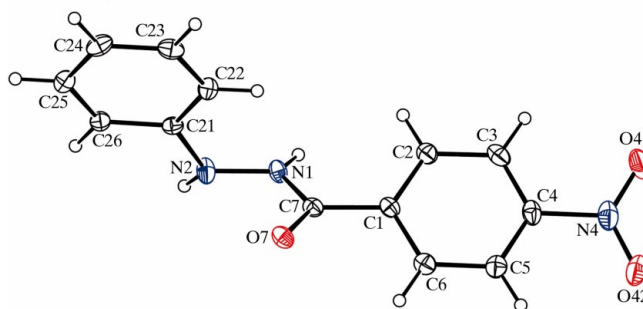


Figure 1

A molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

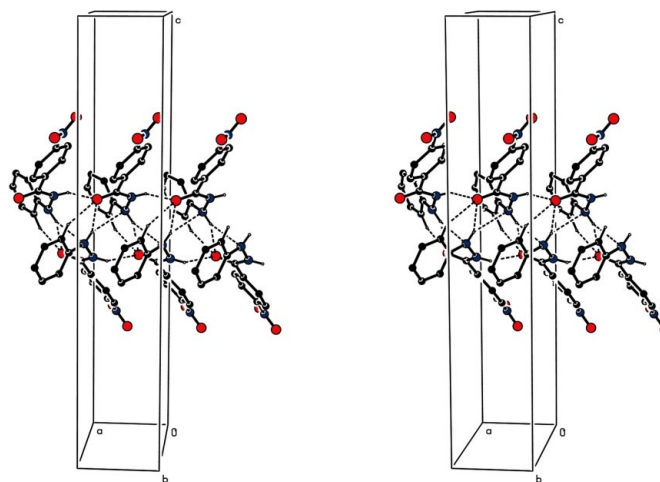


Figure 2

A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings running parallel to the [100] direction. For the sake of clarity, H atoms not involved in the motif have been omitted.

1 - z), so that N2 can be regarded as the donor in an asymmetric but almost planar three-centre N—H...O(N) hydrogen bond. The combination of all these interactions generates a complex chain of rings running parallel to the [100] direction (Fig. 2).

The second substructure is built from a single C—H...O hydrogen bond. Aryl atom C3 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O42 in the molecule at $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$, so forming a $C(5)$ chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$ (Fig. 3).

In combination, the N—H...O and C—H...O hydrogen bonds, which individually generate two independent $C(5)$ helical chains running parallel to [100] and [010], respectively, together generate a $C_2^2(16)$ chain running parallel to the [001] direction (Fig. 4). The combined action of chains parallel to

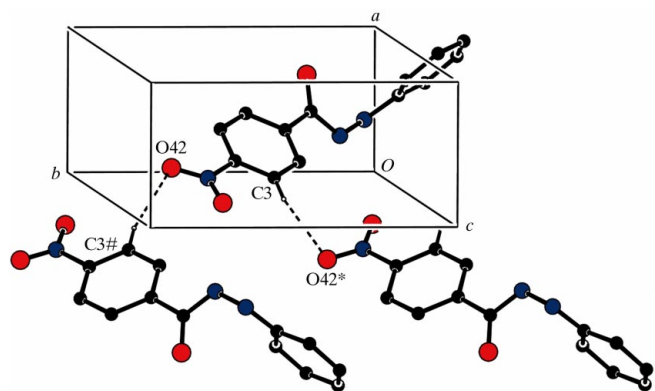


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C(5)$ chain running parallel to the [010] direction. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

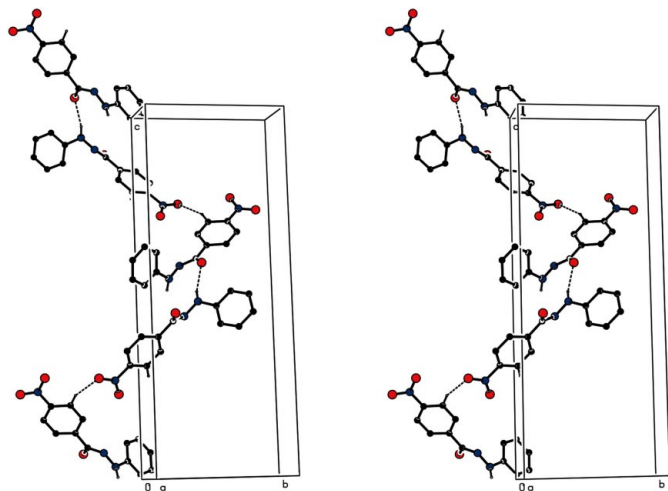


Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C_2^2(16)$ chain running parallel to the [001] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

[100], [010] and [001] (Figs. 2–4) suffices to generate a single three-dimensional framework.

In the related 3,5-dinitro compound, (II) (Wardell *et al.*, 2006), the molecules are again conformationally chiral, with a C7—N1—N2—C21 torsion angle of $84.2(2)^\circ$, but the centrosymmetric space group $P2_1/n$ accommodates equal numbers of the two enantiomeric forms. The molecules are linked into sheets by a combination of three independent two-centre hydrogen bonds, one each of N—H...O(carbonyl), N—H...O(nitro) and C—H...O(carbonyl) types.

Experimental

A solution of 4-nitrobenzoyl chloride (2 mmol) and phenylhydrazine (4 mmol) in 1,2-dichloroethane (25 ml) was heated under reflux for 3 h. The reaction mixture was cooled and the solvent was removed under reduced pressure. The solid product was then recrystallized from ethanol to give the title compound, (I) [m.p. 476–478 K; literature values: 476–478 (Kornet *et al.*, 1986) and 471–473 K (Wang *et al.*, 2005)].

Crystal data

$C_{13}H_{11}N_3O_3$
 $M_r = 257.25$
Orthorhombic, $P2_12_12_1$
 $a = 4.6982(6) \text{ \AA}$
 $b = 9.9532(13) \text{ \AA}$
 $c = 25.719(4) \text{ \AA}$

$V = 1202.7(3) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 $0.32 \times 0.16 \times 0.07 \text{ mm}$

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.975$, $T_{\max} = 0.993$

4443 measured reflections
1477 independent reflections
1314 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.149$
 $S = 1.10$
1477 reflections

172 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$

Table 1

Selected torsion angles ($^\circ$).

C2—C1—C7—N1	27.5 (5)	N1—N2—C21—C22	−11.2 (5)
C1—C7—N1—N2	179.3 (3)	C3—C4—N4—O41	8.7 (6)
C7—N1—N2—C21	81.7 (4)		

Table 2

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1...O7 ⁱ	0.88	2.18	2.926 (4)	143
N2—H2A...O7 ⁱⁱ	0.88	2.14	2.952 (4)	154
N2—H2A...N2 ⁱⁱ	0.88	2.62	3.302 (4)	135
C3—H3...O42 ⁱⁱⁱ	0.95	2.52	3.419 (5)	158
C26—H26...O7 ⁱⁱ	0.95	2.50	3.285 (5)	140

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

The space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and

then treated as riding atoms, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. In the absence of significant resonant scattering, it was not possible to determine the absolute configuration of the molecules in the crystal selected for data collection. However, this has no chemical significance and the Friedel-equivalent reflections were merged prior to the final refinements.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3075). Services for accessing these data are described at the back of the journal.

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