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2-Nitrobenzaldehyde 4-nitrophenylhydrazone

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.101
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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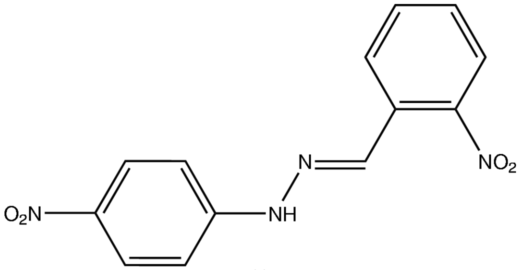
Crystals of the title compound, $C_{13}H_{10}N_4O_4$, were obtained from a condensation reaction of 2-nitrobenzaldehyde and 4-nitrophenylhydrazine. Significantly different C—N(nitro) and N—O bond distances are observed for the *o*- and *p*-nitro groups. The aromatic C—C bonds close to the imino group are longer than the others in the same benzene ring. The overlapped arrangement of nearly parallel benzene rings from neighboring molecules and centroid-to-centroid distance of 3.9370 (9) Å suggest π–π stacking.

Comment

Phenylhydrazone has recently attracted our attention as its derivatives show potential application in the field of biochemistry (Okabe *et al.*, 1993). A series of phenylhydrazones formed by nitrophenylhydrazine and various aldehydes were prepared in Shan's laboratory (Shan *et al.*, 2003). Recently, the title phenylhydrazone, (I), containing two nitrophenyl groups, has been prepared and its structure is presented here for comparison with those reported previously.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule of (I) is planar except for the N4-nitro group. Two nitrophenyl groups are in the molecule of (I). Significantly different geometrical parameters are observed in the two nitro groups. The C—N(nitro) bond in the *o*-nitro group is longer

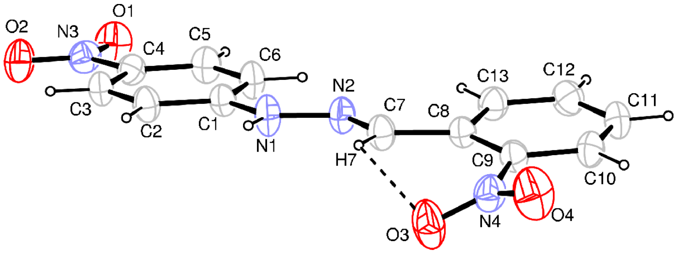


Figure 1
The molecular structure of (I) with 40% probability displacement ellipsoids. The dashed line indicates an intramolecular hydrogen bond.

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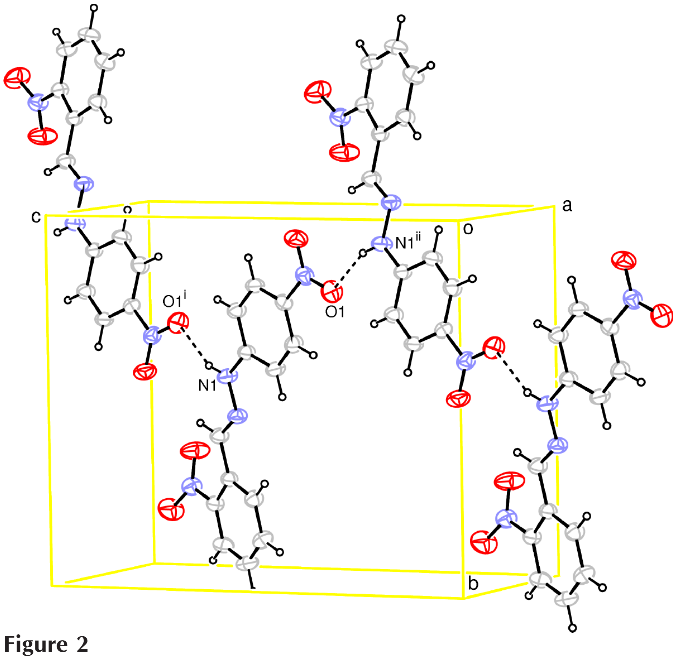

Figure 2
The hydrogen-bonded (dashed lines) supramolecular chain in the unit cell. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$].

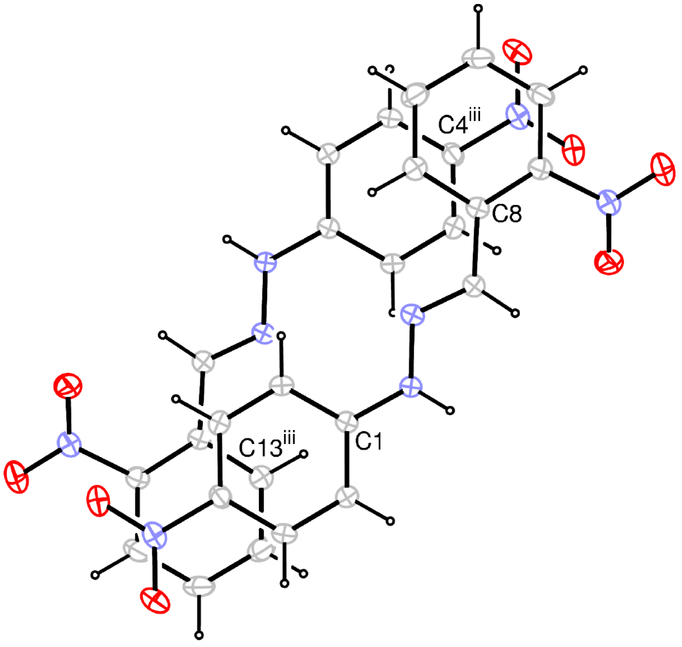

Figure 3
The overlapped arrangement of nearly parallel benzene rings from neighboring molecules, suggesting π–π stacking. [Symmetry code: (iii) $1-x, 1-y, 1-z$].

than that in *p*-nitro group by 0.031 (3) Å (Table 1). Correspondingly the N—O bonds in the *o*-nitro group are significantly shorter than those in the *p*-nitro group. The longer N4—C9 bond implies typical single-bond character and is consistent with the larger dihedral angle of 23.72 (19)° between the N4-nitro plane and the C8-benzene plane. The tilt of the N4-nitro group with respect to the C8-benzene plane may be due to the weak intramolecular C7—H7$\cdots$O3 hydrogen bonding (Table 2).

The C—N(imino) bond is appreciably shorter than the C—N(nitro) bonds and suggests a partial double bond between the imino N atom and the benzene ring. The C1—C2 and C1—C6 bonds, both close to the imino group, are appreciably longer than other aromatic C—C bonds in the same benzene ring. This agrees with the situation found in a 4-nitrophenylhydrazone (Shan *et al.*, 2003) and in a 2,4-dinitrophenylhydrazone reported previously (Bolte & Dill, 1998; Ohba, 1996; Borwick *et al.*, 1997; Naidu *et al.*, 1996; Fan *et al.*, 2004).

The molecules are linked to each other *via* an intermolecular N—H$\cdots$O hydrogen bond between the imino and nitro groups to form a supramolecular chain, extending along the [101] direction, as shown in Fig. 2.

The partially overlapped arrangement of nearly parallel C1-benzene and C8^{iii}-benzene rings is illustrated in Fig. 3. The dihedral angle and centroid-to-centroid distance between the C1-benzene and C8^{iii}-benzene rings are 7.49 (7)° and 3.9397 (9) Å, respectively [symmetry code: (iii) $1-x, 1-y, 1-z$]. The distances of C13^{iii} to the C1-benzene plane and C4^{iii} to the C8-benzene plane are 3.5887 (17) and 3.4640 (16) Å, respectively. These findings suggest the existence of π–π stacking between the benzene rings in the crystal structure.

Experimental

4-Nitrophenylhydrazine (0.31 g, 2 mmol) was dissolved in ethanol (10 ml), then acetic acid (0.2 ml) was added slowly to the ethanol solution with stirring. The solution was heated at 333 K for several minutes until the solution cleared. 2-Nitrobenzaldehyde (0.30 g, 2 mmol) was then dropped slowly into the solution, and the mixture was kept at 333 K with continuous stirring for 30 min. After the solution had cooled to room temperature, fine red crystals appeared and were separated form the solution and washed with cold water. Recrystallization twice, from ethanol and acetone, respectively, gave well shaped single crystals.

Crystal data

$C_{13}H_{10}N_4O_4$
$M_r = 286.25$
Monoclinic, $P2_1/n$
$a = 7.2570$ (7) Å
$b = 12.0869$ (11) Å
$c = 14.4455$ (11) Å
$\beta = 93.465$ (2)°
$V = 1264.77$ (19) Å^3
$Z = 4$

$D_x = 1.503$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9018 reflections
$\theta = 2.5$–25.0°
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Prism, red
$0.31 \times 0.30 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: none
9588 measured reflections
2322 independent reflections

1936 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 25.5$°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.101$
$S = 1.06$
2322 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.2408P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected bond lengths (Å;).

O1—N3	1.2397 (16)	N4—C9	1.4706 (19)
O2—N3	1.2217 (16)	C1—C2	1.398 (2)
O3—N4	1.2120 (17)	C1—C6	1.4002 (19)
O4—N4	1.2145 (16)	C2—C3	1.3680 (19)
N1—N2	1.3506 (16)	C3—C4	1.386 (2)
N2—C7	1.2750 (17)	C4—C5	1.383 (2)
N3—C4	1.4390 (17)	C5—C6	1.367 (2)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1^{i}	0.86	2.10	2.9193 (16)	160
C7—H7⋯O3	0.93	2.27	2.787 (2)	114

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and included in the final cycles of refinement in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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