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3,4-Dimethoxybenzaldehyde 4-nitrophenylhydrazone

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.087
Data-to-parameter ratio = 8.5

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

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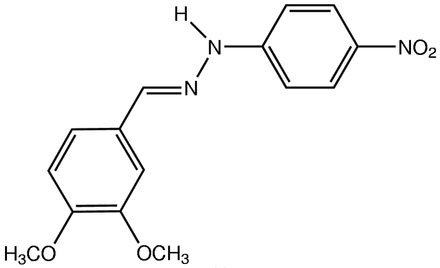
The crystals of the title compound, $C_{15}H_{15}N_3O_4$, were obtained from a condensation reaction of 2,4-dimethoxybenzaldehyde and 4-nitrophenylhydrazine. The molecule displays a nearly planar structure. The overlapped arrangement of nearly parallel benzene rings of neighboring molecules and centroid–centroid distance of 3.5642 (16) Å suggest π–π stacking. Adjacent molecules are linked to each other *via* N—H···O hydrogen bonds to form a helical supramolecular structure.

Comment

Phenylhydrazone has recently attracted our attention as its derivatives showed potential application in biochemistry (Okabe *et al.*, 1993). A series of phenylhydrazones formed from nitrophenylhydrazine and various aldehydes was prepared in our laboratory (Shan *et al.*, 2003). Recently, the 4-nitrophenylhydrazone, (I), containing two benzene rings, 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 essentially planar. While the nitro group is coplanar with the C1-containing benzene ring [maximum atomic deviation of 0.039 (2) Å for atom C4], both methoxy groups are coplanar with the C8-containing benzene ring [maximum atomic deviation of 0.045 (2) Å for atom C14]. The C1-ring is nearly coplanar with the C8-ring, the dihedral angle being 8.05 (12)° between the two mean planes.

The C—N(imine) bond is significantly shorter than the C—N(nitro) bond; the difference of 0.088 (5) Å implies a partial double bond between the atom N2 and the C1-benzene ring. This results in the overlap of the non-bonding orbital of the imine N with the π orbitals of the arene, contributing to the iminocyclohexadiene resonance structure. Thus, both C4—C3 and C4—C5 are appreciably longer than C2—C3 and C5—C6 in the same benzene ring (Table 1). This is similar to the situation found in other phenylhydrazones (Bolte & Dill, 1998; Borwick *et al.*, 1997; Naidu *et al.*, 1996; Ohba, 1996; Shan *et al.*, 2002, 2003).

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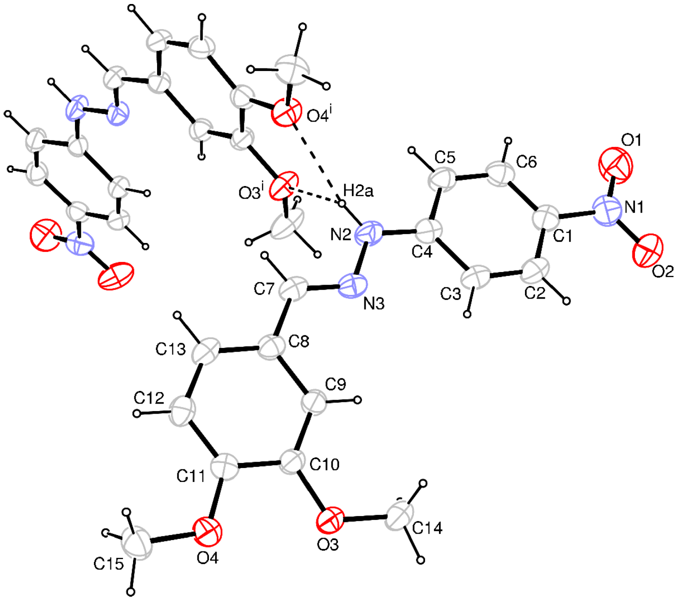

Figure 1

Two molecules of (I) drawn with 30% probability displacement ellipsoids. Dashed lines indicate intermolecular hydrogen bonds [symmetry code: (i) $y+1, 1-x, z-\frac{1}{4}$].

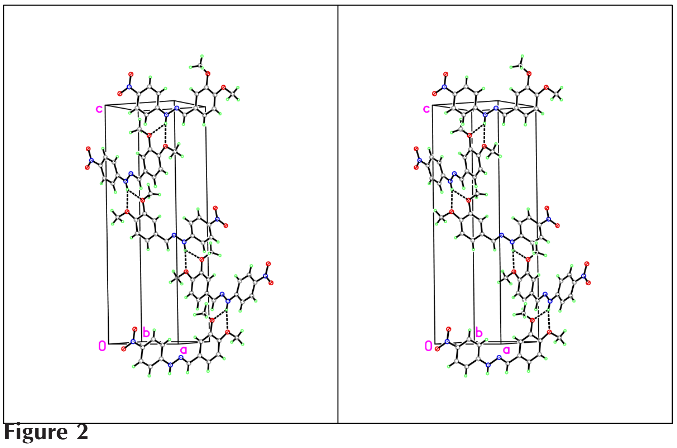

Figure 2

Stereoview of the crystal packing, showing the hydrogen-bonded helical structure.

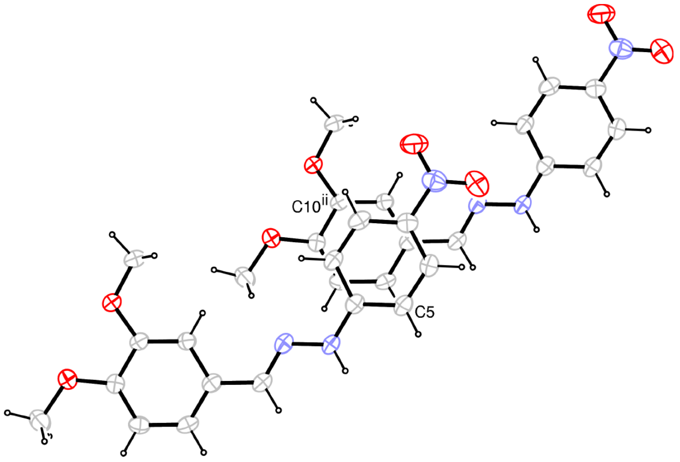

Figure 3

The π–π stacking of neighboring molecules [symmetry code: (ii) $x, y+1, z$].

The molecules are linked to each other *via* bifurcated intermolecular N—H⋯O hydrogen bonds between the imine and methoxy groups (Table 2 and Fig. 1), forming a helical supramolecular structure, as shown in Fig. 2.

The partially overlapped arrangement of nearly parallel C5-containing and C10^{ii}-containing rings [symmetry code: (ii) $x, y+1, z$] is illustrated in Fig. 3. The dihedral angle and centroid-to-centroid distance between the C5-ring and the C10^{ii}-ring are 8.05 (12)° and 3.5642 (16) Å, respectively. These findings suggest the existence of π–π stacking between benzene rings in the crystal structure.

Experimental

4-Nitrophenylhydrazine (0.31 g, 2 mmol) was dissolved in ethanol (10 ml), and an H_2SO_4 solution (98%, 0.5 ml) was slowly added with stirring. The solution was heated at about 333 K for several minutes until it became clear. An ethanol solution (10 ml) of 3,4-dimethoxybenzaldehyde (0.33 g, 2 mmol) was added dropwise to the above solution with continuous stirring. The mixture was kept at about 333 K for half an hour. After cooling to room temperature, yellow microcrystals appeared in the solution. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice from chloroform, producing single crystals of (I).

Crystal data

$C_{15}H_{15}N_3O_4$
$M_r = 301.30$
Tetragonal, $P4_1$
$a = 7.7618\ (12)$ Å
$c = 24.3500\ (17)$ Å
$V = 1467.0\ (3)$ Å^3
$Z = 4$
$D_x = 1.364$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11397 reflections
$\theta = 3.0$–$27.0°$
$\mu = 0.10$ mm^{-1}
$T = 295\ (2)$ K
Prism, yellow
0.40 × 0.24 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: none
13519 measured reflections
1684 independent reflections
1399 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\rm max} = 27.3°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 9$
$l = -31 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.087$
$S = 1.13$
1684 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.1321P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}

Table 1

Selected bond lengths (Å).

N1—C1	1.443 (4)	C2—C3	1.367 (4)
N2—C4	1.357 (3)	C3—C4	1.407 (4)
N3—C7	1.274 (3)	C4—C5	1.399 (4)
C1—C2	1.379 (4)	C5—C6	1.362 (4)
C1—C6	1.389 (4)		

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{N2-H2}A\cdots\mathrm{O3}^{\mathrm{i}}$	0.86	2.44	3.038 (3)	127
$\mathrm{N2-H2}A\cdots\mathrm{O4}^{\mathrm{i}}$	0.86	2.22	3.063 (3)	166

Symmetry code: (i) $1+y, 1-x, z-\frac{1}{4}$.

Methyl H atoms were placed in calculated position, with C—H = 0.96 Å, and the torsion angle was refined to fit the electron density, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$. Other 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, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ of the carrier atom. Owing to the absence of any significant anomalous scatterers in the structure, Friedel pairs were merged before the final refinement and the choice of chiral space group was made arbitrarily.

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) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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