

## 2-Chloro-3,4-dimethoxybenzaldehyde (4-nitrophenyl)hydrazone

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## Key indicators

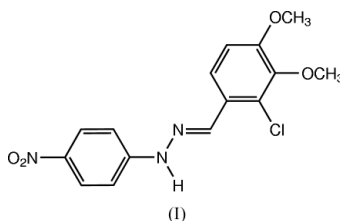
Single-crystal X-ray study  
*T* = 295 K  
Mean  $\sigma$ (C–C) = 0.003 Å  
*R* factor = 0.028  
*wR* factor = 0.078  
Data-to-parameter ratio = 15.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title compound, C<sub>15</sub>H<sub>14</sub>ClN<sub>3</sub>O<sub>4</sub>, were obtained from a condensation reaction of 2-chloro-3,4-dimethoxybenzaldehyde and 4-dinitrophenylhydrazine. Within the nitrophenyl moiety, the distances of 1.401 (2) and 1.399 (2) Å for the two C–C bonds adjacent to the imino group are appreciably longer than the average distance of 1.377 (2) Å for the other aromatic C–C bonds in the same benzene ring. The crystal packing involves  $\pi$ – $\pi$  stacking effects.

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## Comment

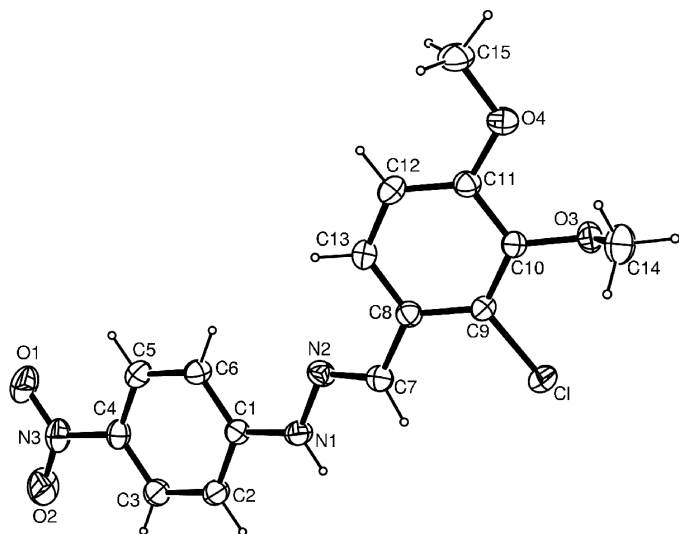
Phenylhydrazones have recently attracted our attention as derivatives show potential applications in biochemistry (Okabe *et al.*, 1993). A series of dinitrophenylhydrazone compounds have been prepared in our laboratory and their crystal structures showed that, within the dinitrophenyl moiety, the C–C bonds adjacent to the imino group were appreciably longer than the other C–C bonds in the same benzene ring. The crystal structure of the title nitrophenylhydrazone, (I) (Fig. 1), is presented here to compare with the corresponding dinitro compound (Shan *et al.*, 2003).



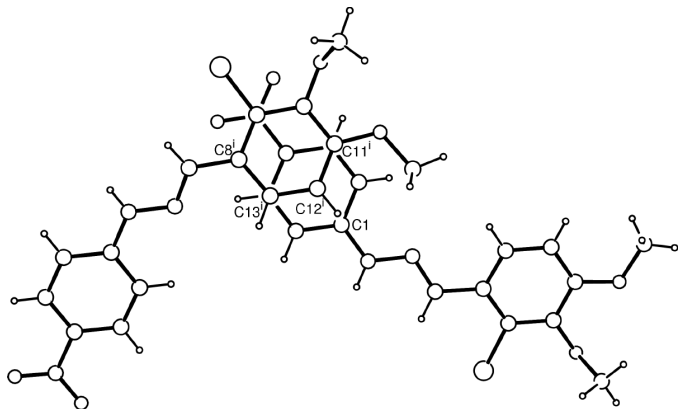
The C1-benzene plane is tilted with respect to the C8-benzene plane by a dihedral angle of 18.17 (11)°. The nitro group is coplanar with the C1-benzene plane, the dihedral angle being 1.4 (3)°. The O4-methoxy group is coplanar with the C8-benzene plane, the maximum atomic deviation from the mean plane being 0.048 (3) Å for atom C15. Conversely, atoms O3 and C14 of the O3-methoxy group are located on opposite sides of the C8-benzene plane, with displacements of 0.112 (2) and 1.106 (3) Å, respectively.

The C1–C2 bond of 1.401 (2) Å and the C1–C6 bond of 1.399 (2) Å, both adjacent to the imino group, are appreciably longer than the other aromatic C–C bonds in the same benzene ring, ranging from 1.371 (2) to 1.385 (2) Å (see Table 1). This agrees with the situation found in chlorodimethoxybenzaldehyde dinitrophenylhydrazone (Shan *et al.*, 2003).

The overlapped arrangement of nearly parallel C1-benzene and C8<sup>i</sup>-benzene rings [symmetry code: (i)  $x, 1 - y, \frac{1}{2} + z$ ] is illustrated in Fig. 2. The dihedral angle and centroid–centroid



**Figure 1**  
The molecular structure of (I), shown with 30% probability displacement ellipsoids.



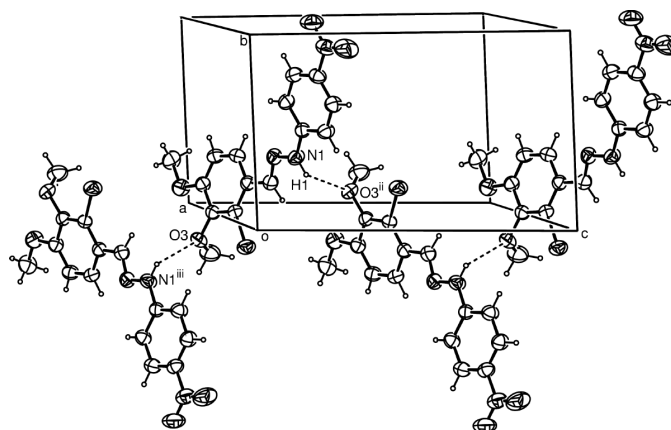
**Figure 2**  
The  $\pi$ - $\pi$  stacking in (I) between neighboring benzene rings [symmetry code: (i)  $x, 1 - y, \frac{1}{2} + z$ ].

distance between the C1-benzene and C8<sup>i</sup>-benzene rings are  $1.39(13)^\circ$  and  $3.6981(10) \text{ \AA}$ , respectively, suggesting the existence of  $\pi$ - $\pi$  stacking between benzene rings in the crystal structure.

The imino atom H1 forms a hydrogen bond with the methoxy O3<sup>iii</sup> atom (Table 2), giving a hydrogen-bonded supramolecular structure, as shown in Fig. 3.

## 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. An ethanol solution (10 ml) containing 2-chloro-3,4-dimethoxybenzaldehyde (0.4 g, 2 mmol) was added dropwise to the above solution with continuous stirring, and the mixture was kept at about 333 K for half a hour. After cooling to room temperature, orange microcrystals appeared. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice with chloroform, resulting in well shaped single crystals.



**Figure 3**  
A molecular packing diagram for (I). Dashed lines indicate the hydrogen bonding [symmetry codes: (ii)  $x, -y, \frac{1}{2} + z$ ; (iii)  $x, -y, z - \frac{1}{2}$ ].

## Crystal data

$C_{15}H_{14}ClN_3O_4$	$D_x = 1.439 \text{ Mg m}^{-3}$
$M_r = 335.74$	Mo $K\alpha$ radiation
Monoclinic, $Cc$	Cell parameters from 5900 reflections
$a = 16.4537(10) \text{ \AA}$	$\theta = 2.5\text{--}25.0^\circ$
$b = 8.1471(11) \text{ \AA}$	$\mu = 0.27 \text{ mm}^{-1}$
$c = 14.5814(12) \text{ \AA}$	$T = 295(2) \text{ K}$
$\beta = 127.535(12)^\circ$	Prism, orange
$V = 1550.0(4) \text{ \AA}^3$	$0.50 \times 0.46 \times 0.38 \text{ mm}$
$Z = 4$	

## Data collection

Rigaku R-Axis RAPID diffractometer	3071 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.016$
Absorption correction: none	$\theta_{\text{max}} = 27.4^\circ$
6761 measured reflections	$h = -21 \rightarrow 21$
3216 independent reflections	$k = -10 \rightarrow 10$
	$l = -18 \rightarrow 18$

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
$wR(F^2) = 0.078$	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
$S = 1.03$	Extinction correction: SHELXL97
3216 reflections	Extinction coefficient: 0.0073(8)
209 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1455 Friedel Pairs
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.0873P]$	Flack parameter = 0.09(4)
where $P = (F_o^2 + 2F_c^2)/3$	

**Table 1**

Selected bond distances ( $\text{\AA}$ ).

Cl—C9	1.7352(14)	N2—C7	1.278(2)
O3—C10	1.3694(17)	C1—C2	1.401(2)
O3—C14	1.432(2)	C1—C6	1.399(2)
O4—C11	1.3616(18)	C2—C3	1.374(2)
O4—C15	1.432(2)	C3—C4	1.385(2)
N1—N2	1.3619(17)	C4—C5	1.379(3)
N1—C1	1.3725(18)	C5—C6	1.371(2)

**Table 2**

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O3 <sup>ii</sup>	0.86	2.36	2.8975(19)	121

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

H atoms were placed in calculated positions, with C–H = 0.93 (aromatic) or 0.96 Å (methyl) and N–H = 0.86 Å, and included in the final cycles of refinement in the riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  or  $1.5U_{\text{eq}}$  of the carrier atoms.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* **C49**, 1678–1680.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSK (2002). *CrystalStructure*. Version 3.00. Rigaku/MSK, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Shan, S., Chen, W.-R., Hu, W.-X. & Xu, D.-J. (2003). *Acta Cryst.* **E59**, o1723–o1725.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.