2-Chloro-3,4-dimethoxybenzaldehyde 2,4-dinitrophenylhydrazone

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.003 Å

R factor = 0.045

wR factor = 0.115

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.

Crystals of the title compound, $C_{15}H_{13}ClN_4O_6$, were obtained from a condensation reaction of 2-chloro-3,4-dimethoxybenzaldehyde and 2,4-dinitrophenylhydrazine. Within the dinitrophenyl group, the distances of 1.413 (3) and 1.405 (3) Å for the C—C bonds close to the imino group are appreciably longer than the average distance of 1.372 (4) Å for other aromatic C—C bonds in the same benzene ring. The benzene rings in the molecule are nearly coplanar, and the overlapped arrangement of benzene rings of neighboring molecules shows the existence of a π–π stacking interaction.

Comment

As some phenylhydrazone derivatives show potential application in biochemistry (Okabe *et al.*, 1993), phenylhydrazone has recently attracted our attention. A series of phenylhydrazone derivatives has been prepared in our laboratory, from which several X-ray structures have been reported (Shan *et al.*, 2003). The molecular structure of the title compound, (I), is shown in Fig. 1.
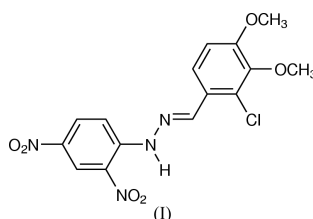
The molecule has a nearly planar structure. Within the dinitrophenyl moiety, one nitro group is coplanar with the benzene ring, but the other is tilted with respect to the ring by 15.9 (3)°. Within the dimethoxyphenyl moiety, one methyl C atom is located in the benzene-ring plane, but the other is out of the plane by 0.985 (5) Å. Atom O5 is out of the benzene plane on the other side by 0.163 (3) Å due to the repulsion between the C14-methyl group and the N2-nitro group of a neighboring molecule, as verified by the C14···O3($-x$, $1 - y$, $1 - z$) separation of 3.446 (5) Å. The two benzene rings are nearly coplanar, the dihedral angle being 6.63 (11)°. The C1—C2 bond of 1.413 (3) Å and the C1—C6 bond of 1.405 (3) Å, both close to the imino group, are appreciably longer than other aromatic C—C bonds in the same benzene ring, ranging from 1.357 (3) to 1.386 (3) Å (see Table 1). This agrees with the situation found in 2,4-dinitrophenylhydrazone derivatives reported previously (Bolte & Dill, 1998; Ohba, 1996; Borwick *et al.*, 1997; Naidu *et al.*, 1996; Shan *et al.*, 2002). The imino H3 atom is intramolecularly hydrogen bonded to the adjacent
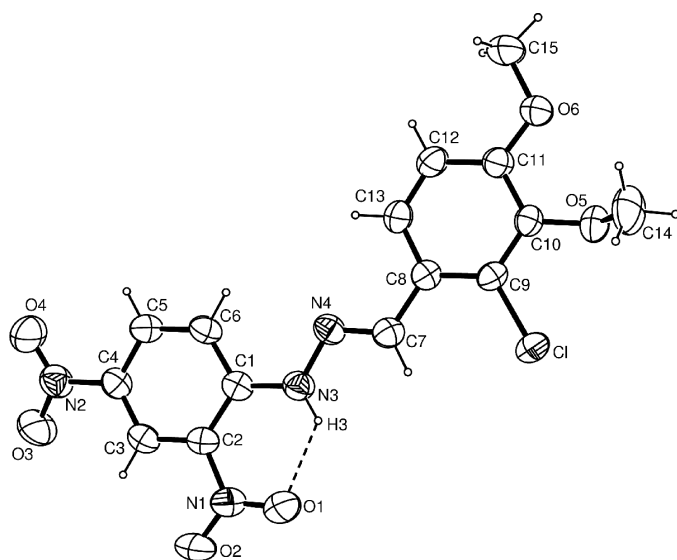
Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. The dashed line indicates hydrogen bonding.
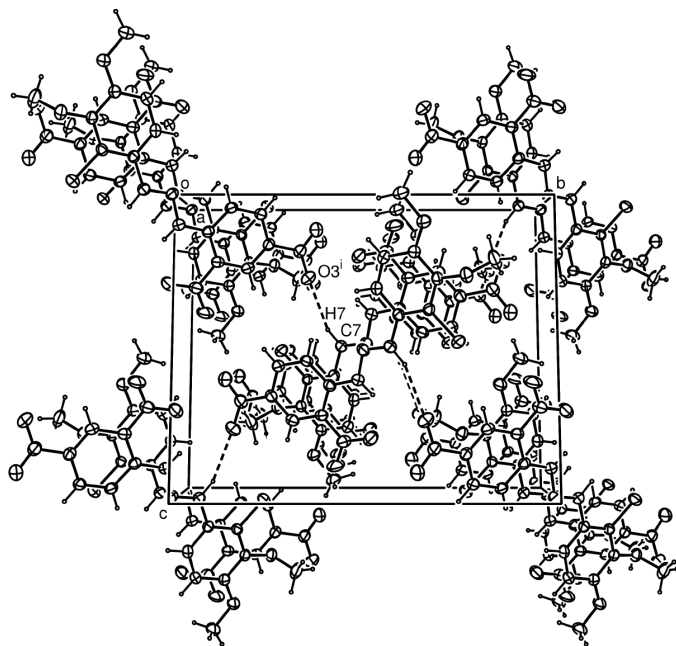

Figure 2
A molecular packing diagram. Dashed lines indicate the weak intermolecular C—H···O hydrogen bonds. [Symmetry code: (i) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$.]

nitro group, with an N3···O1 distance of 2.602 (3) Å and an N3—H3···O1 angle of 127°. Weak C—H···O hydrogen bonding exists between neighboring molecules, as shown in Fig. 2, with a C7···O3^i [symmetry code (i): $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$] distance of 3.297 (3) Å and a C7—H7···O3^i angle of 161°. The overlapped arrangement of benzene rings is illustrated in Fig. 3. Atoms C8 and C13 are out of the C1^{ii} benzene plane by 3.404 (3) and 3.402 (3) Å, respectively [symmetry code: (ii) $-x$, $1 - y$, $1 - z$]. These findings suggest the existence of a π–π stacking interaction between neighboring molecules.
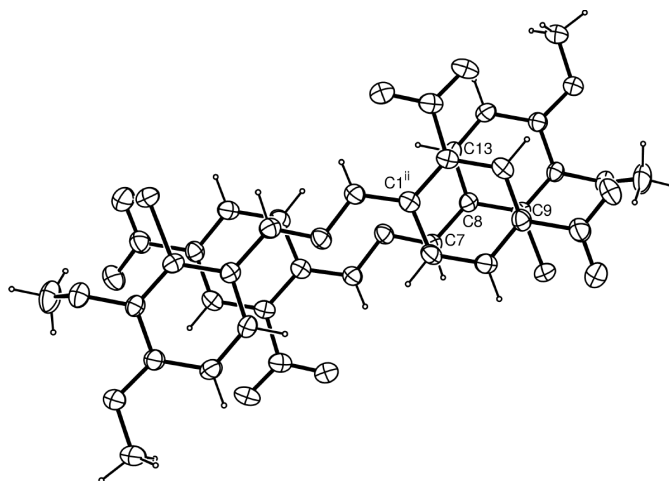

Figure 3
A diagram showing π–π stacking between neighboring benzene rings. [Symmetry code: (ii) $-x$, $1 - y$, $1 - z$.]

Experimental

2,4-Nitrophenylhydrazine (0.4 g, 2 mmol) was dissolved in ethanol (10 ml). H_2SO_4 solution (98%, 0.5 ml) was then slowly added to the ethanol solution with stirring. The resulting solution was heated at about 333 K for several minutes until the solution cleared. An ethanol solution containing 2-chloro-3,4-dimethoxybenzaldehyde (0.4 g, 2 mmol) was dropped slowly into the above solution with continuous stirring at 333 K. The mixture was kept at 333 K for 30 min. When the solution had cooled 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 toluene, resulting in well shaped single crystals.

Crystal data

$C_{15}H_{13}ClN_4O_6$	$D_x = 1.546$ Mg m^{-3}
$M_r = 380.74$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 9318
$a = 7.8251$ (11) Å	reflections
$b = 16.1448$ (13) Å	$\theta = 2.0$–$24.0°$
$c = 13.2147$ (11) Å	$\mu = 0.28$ mm^{-1}
$\beta = 101.508$ (13)°	$T = 293$ (2) K
$V = 1635.9$ (3) Å^3	Prism, orange
$Z = 4$	$0.42 \times 0.20 \times 0.16$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	2873 independent reflections
ω scans	2477 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.023$
(*ABSCOR*; Higashi, 1995)	$\theta_{max} = 25.1°$
$T_{min} = 0.890$, $T_{max} = 0.952$	$h = -8 \rightarrow 9$
12 157 measured reflections	$k = -19 \rightarrow 19$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 1.1385P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} < 0.001$
2873 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
236 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0050 (9)

Table 1
Selected geometric parameters (Å).

Cl—C9	1.727 (2)	C1—C2	1.413 (3)
N3—C1	1.357 (3)	C2—C3	1.382 (4)
N3—N4	1.370 (3)	C3—C4	1.357 (3)
N4—C7	1.276 (3)	C4—C5	1.386 (3)
C1—C6	1.405 (3)	C5—C6	1.363 (4)

H atoms were placed in calculated positions, with C—H = 0.93 or 0.96 Å and N—H = 0.86 Å, and included in the final cycles of refinement as riding, with $U_{iso}(H) = 1.2U_{eq}$ or $1.5U_{eq}$ 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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