

## Benzylideneacetone 2,4-dinitrophenylhydrazone

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## Key indicators

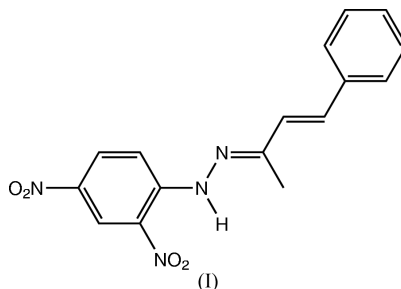
Single-crystal X-ray study  
*T* = 295 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
*R* factor = 0.048  
*wR* factor = 0.127  
Data-to-parameter ratio = 12.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title compound,  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_4$ , were obtained from a condensation reaction of benzylideneacetone and 2,4-dinitrophenylhydrazine. The molecule has a nearly planar structure with a dihedral angle of  $7.57(4)^\circ$  between the dinitrophenyl and benzylidene mean planes. Within the dinitrophenyl moiety, the distances of 1.420(2) and 1.411(3)  $\text{\AA}$  for the C—C bonds near the imine group are longer than the average distance of 1.374(3)  $\text{\AA}$  for the other C—C bonds in the same benzene ring. The short N—C distance of 1.338(2)  $\text{\AA}$  indicates electron delocalization between the imine group and dinitrophenyl ring.

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## Comment

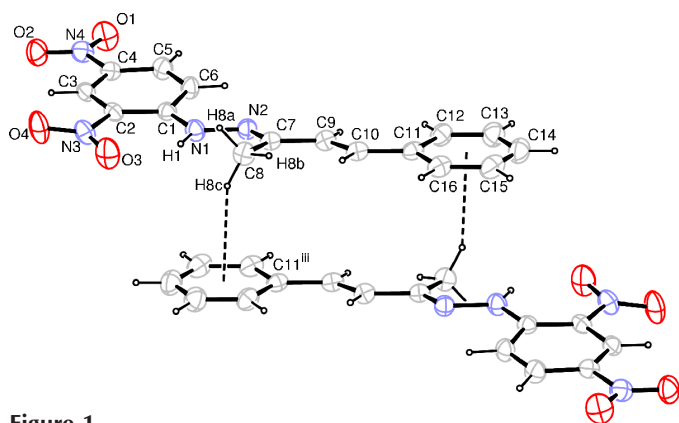
In view of the potential application of phenylhydrazone derivatives in biochemistry (Okabe *et al.*, 1993), a series of phenylhydrazone derivatives has been prepared in our laboratory. We present here the X-ray structure of the title compound, (I), and compare it with those reported previously (Shan *et al.*, 2002, 2003).



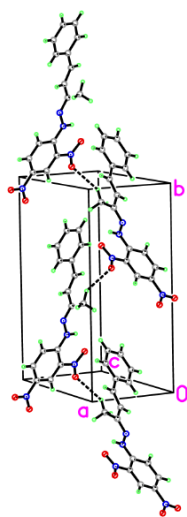
The molecule of (I) is nearly planar, except for the methyl H atoms (Fig. 1). The dinitrophenyl mean plane is inclined with respect to the benzylidene mean plane by a small dihedral angle of  $7.57(4)^\circ$ .

The  $\text{N}2=\text{C}7$  distance (Table 1) is typical of a double bond, and the methyl group and imine  $\text{N}1-\text{H}1$  bond are on the same side of the  $\text{N}2=\text{C}7$  double bond. The methyl group, refined with torsional freedom about the C—C bond to optimise the fit to the electron density, shows a different conformation from that calculated by *SXGRAPH* (Farrugia, 1999). The torsion angles  $\text{N}2-\text{C}7-\text{C}8-\text{H}8a = -50.2^\circ$  and  $\text{N}2-\text{C}7-\text{C}8-\text{H}8c = 69.8^\circ$  show that the observed methyl conformation minimizes the steric hindrance between the methyl group and the  $\text{N}1-\text{H}1$  bond.

The  $\text{C}1-\text{C}2$  and  $\text{C}1-\text{C}6$  bonds near the imine group are appreciably longer than the average distance of 1.374(3)  $\text{\AA}$  for the other C—C bonds in the same benzene ring (Table 1). This situation agrees with that reported previously for 2,4-



**Figure 1**  
The molecular structure of (I), with 30% probability displacement ellipsoids. Dashed lines indicate C—H...Cg interactions. [Symmetry code: (iii)  $-x, 1 - y, 1 - z$ ].



**Figure 2**  
A stereoview of the unit-cell packing diagram, showing the intermolecular C—H...O hydrogen bonding.

dinitrophenylhydrazone derivatives (Ohba, 1996; Naidu *et al.*, 1996; Borwick *et al.*, 1997; Bolte & Dill, 1998; Shan *et al.*, 2003). The N1—C1 bond is significantly shorter than the N1—N2 bond, suggesting electron delocalization between imine atom N1 and the C1-containing benzene ring. This may be the reason for the longer C1—C2 and C1—C6 bonds.

The  $\pi$ - $\pi$  stacking usually observed in reported phenylhydrazone derivatives (Shan *et al.*, 2003) is not observed in (I). A C—H... $\pi$  interaction occurs between the methyl group and the C11<sup>iii</sup>-containing benzene ring of a neighboring molecule, as shown in Fig. 1 [symmetry code: (iii)  $-x, 1 - y, 1 - z$ ]. The C8—H8c...Cg angle and H8c...Cg distance are  $152^\circ$  and 2.67 Å, respectively (Cg denotes the centroid of the benzene ring). The crystal packing (Fig. 2) is stabilized by weak intermolecular C—H...O hydrogen bonds (Table 2).

## Experimental

2,4-Dinitrophenylhydrazine (0.4 g, 2 mmol) was dissolved in ethanol (10 ml), and H<sub>2</sub>SO<sub>4</sub> solution (98%, 0.5 ml) was added slowly with ethanol solution with stirring. The solution was heated at about 333 K

for several minutes until it cleared. An ethanol solution (2 ml) of benzylideneacetone (0.29 g, 2 mmol) was dropped slowly into the above solution with continuous stirring. The mixture was refluxed for half an hour. After cooling to room temperature, red microcrystals appeared in the solution. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice with a mixed solution of acetone and ethyl acetate (1:1).

## Crystal data

C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 326.31  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 7.3916 (3) Å  
*b* = 15.7043 (7) Å  
*c* = 13.7350 (5) Å  
 $\beta$  = 102.4362 (13) $^\circ$   
*V* = 1556.95 (11) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.392 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 7517 reflections  
 $\theta$  = 2.5–24.0 $^\circ$   
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Prism, red  
 0.27 × 0.15 × 0.13 mm

## Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 10 933 measured reflections  
 2696 independent reflections

2072 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.043  
 $\theta$ <sub>max</sub> = 25.0 $^\circ$   
*h* = -8 → 8  
*k* = -18 → 18  
*l* = -16 → 16

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 0.127  
*S* = 1.02  
 2696 reflections  
 218 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.3839P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$

**Table 1**

Selected interatomic distances (Å).

N1—C1	1.338 (2)	C2—C3	1.380 (3)
N1—N2	1.379 (2)	C3—C4	1.368 (3)
N2—C7	1.293 (2)	C4—C5	1.391 (3)
C1—C2	1.420 (2)	C5—C6	1.356 (3)
C1—C6	1.411 (3)		

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O3	0.86	1.98	2.610 (2)	130
C8—H8b...O4 <sup>i</sup>	0.96	2.57	3.410 (3)	146
C13—H13...O2 <sup>ii</sup>	0.93	2.56	3.406 (3)	151

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

Methyl H atoms were placed in calculated positions, with C—H = 0.96 Å, and the torsion angle was refined to fit the electron density, with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(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 a riding model, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N).

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure*

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

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