

## Acetophenone 2,4,6-trinitrophenylhydrazone

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## Key indicators

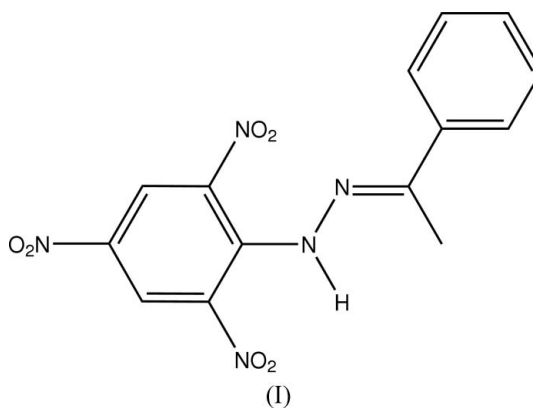
Single-crystal X-ray study  
 $T = 295\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.049  
 $wR$  factor = 0.155  
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Molecules of the title compound,  $\text{C}_{14}\text{H}_{11}\text{N}_5\text{O}_6$ , display an *E* configuration about the  $\text{C}=\text{N}$  bond and an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond. The crystal packing is consolidated by aromatic  $\pi-\pi$  stacking and  $\text{C}-\text{H}\cdots\text{O}$  interactions.

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## Comment

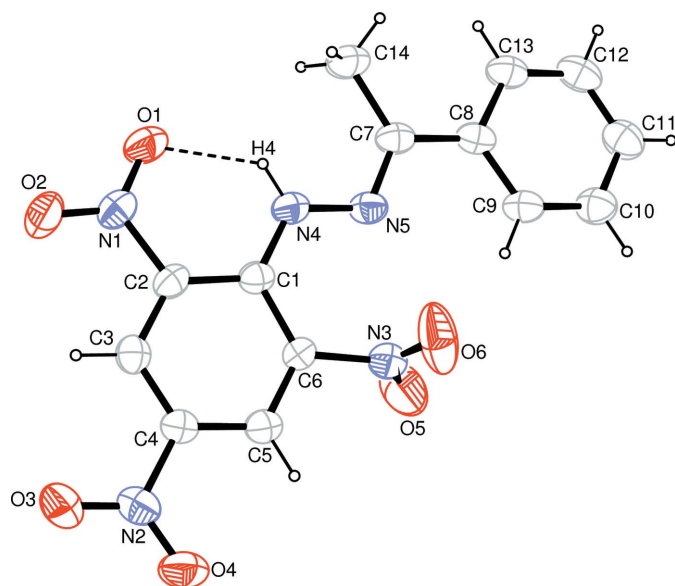
As some phenylhydrazone derivatives have been shown to be potential DNA-damaging or mutagenic agents (Okabe *et al.*, 1993), a series of nitrophenylhydrazone derivatives has been synthesized in our laboratory in order to investigate the relationship between structure and bioactivity (Shan *et al.*, 2003). As part of this ongoing work, we synthesized the title trinitrophenylhydrazone compound, (I) (Fig. 1), and present its crystal structure here.



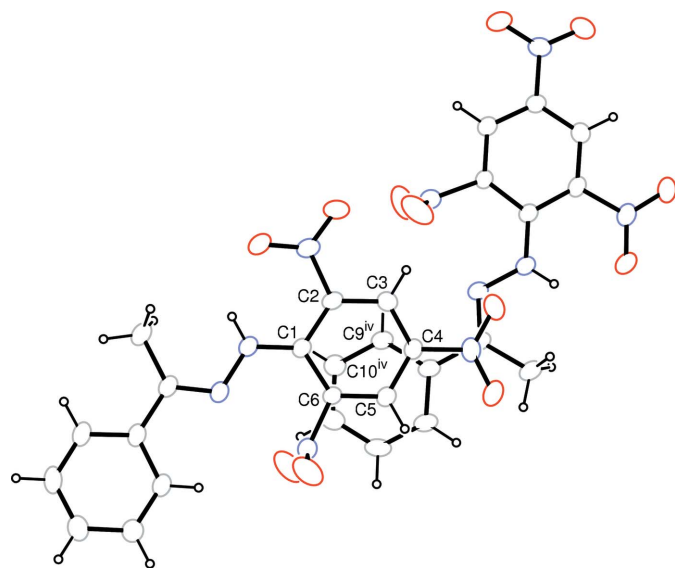
The molecule of (I) displays an *E* configuration, the two benzene rings being located on opposite sides of the  $\text{C}7=\text{N}5$  double bond. The non-H atoms of the molecule are roughly coplanar, except for the  $\text{N}3/\text{O}5/\text{O}6$  nitro group which is nearly perpendicular to the mean plane of the molecule with a dihedral angle of  $78.96(12)^\circ$ . The dihedral angle between the two benzene ring planes is  $5.11(9)^\circ$ . An intramolecular  $\text{N}-\text{H}\cdots\text{O}$  bond occurs between the imine NH group and a nitro O atom (Table 2).

The  $\text{C}1-\text{C}2$  and  $\text{C}1-\text{C}6$  bonds, which are adjacent to the imino N4 atom, are significantly longer than the average distance of  $1.371(3)\text{ \AA}$  for the other  $\text{C}-\text{C}$  bonds in the same benzene ring (Table 1). This is consistent with the situation found in similar trinitrophenylhydrazone compounds reported recently (Fan *et al.*, 2005; Shan *et al.*, 2006).

An off-set overlapping arrangement of nearly parallel benzene rings is observed (Fig. 2) in the crystal packing of (I). The centroid-to-centroid separation of  $3.7825(19)\text{ \AA}$  between nearly parallel [dihedral angle  $5.11(9)^\circ$ ]  $\text{C}1$ -benzene and  $\text{C}9^{\text{iv}}$ -



**Figure 1**  
The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms), and a dashed line showing the intramolecular hydrogen bond.



**Figure 2**  
A diagram showing the  $\pi$ - $\pi$  stacking between benzene rings in (I) [symmetry code: (iv)  $\frac{3}{2} - x, 1/2 + y, \frac{1}{2} - z$ ].

benzene rings (for symmetry code see Fig. 2) and the separation of 3.486 (3) Å from the C9<sup>iv</sup> atom to the C1-benzene plane suggest the existence of  $\pi$ - $\pi$  stacking in (I). Finally, several weak C—H $\cdots$ O intermolecular interactions occur in (I) (Table 2).

## Experimental

2,4,6-Trinitrophenylhydrazine (0.24 g, 1 mmol) was dissolved in ethanol (18 ml) and acetic acid (0.3 ml) was added slowly with stirring. The solution was heated at about 333 K for several minutes until

it became clear. Acetophenone (0.12 g, 1 mmol) was added dropwise with continuous stirring, and the resulting mixture was refluxed for 4 h. When the solution cooled to room temperature, red microcrystals appeared. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice using a mixed solvent of acetone/ethanol (3:1 v/v), to obtain well faceted red single crystals of (I).

### Crystal data

C<sub>14</sub>H<sub>11</sub>N<sub>5</sub>O<sub>6</sub>  
*M<sub>r</sub>* = 345.28  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 10.318 (4) Å  
*b* = 13.850 (5) Å  
*c* = 10.385 (4) Å  
 $\beta$  = 93.952 (12)°  
*V* = 1480.5 (10) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 1.549 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 $\mu$  = 0.13 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Prism, red  
 0.32 × 0.29 × 0.26 mm

### Data collection

Rigaku R-Axis RAPID  
 diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 14339 measured reflections

3395 independent reflections  
 1634 reflections with *I* > 2 $\sigma$ (*I*)  
*R*<sub>int</sub> = 0.033  
 $\theta$ <sub>max</sub> = 27.5°

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.049  
*wR*(*F*<sup>2</sup>) = 0.155  
*S* = 0.96  
 3395 reflections  
 228 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0074 (18)

**Table 1**  
Selected bond lengths (Å).

N4—N5	1.372 (2)	C2—C3	1.379 (3)
C1—N4	1.342 (2)	C3—C4	1.364 (3)
C7—N5	1.294 (2)	C4—C5	1.379 (3)
C1—C2	1.422 (3)	C5—C6	1.360 (3)
C1—C6	1.421 (3)		

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N4—H4 $\cdots$ O1	0.86	1.94	2.584 (2)	130
C10—H10 $\cdots$ O4 <sup>i</sup>	0.93	2.59	3.388 (3)	144
C13—H13 $\cdots$ O1 <sup>ii</sup>	0.93	2.53	3.352 (3)	148
C14—H14A $\cdots$ O5 <sup>iii</sup>	0.96	2.58	3.538 (4)	174

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

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;  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The other H atoms were placed in calculated positions with C—H = 0.93 Å and N—H = 0.86 Å, and refined in the riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

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