

## Acetophenone (2,4-dinitrophenyl)hydrazone

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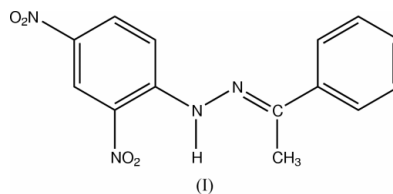
## Key indicators

Single-crystal X-ray study  
T = 298 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
R factor = 0.041  
wR factor = 0.142  
Data-to-parameter ratio = 13.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Crystals of the title compound,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_4$ , were obtained from a condensation reaction of acetophenone and 2,4-dinitrophenylhydrazine. The molecule exhibits a planar structure, with the *p*-nitro group slightly inclined to the plane. A delocalized double bond is observed in the hydrazone moiety. The separation distances, 3.404 (2) and 3.416 (4)  $\text{\AA}$ , between adjacent parallel phenyl rings indicate  $\pi$ - $\pi$  aromatic stacking interactions.

## Comment

Some phenylhydrazone derivatives have been shown to be potentially DNA-damaging and mutagenic agents (Okabe *et al.*, 1993). In order to investigate the relationship of the biological activity and the molecular structure, a number of new phenylhydrazone derivatives have been synthesized in this laboratory.



The molecular structure of the title compound, (I), is shown in Fig. 1. The molecule has an approximately planar structure, except for the N2-nitro group, which is tilted slightly due to intermolecular hydrogen bonding; thus, atoms O3 and O4 deviate from the mean plane of the molecule by 0.284 (3) and  $-0.199$  (3)  $\text{\AA}$ , respectively.

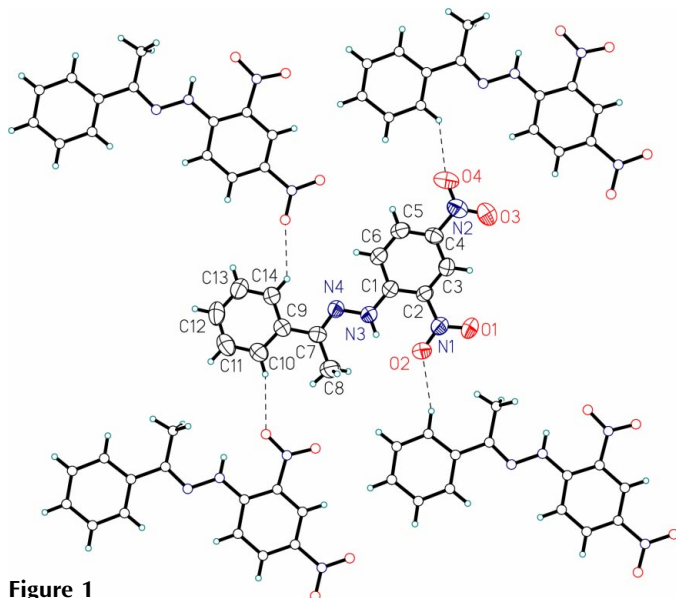
The N3–C1 bond distance of 1.351 (3)  $\text{\AA}$  indicates partial double-bond character. It should be noted that, within the phenyl ring attached to N3, both the C1–C2 bond [1.411 (3)  $\text{\AA}$ ] and the C1–C6 bond [1.415 (3)  $\text{\AA}$ ] are significantly longer than the average distance of 1.375 (3)  $\text{\AA}$  for the other four C–C bonds; these range from 1.360 (3) to 1.389 (3)  $\text{\AA}$ . A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals appreciable differences in the C–C distances in free 2,4-dinitrophenylhydrazine (Okabe *et al.*, 1993; Hilgenfeld & Saenger, 1981) and many of its derivatives (Bolte & Dill, 1998; Ohba, 1996; Borwick *et al.*, 1997; Naidu *et al.*, 1996). This is presumably due to the fact that the non-bonding orbital of nitrogen can overlap with the  $\pi$  orbitals of the arene, thus contributing to the iminocyclohexadiene resonance structure.

The N3–N4 bond distance of 1.367 (3)  $\text{\AA}$  is shorter than that found in free 2,4-dinitrophenylhydrazine [1.405 (6)  $\text{\AA}$ ; Okabe *et al.*, 1993], while the N4=C7 bond distance of 1.286 (3)  $\text{\AA}$  is longer than the typical N=C bond distance. These values suggest a delocalized double bond in the

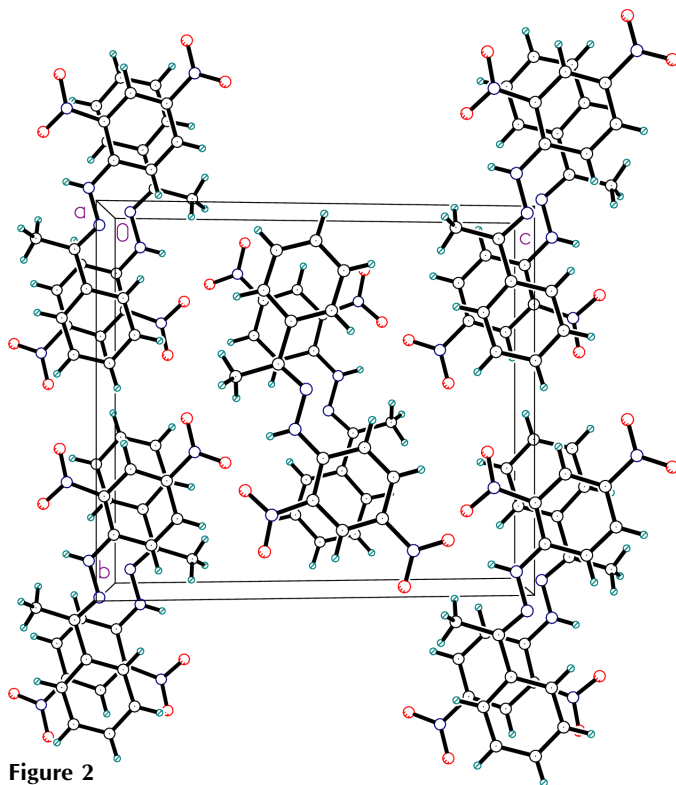
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**Figure 1**  
The structure of (I), with 50% probability displacement ellipsoids. The dashed lines indicate intermolecular hydrogen bonds.



**Figure 2**  
A molecular packing diagram, showing the overlap of aromatic rings of neighboring molecules.

hydrazone moiety, but not involving C7—C9 [1.480 (3) Å].

The title molecule crystallizes in the *E* configuration, with the phenyl group (C9—C14) and the N3 2,4-dinitrophenyl group on opposite sides of the C7=N4 double bond; this also means that the methyl group and the N3—H1 bond are on the same side of the N3—N4 bond. The methyl H atoms were located in a difference Fourier map and a torsional parameter was refined for the methyl group. In the present structure, one

methyl H atom (H8B) is *syn* with respect to the C7—C9 bond, the C9—C7—C8—H8B torsion angle being 9.5°. The methyl conformation in this structure is quite different from that calculated by *SXGRAPH* (Farrugia, 1999) or that reported for *p*-cyclopropylacetonephenone 2,4-dinitrophenylhydrazone (Drumright *et al.*, 1990). In the former, the H8B···H1 separation is 1.67 Å, whereas in the latter, it is 1.69 Å; in the present structure H8B···H1 is 2.09 Å and thus the methyl conformation better minimizes the steric hindrance between the methyl group and the N3—H1 bond.

An intramolecular hydrogen bond is formed between the N3—H1 group and the adjacent N nitro group; this is a common feature of *o*-nitrophenylhydrazine (Vickery *et al.*, 1985). Intermolecular C—H···O hydrogen bonds exist between the phenyl and nitro groups, as shown in Fig. 1 and Table 2. With the aid of these C—H···O hydrogen bonds, the title molecules are linked to form the supramolecular layered structure. A molecular packing diagram (Fig. 2) shows how neighboring molecules overlap. The separations between adjacent parallel phenyl rings are 3.404 (2) Å (1 - *x*, -*y*, -*z*) and 3.416 (4) Å (2 - *x*, -*y*, -*z*), respectively, indicative of  $\pi$ - $\pi$  aromatic stacking interactions in the crystal.

## Experimental

2,4-Dinitrophenylhydrazine (0.4 g, 0.2 mmol) was dissolved in ethanol (10 ml), then H<sub>2</sub>SO<sub>4</sub> solution (98%, 0.5 ml) was added slowly to the ethanol solution with stirring. The solution was heated at about 333 K for several minutes until the solution cleared. Acetophenone (0.24 g, 0.2 mmol) was slowly dropped into the solution with continuous stirring, and the mixture solution was kept at about 333 K for 30 min. When the solution had cooled to room temperature, red powdery crystals appeared. The powdery crystals were separated from the solution and washed with water three times. Recrystallization was performed twice, from chloroform and acetone, respectively, to obtain well-shaped crystals.

### Crystal data

C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 300.28  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 7.0169 (15) Å  
*b* = 13.263 (3) Å  
*c* = 14.8568 (19) Å  
 $\beta$  = 97.938 (16)°  
*V* = 1369.4 (5) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.456 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 24 reflections  
 $\theta$  = 5.7–12.3°  
 $\mu$  = 0.11 mm<sup>-1</sup>  
*T* = 298 (2) K  
 Prism, orange  
 0.42 × 0.32 × 0.22 mm

### Data collection

Rigaku AFC-7S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 2921 measured reflections  
 2694 independent reflections  
 1212 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.025

$\theta_{\max}$  = 26.0°  
*h* = 0 → 8  
*k* = 0 → 16  
*l* = -18 → 18  
 3 standard reflections  
 every 150 reflections  
 intensity decay: 0.7%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR*(*F*<sup>2</sup>) = 0.142  
*S* = 0.96  
 2694 reflections  
 201 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0070 (14)

**Table 1**  
Selected geometric parameters (Å, °).

O1—N1	1.220 (3)	C3—C4	1.365 (3)
O2—N1	1.234 (2)	C4—C5	1.387 (3)
O3—N2	1.223 (3)	C5—C6	1.360 (3)
O4—N2	1.222 (3)	C7—C9	1.480 (3)
N1—C2	1.450 (3)	C7—C8	1.500 (3)
N2—C4	1.454 (3)	C9—C14	1.389 (3)
N3—C1	1.351 (3)	C9—C10	1.392 (3)
N3—N4	1.367 (3)	C10—C11	1.388 (4)
N4—C7	1.286 (3)	C11—C12	1.358 (4)
C1—C2	1.411 (3)	C12—C13	1.376 (4)
C1—C6	1.415 (3)	C13—C14	1.376 (3)
C2—C3	1.389 (3)		
C1—N3—N4	120.39 (19)	N4—C7—C8	123.4 (2)
C7—N4—N3	116.7 (2)	C9—C7—C8	121.3 (2)
N4—C7—C9	115.4 (2)		

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

<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>
N3—H1...O2	0.86	1.97	2.607 (3)	130
C10—H10...O2 <sup>i</sup>	0.93	2.60	3.450 (3)	153
C14—H14...O4 <sup>ii</sup>	0.93	2.44	3.174 (4)	136

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

Guided by a difference Fourier map, the methyl H atoms were placed in calculated positions, with C—H = 0.96 Å. A torsional parameter was refined for the methyl group. Other H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å; H atoms were included in the final cycles of refinement in the riding mode, with isotropic displacement parameters of  $1.2U_{eq}$  of the carrier atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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