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(*E*)-4-Methylbenzaldehyde 2,4,6-trinitrophenylhydrazone

Gen-Rong Qiang,[a] Zheng Fan,[b] Shang Shan,[a]* Yu-Liang Tian[a] and Xu-Chun Fu[c]

[a]College of Chemical Engineering and Materials Science, Zhejiang University of Technology, People's Republic of China, [b]College of Biological and Environmental Engineering, Zhejiang University of Technology, People's Republic of China, and [c]Department of Pharmacy, Zhejiang University City College, People's Republic of China

Correspondence e-mail:
shanshang@mail.hz.zj.cn

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.066
wR factor = 0.245
Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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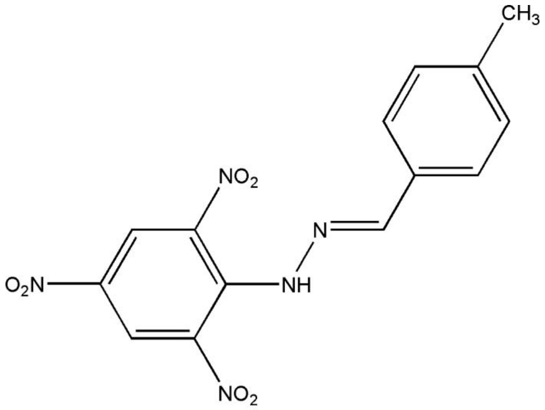
The crystals of the title compound, $C_{14}H_{11}N_5O_6$, were obtained from a condensation reaction of 4-methylbenzaldehyde and 2,4,6-trinitrophenylhydrazine. The molecule displays an *E* configuration. The centroid-to-centroid separation of 3.885 (2) Å indicates the existence of π–π stacking between nearly parallel benzene rings of neighboring molecules.

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; Fan *et al.*, 2005). Here we present the crystal structure of the title trinitrophenylhydrazone compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule displays an *E* configuration, with the methylphenyl and trinitrophenyl groups located on opposite sides of the C7═N2 double bond. This agrees with the configuration commonly found in phenylhydrazones (Bolte & Dill, 1998). The molecule of (I) is approximately planar [dihedral angle between the two benzene rings is 4.86 (16)°], apart from the N3-nitro group being nearly perpendicular [dihedral angle 82.70 (17)°] to the C1-benzene ring to minimize the repulsion between the N3-nitro group and atom N2 [O2···N2 separation 2.937 (4) Å]. Within the trinitrophenyl group, both the C1—C2 and C1—C6 bonds (adjacent to the N1-imino group) are significantly longer than the average distance of 1.374 (5) Å for the other C—C bonds in the same benzene ring (Table 1). This is consistent with that found in a trinitrophenylhydrazone compound reported previously (Fan *et al.*, 2005).

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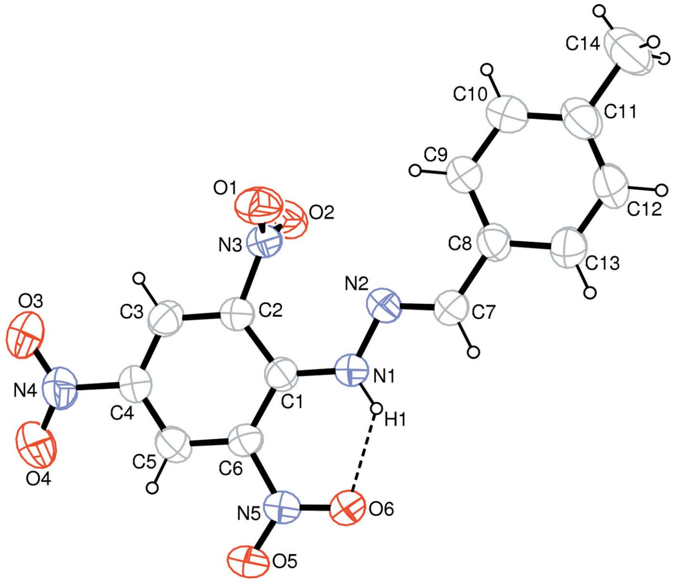

Figure 1
The molecular structure of (I) with 40% probability displacement ellipsoids (arbitrary spheres for H atoms); the dashed line shows the intramolecular hydrogen bonding.

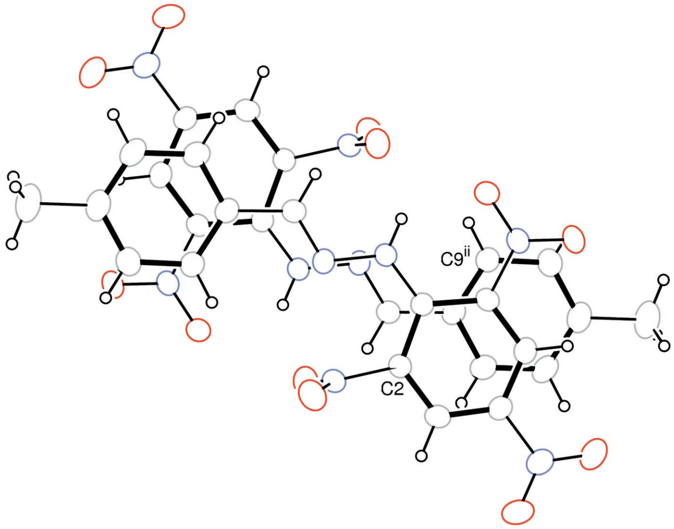

Figure 2
A diagram showing π–π stacking [symmetry code: (ii) $1 - x, -y, 1 - z$].

The centroid-to-centroid separation of 3.885 (2) Å between nearly parallel C2-benzene and C9^{ii}-benzene rings [dihedral angle 4.86 (16)°] indicates the existence of π–π stacking (Fig. 2) [symmetry code: (ii) $1 - x, -y, 1 - z$]. Intermolecular C—H···O hydrogen bonding (Table 2) helps to stabilize the crystal structure of (I).

Experimental

2,4,6-Trinitrophenylhydrazine (0.24 g, 1 mmol) was dissolved in ethanol (18 ml), then acetic acid (0.3 ml) was added slowly with stirring. The solution was heated at 333 K for several minutes until it became clear. To the above solution 4-methylbenzaldehyde (0.12 g, 1 mmol) was added dropwise with continuous stirring, then the 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 from ethanol to obtain single crystals of (I).

Crystal data

$C_{14}H_{11}N_5O_6$
$M_r = 345.28$
Triclinic, $P\bar{1}$
$a = 7.1378$ (12) Å
$b = 7.4914$ (14) Å
$c = 14.9950$ (19) Å
$\alpha = 76.191$ (9)°
$\beta = 79.469$ (7)°
$\gamma = 83.606$ (6)°
$V = 763.6$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 294$ (2) K
0.31 × 0.23 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: none
6162 measured reflections
2746 independent reflections
1690 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.245$
$S = 1.11$
2746 reflections
228 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 1
Selected bond lengths (Å).

N1—C1	1.341 (4)	C2—C3	1.370 (4)
N1—N2	1.370 (3)	C3—C4	1.377 (5)
N2—C7	1.276 (4)	C4—C5	1.363 (5)
C1—C2	1.424 (4)	C5—C6	1.385 (5)
C1—C6	1.429 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6	0.86	1.96	2.601 (4)	130
C3—H3···O1^i	0.93	2.44	3.302 (5)	155

Symmetry code: (i) $-x, -y + 1, -z + 1$.

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; $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. 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 $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N})$.

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