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(*E*)-3-Methoxyacetophenone 2,4,6-trinitrophenylhydrazone

Zheng Fan,[a] Shang Shan[b]* and Duan-Jun Xu[c]

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

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

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.134
Data-to-parameter ratio = 14.4

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

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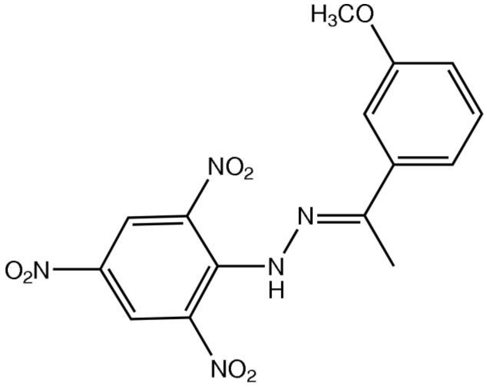
Crystals of the title compound, $C_{15}H_{13}N_5O_7$, were obtained by a condensation reaction of 3-methoxyacetophenone and 2,4,6-trinitrophenylhydrazine. The molecule adopts an *E* configuration about the C8═N5 bond. π-π stacking is observed between the methoxyphenyl and trinitrophenyl rings of neighbouring 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 and dinitrophenylhydrazone derivatives has been synthesized in our laboratory in order to investigate the relationship between structure and bioactivity. As part of the ongoing work, we recently synthesized the title trinitrophenylhydrazone compound, (I), and determined its crystal structure.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule of (I) crystallizes in the *E* configuration, with the trinitrophenyl and methoxyphenyl groups located on opposite sides of the C8═N5 double bond (Table 1) as commonly found in phenylhydrazone (Bolte & Dill,1998), nitrophenylhydrazone (Shan *et al.*, 2004) and dinitrophenylhydrazone (Shan *et al.*, 2003). The molecule of (I) is nearly planar, except that the N1-nitro group is almost perpendicular to the aromatic plane [dihedral angle = 80.70 (16)°] to minimize the repulsion between the N1-nitro group and hydrazone atom N5. The dihedral angles between the C1/N4/N5/C8 hydrazone group and the trinitrophenyl group [6.9 (3)°], and between the hydrazone and methoxyphenyl groups [7.9 (3)°], illustrate the planarity of the main body of the molecule.

The N4—C1 bond distance of 1.338 (2) Å indicates a partial double bond between the imino and the trinitrophenyl groups. Both the C1—C2 and C1—C6 bonds are significantly longer

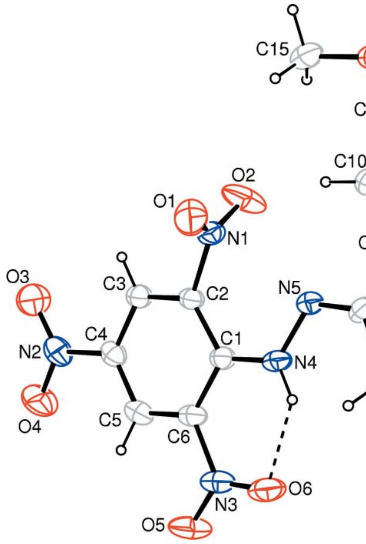


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. The intramolecular hydrogen bond is indicated by a dashed line.

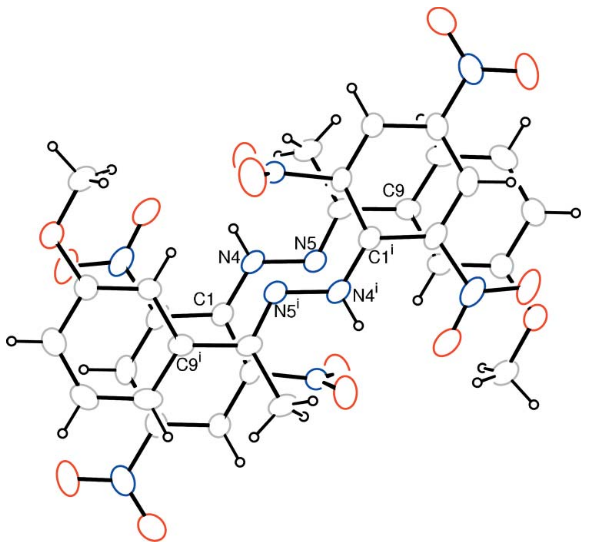


Figure 2
π–π stacking between trinitrophenyl rings [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

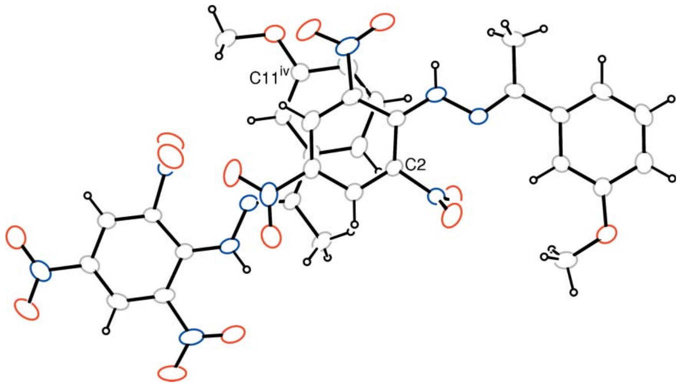


Figure 3
π-π stacking between methoxyphenyl rings [symmetry code: (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$].

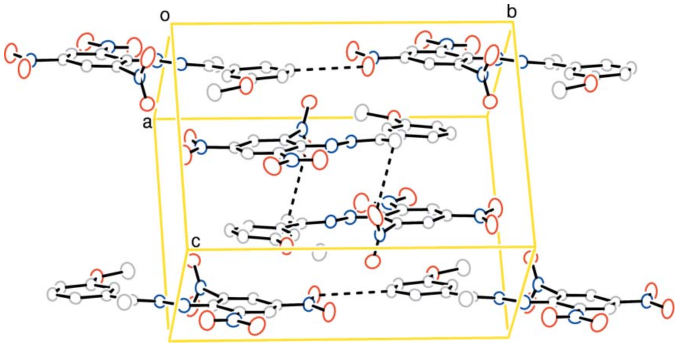


Figure 4
The packing, showing the weak intermolecular C—H$\cdots$O hydrogen bonds (dashed lines). H atoms have been omitted for clarity.

than the average distance of 1.375 (3) Å for other C—C bonds in the same aromatic ring. This effect is found in nitrophenylhydrazone and dinitrophenylhydrazone compounds reported previously (Bolte & Dill, 1998; Ohba, 1996; Borwick *et al.*, 1997; Naidu *et al.*, 1996; Shan *et al.*, 2003, 2004). This might be due to the overlap of the non-bonding orbital of the imine Natom and the π orbitals of the arene, thus contributing to the iminocyclohexadiene resonance structure.

Partially overlapped trinitrophenyl and methoxyphenyl rings are observed in (I) (Figs. 2 and 3). The dihedral angle between the trinitrophenyl ring and the methoxyphenyl ring at ($1 - x$, $1 - y$, $1 - z$) is 6.3 (1)°, with a centroid–centroid separation of 3.745 (1) Å; the dihedral angle between the trinitrophenyl ring and the methoxyphenyl ring at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) is 2.19 (12)°, with a centroid–centroid separation of 3.7034 (11) Å. These values suggest the existence of π–π stacking between nearly parallel but laterally displaced trinitrophenyl and methoxyphenyl rings.

Both intramolecular N—H$\cdots$O hydrogen bonding and weak intermolecular C—H$\cdots$O hydrogen bonding exist in (I) (Table 2 and Fig. 4).

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. 3-Methoxyacetophenone (0.15 g, 1 mmol) was added dropwise with continuous stirring, and the mixture solution was refluxed for 2 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 twice from a mixture of dichloromethane and toluene (4:1 *v*/*v*) produced well shaped single crystals of (I).

Crystal data

$C_{15}H_{13}N_5O_7$
$M_r = 375.30$
Monoclinic, $P2_1/n$
$a = 9.7926$ (4) Å
$b = 14.6633$ (7) Å
$c = 11.6359$ (4) Å
$\beta = 100.576$ (2)°
$V = 1642.44$ (12) Å^3
$Z = 4$
$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9592 reflections
$\theta = 3.0$–26.0°
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Block, red
0.32 × 0.20 × 0.18 mm

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Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: none
14416 measured reflections
3543 independent reflections
2301 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\rm max} = 27.0°$
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 18$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.134$
$S = 1.02$
3543 reflections
246 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.159P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N4—C1	1.338 (2)	N5—C8	1.287 (2)
N4—N5	1.376 (2)		
C1—N4—N5	121.22 (15)	C8—N5—N4	116.76 (15)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$\cdots$O6	0.86	1.96	2.600 (2)	131
C7—H7$C\cdots$O2$^{\rm i}$	0.96	2.41	3.293 (3)	152
C13—H13$\cdots$O3$^{\rm ii}$	0.93	2.47	3.393 (3)	170
C15—H15$B\cdots$O4$^{\rm iii}$	0.96	2.53	3.309 (3)	138

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

Methyl H atoms were placed in calculated positions, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(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 $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier).

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: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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