Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Chloroacetophenone 2,4,6-trinitrophenylhydrazone

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

[a]Department of Chemical Engineering, West Branch, 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 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 = 0.048
wR factor = 0.147
Data-to-parameter ratio = 12.9

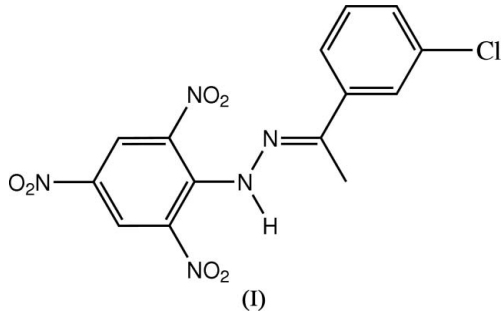
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 September 2005
Accepted 17 February 2006

Crystals of the title compound {systematic name [(1*E*)-1-aza-2-(3-chlorophenyl)prop-1-enyl](2,4,6-trinitrophenyl)amine}, $C_{14}H_{10}ClN_5O_6$, were obtained from a condensation reaction of 3-chloroacetophenone and 2,4,6-trinitrophenylhydrazine. There are two molecules in the asymmetric unit. The double bond in the bridge between the benzene rings displays an *E* configuration. π–π stacking is observed between parallel and nearly parallel benzene rings.

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 (Shan *et al.*, 2003; Fan *et al.*, 2004). As part of this ongoing work, we recently synthesized the title trinitrophenylhydrazone compound, (I), and present here its crystal structure.



(I)

There are two crystallographically independent molecules of (I) in the crystal structure (Fig. 1). Both molecule *A* and molecule *B* display an *E* configuration, where the chlorophenyl and the trinitrophenyl rings are located on opposite sides of the C=N double bonds (N5=C8 in *A* and N10=C22 in *B*). This matches the configuration found in a related compound, 3-methoxyacetophenone 2,4,6-trinitrophenylhydrazone (Fan *et al.*, 2005). In molecule *B*, the C15–C20 benzene plane is nearly parallel to the C23–C28 benzene plane [dihedral angle 5.65 (18)°], but molecule *A* displays a significantly more twisted conformation, with a dihedral angle of 11.26 (25)° between the C1–C6 and the C9–C14 planes. In molecule *A*, the N1-nitro group is nearly perpendicular to the C1–C6 benzene plane [dihedral angle 68.46 (19)°]; a similar situation is observed in molecule *B* [dihedral angle 70.9 (2)°].

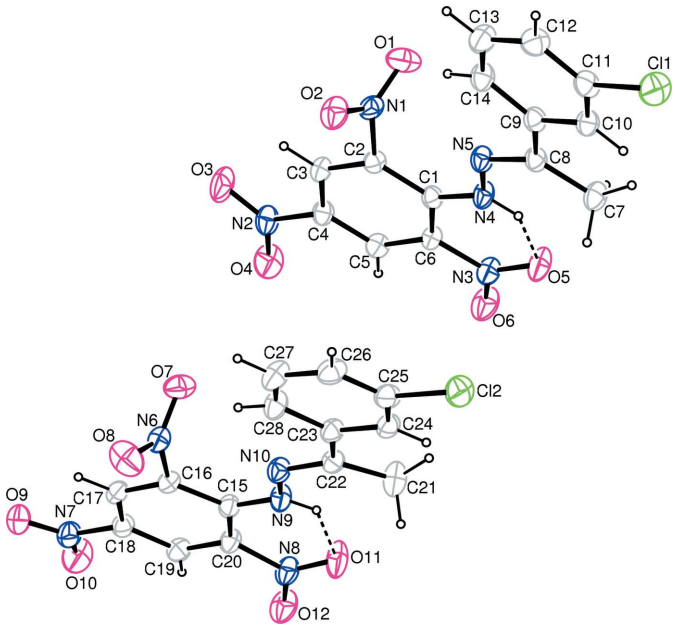


Figure 1
The asymmetric unit of (I), with 30% probability displacement ellipsoids and dashed lines indicating hydrogen bonds.

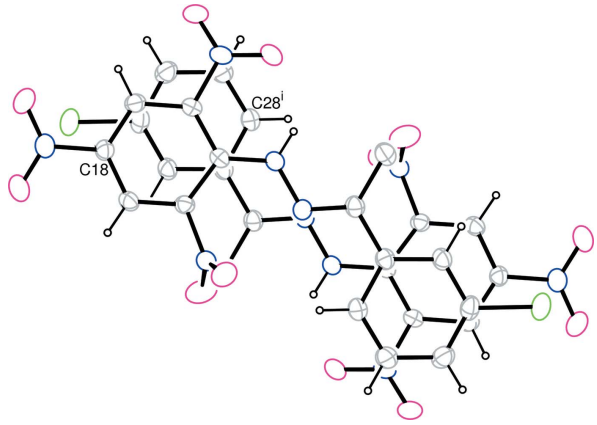


Figure 2
A diagram showing π–π stacking [symmetry code: (i) $2-x,1-y,1-z$].

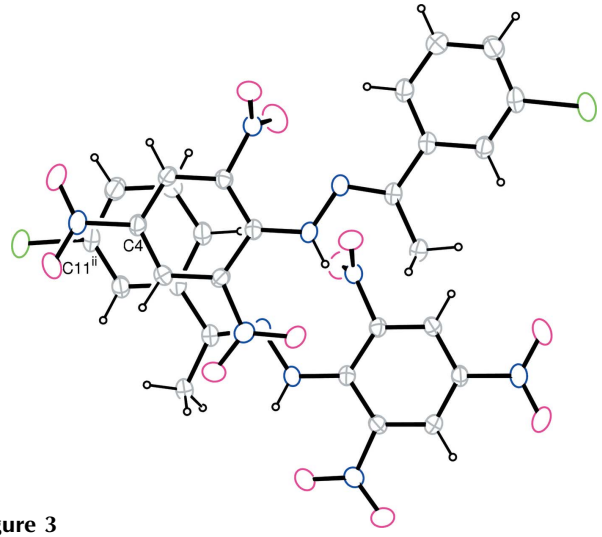


Figure 3
A diagram showing π–π stacking [symmetry code: (ii) $x,\frac{3}{2}-y,-\frac{1}{2}+z$].

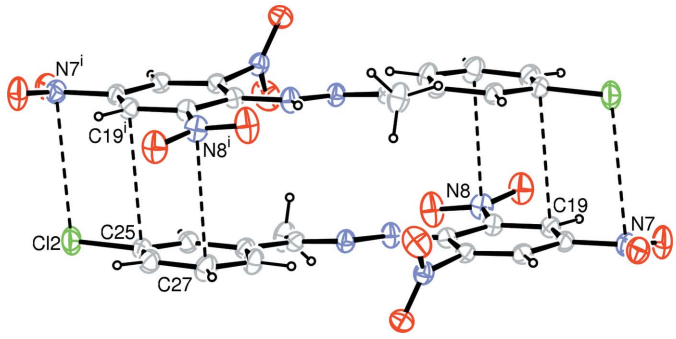


Figure 4
A diagram showing, with dashed lines, the shorter contacts between non-H atoms [symmetry code: (i) $2-x,1-y,1-z$].

This large out-of-plane twist reduces the repulsion between the hydrazone N atom and the adjacent nitro group.

Both the C1—C2 and C1—C6 bonds, which are adjacent to the imino N4 atom, are significantly longer than the average distance of 1.375 (3) Å for the other C—C bonds in the same benzene ring (Table 1), and this is also true for molecule *B*. This same pattern of distances was found in a previously reported trinitrophenylhydrazone compound (Fan *et al.*, 2005).

An off-set overlapping arrangement of nearly parallel benzene planes is observed (Figs. 2 and 3). The centroid-to-centroid separations of 3.6638 (15) Å between the C15–C20 and the C23^{i}–C28^{i} benzene planes [symmetry code: (i) $2-x$, $1-y$, $1-z$] and 3.6974 (14) Å between the C1–C6 and the C9^{ii}–C14^{ii} benzene planes [symmetry code: (ii) $x,\frac{3}{2}-y,-\frac{1}{2}+z$] suggest the existence of π–π stacking in the crystal structure of (I). This is also shown by a number of short (3.0–3.5 A) contacts between non-H atoms of neighboring molecules (Fig. 4 and Table 1).

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-Chloroacetophenone (0.16 g, 1 mmol) was added dropwise with continuous stirring, and the mixture was refluxed for 2 h. When the solution had cooled to room temperature, orange microcrystals appeared. The microcrystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice with a solvent mixture of acetone/ethanol (3:1 *v*/*v*), to yield well shaped single crystals of (I).

Crystal data

$C_{14}H_{10}ClN_5O_6$
M_r = 379.72
Monoclinic, $P2_1/c$
a = 13.1335 (5) Å
b = 24.5909 (8) Å
c = 10.0806 (3) Å
β = 104.328 (2)°
V = 3154.41 (18) Å^3
Z = 8
D_x = 1.599 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12806 reflections
θ = 2.3–24.5°
μ = 0.29 mm^{-1}
T = 295 (2) K
Prism, yellow
0.38 × 0.36 × 0.28 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	4052 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.046$
Absorption correction: none	$\theta_{max} = 25.9^\circ$
25647 measured reflections	$h = -16 \rightarrow 16$
6085 independent reflections	$k = -30 \rightarrow 30$
	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
6085 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
471 parameters	

Table 1
Selected interatomic distances (Å).

C1—N4	1.350 (3)	C15—N9	1.349 (3)
C1—C2	1.413 (3)	C15—C16	1.423 (3)
C1—C6	1.417 (3)	C15—C20	1.413 (3)
C2—C3	1.363 (3)	C16—C17	1.364 (3)
C3—C4	1.382 (3)	C17—C18	1.376 (3)
C4—C5	1.362 (3)	C18—C19	1.368 (3)
C5—C6	1.389 (3)	C19—C20	1.381 (3)
C8—N5	1.295 (3)	C22—N10	1.287 (3)
Cl2···N7^{i}	3.430 (3)	C27···N8^{i}	3.361 (4)
C25···C19^{i}	3.420 (4)	N4···O2^{ii}	3.029 (3)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsionally refined to fit the electron density with $U_{iso}(H) = 1.5U_{eq}(C)$. Other H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in the riding mode, with $U_{iso}(H) = 1.2U_{eq}$(carrier).

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

The project was supported by the Natural Science Foundation of Zhejiang Province of China (grant No. M203027).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Fan, Z., Shan, S., Hu, W.-X. & Xu, D.-J. (2004). *Acta Cryst.* E**60**, o1102–o1104.
Fan, Z., Shan, S. & Xu, D.-J. (2005). *Acta Cryst.* E**61**, o2758–o2760.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* C**49**, 1678–1680.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC and Rigaku Corporation. (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, 900 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Shan, S., Xu, D.-J., Hung, C.-H., Wu, J.-Y. & Chiang, M. Y. (2003). *Acta Cryst.* C**59**, o135–o136.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.