Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3-Chloroacetophenone 2,4-dinitrophenylhydrazone

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Received 12 May 2004
Accepted 24 May 2004
Online 29 May 2004

Crystals of the title compound, $C_{14}H_{11}ClN_4O_4$, were obtained from a condensation reaction of *m*-chloroacetophenone and 2,4-dinitrophenylhydrazine. The two benzene rings of the title molecule have a dihedral angle of 16.17 (6)°. Within the dinitrophenyl moiety, the distances of 1.422 (3) and 1.415 (3) Å for the C—C bonds close to the imine group are appreciably longer than the average distance of 1.376 (3) Å for other aromatic C—C bonds in the same benzene ring. The overlapped arrangement of chlorophenyl rings of neighbouring molecules shows the existence of a π–π stacking interaction.

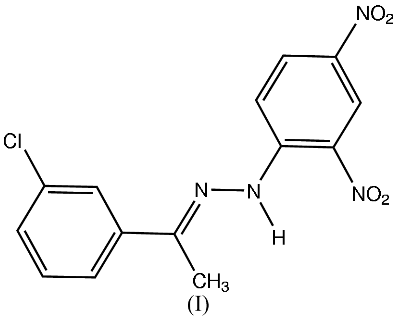
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.127
Data-to-parameter ratio = 16.0

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

Comment

As some phenylhydrazone derivatives show potential applications in the biochemistry field (Okabe *et al.*, 1993), phenylhydrazone has attracted our attention recently. A series of phenylhydrazone derivatives have been prepared in our laboratory. We present here the crystal structure of the title compound, (I), to compare with those reported previously for related compounds (Shan *et al.*, 2002; Shan *et al.*, 2003).



(I)

The molecular structure of (I) is shown in Fig. 1. Atoms N3 and N4 are displaced on opposite sides from the weighted least-squares plane through the C1 benzene ring by 0.042 (2) and 0.040 (2) Å, respectively. Of the two nitro groups, one is coplanar with the C1 benzene ring, but the other has an 8.1 (4)° dihedral angle. The C9 benzene ring mean plane is tilted with respect to the C1 benzene ring, the dihedral angle being 16.17 (6)°. Thus the C8 methyl group deviates from the C9 benzene ring plane by 0.235 (5) Å. This configuration is different from the coplanar configuration found in acetophenone 2,4-dinitrophenylhydrazone (Shan *et al.*, 2002).

The C1—C2 and C1—C6 bonds close to the imine group are appreciably longer than other C—C bonds in the same benzene ring (Table 1). This agrees with the situation found in 2,4-dinitrophenylhydrazone derivatives reported previously

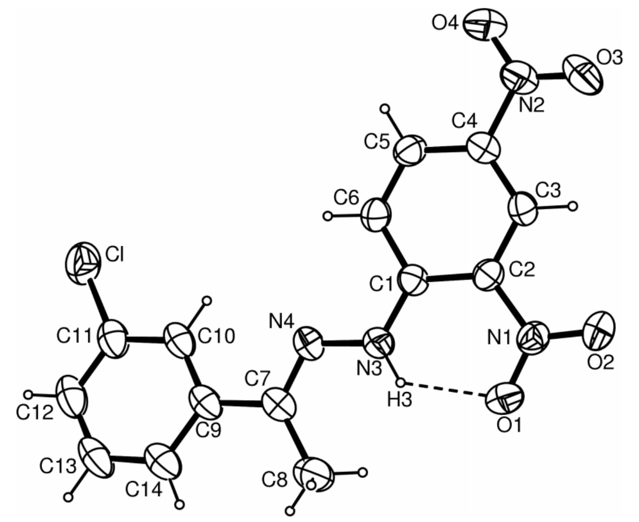


Figure 1
The molecular structure of (I), with 40% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

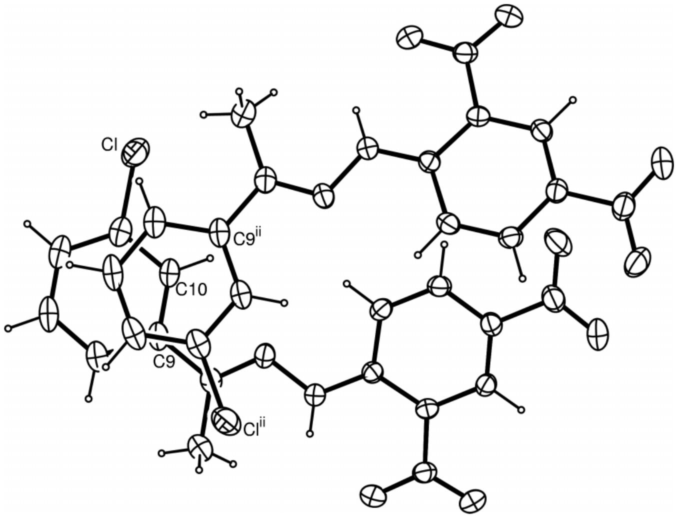


Figure 3
A diagram showing π–π stacking between neighbouring benzene rings. [Symmetry code: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

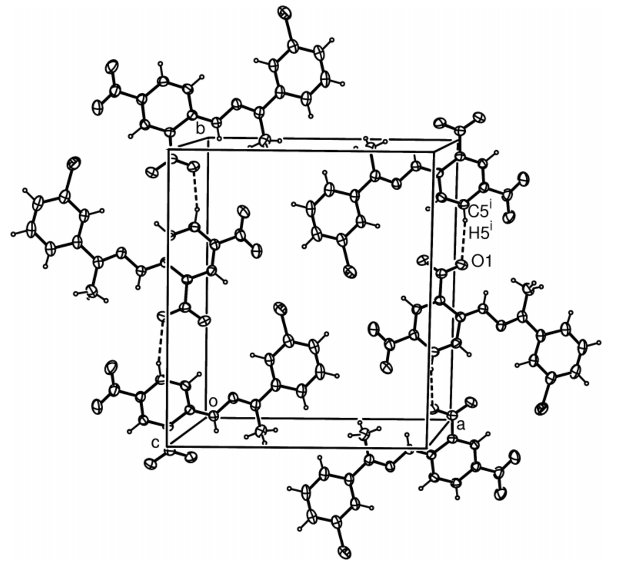


Figure 2
A molecular packing diagram. Dashed lines indicate weak intermolecular C—H$\cdots$O hydrogen bonds. [Symmetry code: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.]

(Ohba, 1996; Naidu *et al.*, 1996; Borwick *et al.*, 1997; Bolte & Dill, 1998; Shan *et al.*, 2002).

The N4═C7 distance of 1.290 (3) Å is typical of a double bond. The C9 and C1 benzene rings lie on opposite sides of the N4═C7 double bond; the methyl group and imine N3—H3 bond are on the same side of the N4═C7 bond. The methyl H atoms were placed in calculated positions and then the torsion angle was refined to fit the electron density. The present methyl conformation is very different from that calculated by *SXGRAPH* (Farrugia, 1999) (N4—C7—C8—H8*A* = 38°, C9—C7—C8—H8*B* = 22°, H3$\cdots$H8*A* = 1.95 Å and H14$\cdots$H8*B* = 2.09 Å). These values show that the methyl conformation better minimizes the steric hindrance between the methyl group and the C9 benzene ring, and between the methyl group and the N3—H3 bond.

With the aid of weak C—H$\cdots$O hydrogen bonding, neighbouring molecules are linked to each other to form supramolecular chains along the crystallographic *b* axis, as shown in Fig. 2. The C5—H5$\cdots$O1^{i} [symmetry code: (i) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$] hydrogen bond generates a *C*(7) graph-set chain (Etter *et al.*, 1990). Intramolecular weak hydrogen bonds involving the H atoms on the C1 benzene ring (H3*A*, H5 and H6; Table 2) may have some influence on the molecular conformation.

The partially overlapped arrangement of C9 and C9^{ii} benzene rings [symmetry code (ii): $x, \frac{1}{2} - y, \frac{1}{2} + z$] is illustrated in Fig. 3. The rings are nearly parallel, with an interplanar dihedral angle of only 0.20 (7)°. A centroid separation of 3.793 (3) Å, an interplanar spacing of 3.495 (2) and a centroid offset of 1.474 (10) Å suggest the existence of π–π stacking between them.

Experimental

2,4-Dinitrophenylhydrazine (0.40 g, 2 mmol) was dissolved in ethanol (10 ml), and then H_2SO_4 solution (98%, 0.5 ml) was added slowly with stirring. The solution was heated at 333 K for several minutes until the solution cleared. *m*-Chloroacetophenone (0.31 g, 2 mmol) was added dropwise with continuous stirring, and then the mixture was kept at 333 K for 30 min. When the solution had cooled to room temperature, fine orange crystals appeared. The crystals were separated from the solution and washed with cold water three times. Recrystallization was performed twice with acetone–diethyl ether (4:1).

Crystal data

$C_{14}H_{11}ClN_4O_4$
M_r = 334.72
Monoclinic, $P2_1/c$
a = 13.221 (1) Å
b = 15.1466 (11) Å
c = 7.5827 (6) Å
β = 105.324 (2)°
V = 1464.47 (19) Å^3
Z = 4

D_x = 1.518 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 10 397 reflections
θ = 2.8–27.0°
μ = 0.29 mm^{-1}
T = 295 (2) K
Prism, orange
0.38 × 0.22 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
13 167 measured reflections
3349 independent reflections
2250 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -19 \rightarrow 19$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.127$
$S = 1.02$
3349 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2883P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cl—C11	1.740 (3)	C1—C6	1.415 (3)
N3—N4	1.374 (2)	C2—C3	1.390 (3)
N3—C1	1.349 (2)	C3—C4	1.360 (3)
N4—C7	1.290 (3)	C4—C5	1.392 (3)
C1—C2	1.422 (3)	C5—C6	1.363 (3)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N3—H3$\cdots$O1	0.86	1.97	2.589 (2)	128
C5—H5$\cdots$O1$^{\rm i}$	0.93	2.42	3.205 (2)	142
C3—H3*A*$\cdots$O2	0.93	2.35	2.658 (2)	99
C3—H3*A*$\cdots$O3	0.93	2.42	2.705 (3)	98
C5—H5$\cdots$O4	0.93	2.44	2.725 (3)	98
C6—H6$\cdots$N4	0.93	2.44	2.752 (3)	100

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

H atoms of benzene rings and the imine group were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and included in the final cycles of refinement in a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atoms). 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 [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)].

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the Zhejiang Provincial Natural Science Foundation of China (M203027). The authors thank Dr. Jian-Ming Gu for assistance in data collection.

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