Cyclohexanone 2,4-dinitrophenylhydrazone

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Crystals of the title compound, $C_{12}H_{14}N_4O_4$ were obtained by a condensation reaction between cyclohexanone and 2,4-dinitrophenylhydrazine. Within the dinitrophenyl group, the distances of 1.420 (2) and 1.422 (2) Å for the C—C bonds close to the imino group are appreciably longer than the average distance of 1.377 (2) Å for the rest of the C—C bonds in the ring. The overlapped arrangement and separation of 3.379 (8) Å between parallel aromatic rings suggest the existence of a π–π-stacking interaction between neighboring molecules.

Comment

As part of the structural investigation of phenylhydrazone derivatives (Shan *et al.*, 2003), we present here the crystal structure of the title compound, (I), which was prepared recently using a condensation reaction between cyclohexanone and 2,4-dinitrophenylhydrazine.

(I)
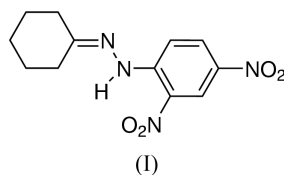
The phenylhydrazone moiety in (I) has a planar structure and the cyclohexane group assumes a chair conformation (Fig. 1). Distances of 1.420 (2) and 1.422 (2) Å for the C1—C2 and C1—C6 bonds, both close to the imino group, are appreciably longer than the average distance of 1.377 (2) Å for the rest of the C—C bonds in the substituted phenyl ring, which range from 1.357 (2) to 1.398 (2) Å (Table 1). This is in agreement with the values found in 2,4-dinitrophenylhydrazone derivatives reported previously (Dinger & Scott, 2000; Shan *et al.*, 2003). The imino atom H3 forms an intramolecular hydrogen bond to the adjacent nitro group, with an N3···O1 distance of 2.6268 (19) Å and an N3—H3···O1 angle of 128°. Another short, though non-bonding, intramolecular contact C—H···H—C, with an H···H distance of 1.90 Å, is also observed between atoms H3 and H12*A* of the cyclohexane group; this is comparable to the distance of 1.97 Å found in quinolylcyclohexanone phenylhydrazone (Bocelli *et al.*, 1984).

A weak intermolecular C—H···O hydrogen bond, with a C5···O4[i] distance of 3.292 (2) Å and a C5—H5···O4[i] angle of 143° [symmetry code: (i) $2 - x$, $1 - y$, $1 - z$], links the molecules in the crystal into centrosymmetric dimers, as shown in Fig. 1. The overlapped arrangement of parallel aromatic rings (Fig. 2) and the separation of 3.379 (8) Å between the C1 and

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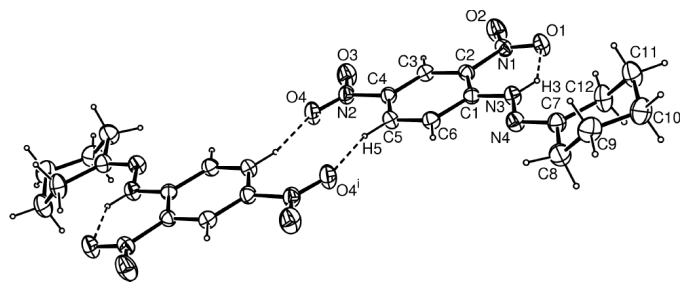
Figure 1
Centrosymmetric molecular dimers in the structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate the intramolecular and intermolecular hydrogen bonding [symmetry code: (i) $2 - x, 1 - y, 1 - z$].

$C1^{ii}$ rings also suggest the existence of π–π-stacking interactions between neighboring molecules [symmetry code: (ii) $1 - x, 1 - y, 1 - z$].

Experimental

2,4–Dinitrophenylhydrazine (0.4 g, 2 mmol) was dissolved in ethanol (10 ml) and H_2SO_4 (98%, 0.5 ml) was added slowly with stirring. The solution was heated at about 333 K for several minutes until it became clear. Cyclohexanone (0.2 g, 2 mmol) was added dropwise with continuous stirring and the resulting mixture was refluxed for 30 min. After the solution had cooled to room temperature, a yellow powder appeared. This was separated and washed with water three times. Recrystallization from absolute ethanol yielded well shaped single crystals of (I).

Crystal data

$C_{12}H_{14}N_4O_4$	$Z = 2$
$M_r = 278.27$	$D_x = 1.433$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.9700 (11)$ Å	Cell parameters from 2694
$b = 8.0438 (10)$ Å	reflections
$c = 11.8063 (13)$ Å	$\theta = 1.8$–$27.4°$
$\alpha = 87.910 (2)°$	$\mu = 0.11$ mm^{-1}
$\beta = 79.862 (4)°$	$T = 296 (2)$ K
$\gamma = 81.879 (3)°$	Plate, yellow
$V = 645.01 (15)$ Å^3	$0.51 \times 0.45 \times 0.09$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	1988 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.015$
Absorption correction: none	$\theta_{max} = 27.4°$
4526 measured reflections	$h = -8 \rightarrow 9$
2883 independent reflections	$k = -10 \rightarrow 10$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 0.0918P]$
$wR(F^2) = 0.123$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2883 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
182 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97
	Extinction coefficient: 0.022 (4)
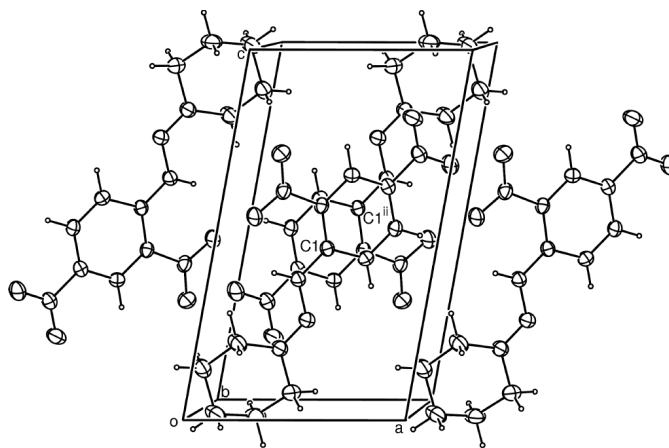
Figure 2
A molecular packing diagram, showing π–π stacking between neighboring aromatic rings [symmetry code: (ii) $1 - x, 1 - y, 1 - z$].

Table 1
Selected geometric parameters (Å).

N3—C1	1.355 (2)	C2—C3	1.386 (2)
N3—N4	1.3860 (18)	C3—C4	1.368 (2)
N4—C7	1.276 (2)	C4—C5	1.398 (2)
C1—C2	1.420 (2)	C5—C6	1.357 (2)
C1—C6	1.422 (2)		

H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and N—H = 0.86 Å, and included in the final cycles of refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$ or $1.5U_{eq}$ of the carrier atoms.

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).

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