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Ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate

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Key indicators

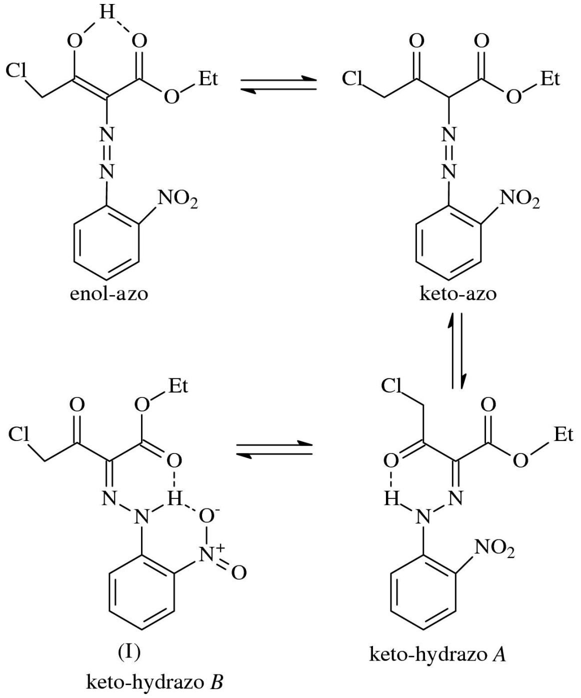
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.190
Data-to-parameter ratio = 15.7

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

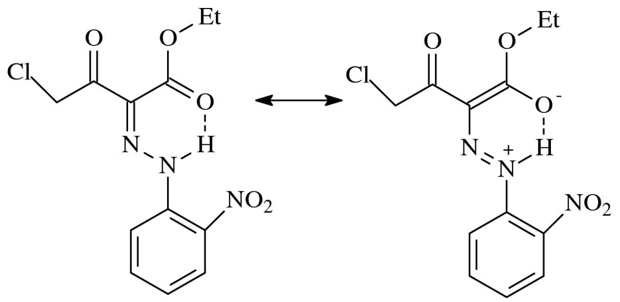
The title compound, $C_{12}H_{12}N_3O_5$, adopts a keto-hydrazo tautomeric form stabilized by intramolecular hydrogen bonds. The aromatic ring and aliphatic chain, which adopt a *trans* configuration about the C═N double bond, are nearly coplanar, with a dihedral angle of 7.56 (1)° between them. The molecules pack *via* weak intermolecular C—H···O hydrogen bonds which, together with intramolecular N—H···O bonds, form an $S(6)S(6)[R_2^2(13)]S(6)S(6)$ motif.

Comment

1,3-Diketones are used in the synthesis of many organic compounds, such as diazepine (Khudina *et al.*, 2004), pyrazole, pyrimidine and their derivatives (Saleh *et al.*, 2003). 3-Phenylhydrazono-2,4-diones and their derivatives are used for the treatment of cancer or AIDS, or of opportunistic infections afflicting patients with cancer or AIDS (Monga & Sausville, 2002). They are also used to inhibit the activity of a newly discovered membrane-bound aminopeptidase, ACE2 (Huentelman *et al.*, 2004). As part of our ongoing research on phenylhydrazonodiones, the title compound, (I), has been synthesized and its crystal structure is reported here.



Phenylhydrazono-1,3-diones can exist in four tautomeric forms (see scheme 1). Our investigations show that, in the solid state, the molecular structure of (I) adopts the keto-hydrazo B form with intramolecular hydrogen bonds (Fig. 1). This is also indicated by the N1—N2 and C1—N2 bond lengths (Table 1). In (I), the imino group adopts a (*Z*) configuration, with bond lengths C9—N1 1.302 (3) Å, C1—N2 1.396 (3) Å and N1—N2 1.316 (3) Å (Table 1). These data show that there is significant elongation of the N1—N2 bond and contraction of the C1—N2 bonds in comparsion with azo compounds. For example, the N═N and C—N bonds in azobenzene are 1.249 (4) and 1.431 (4) Å, respectively (Harada *et al.*, 1997), while the C═N double bonds in imino compounds are in the range 1.270 (5)–1.303 (3) Å (Şahin *et al.*, 2005; Odabaşoğlu *et al.*, 2005; Butcher *et al.*, 2005; Baughman *et al.*, 2004; Ersanlı *et al.*, 2004; Galić *et al.*, 2000). Secondly, atom H1 was located on atom N2, confirming a preference for the keto-hydrazo tautomer in the solid state. Finally, there is a moderately strong intramolecular N2—H1···O1 hydrogen bond, which is a common feature of similar systems {N—H···O = 1.97 Å in 4-chloro-2-(4-oxopent-2-en-2-ylamino)phenol (Arıcı *et al.*, 1999); N—H···O = 1.92 (3) Å in 3,10-bis-[2-(2-pyridinyl)-ethyl]-4,9-dimethyl-5,8-diazododeca-4,8-diene-2,11-dione (Nathan & Silver, 1997)}.



The N1—N2 single bond of 1.316 (3) Å is shorter than that observed in 1,2-bis-[1-(3-pyridyl)3-methyltriazen-3-yl]ethane [1.326 (3) Å; Vaughan *et al.*, 2004] and other triazines (Pottie *et al.*, 1998; Hooper *et al.*, 1998). This shortening in the hydrazone group is consistent with the resonance structures shown in scheme 2, which give the N1—N2 bond some double-bond character. Because of this mesomeric effect, the C8═O3 double bond of 1.208 (3) Å is longer than C10═O1 [1.191 (4) Å] (Table 1).

A significant intramolecular interaction occurs, in which the hydrazo atom H1 forms a three-centred hydrogen bond with atoms O1 and O4, forming two six-membered rings (Fig. 1 and Table 2). The aromatic C1–C6 ring (*A*) and the aliphatic chain (C7–C10/O3) are nearly coplanar, with a dihedral angle of 7.56 (1)° between them. The dihedral angles between the rings formed through intramolecular hydrogen bonding (H1/N2/N1/C9/C10/O1 and H1/N2/C1/C6/N3/O4), the C7/C8/C9/C10/O1/O3/Cl1 plane and ring *A* are 6.80 (1), 2.85 (1) and 5.93 (1)°, respectively.

Further examination of non-bonded contacts in (I) also reveals two intermolecular hydrogen bonds (Table 2). Hence, as shown Fig. 2, pairs of molecules are linked through C5—H5···O3 and C12—H12*B*···O5 hydrogen bonds in a motif described as $S(6)S(6)[R_2^2(13)]S(6)S(6)$ (Bernstein *et al.*, 1995).

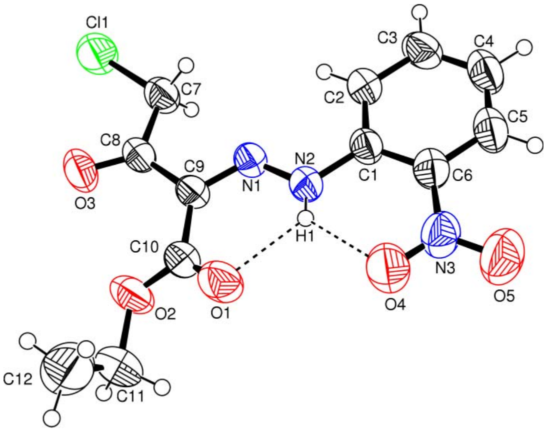


Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. Intramolecular hydrogen bonds are drawn as dashed lines.

The carbonyl groups point in opposite sides of the C8–C10 chain and their bond distances of 1.191 (4) and 1.208 (3) Å are shorter than those observed in similar compounds (Chen *et al.*, 2004; Odabaşoğlu, *et al.*, 2003) but within the normal range for carbonyl compounds (Loudon, 2002).

Experimental

A mixture of 2-nitroaniline (10 mmol), water (50 ml) and concentrated hydrochloric acid (30 mmol) was heated with stirring until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (14 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. The pH was raised to 8–9 by adding dilute NaOH solution. Ethyl 4-chloroacetoacetate (10 mmol) solution in ethanol was gradually added to a cooled solution of the 2-nitrobenzenediazonium chloride, prepared as described above. The resulting mixture was stirred at 273–278 K for 60 min in an ice bath and the pH lowered to 5 with dilute HCl. The product was recrystallized from glacial acetic acid to obtain solid 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyric acid ethyl ester, (I) (yield 95%, m.p. 421–423 K).

Crystal data

$C_{12}H_{12}ClN_3O_5$
M_r = 313.70
Triclinic, $P\overline{1}$
a = 5.1656 (10) Å
b = 7.9102 (16) Å
c = 17.669 (3) Å
α = 83.721 (15)°
β = 82.709 (15)°
γ = 75.683 (15)°
V = 691.6 (2) Å^3
Z = 2
D_x = 1.506 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11207 reflections
θ = 2.3–27.2°
μ = 0.30 mm^{-1}
T = 296 (2) K
Thick plate, red
0.24 × 0.20 × 0.14 mm

Data collection

Stoe IPDS 2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.930, T_{max} = 0.959
11207 measured reflections
3065 independent reflections
1700 reflections with $I > 2\sigma(I)$
R_{int} = 0.099
θ_{max} = 27.2°
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 22$

o2066 Odabaşoğlu *et al.* • $C_{12}H_{12}ClN_3O_5$ *Acta Cryst.* (2005). E**61**, o2065–o2067

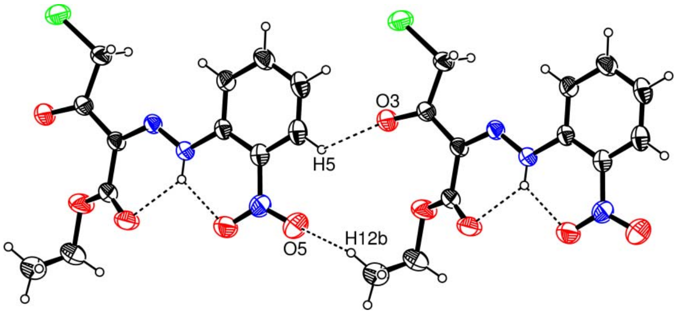


Figure 2
A view of the hydrogen-bonded dimer of (I). Hydrogen bonds are drawn as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.190$
$S = 1.03$
3065 reflections
195 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0974P)^2 + 0.024P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C6—N3	1.453 (4)	C9—N1	1.302 (3)
C1—N2	1.396 (3)	C9—C10	1.491 (4)
C7—Cl1	1.764 (3)	C10—O1	1.191 (4)
C8—O3	1.208 (3)	N2—N1	1.316 (3)
C8—C9	1.468 (4)		
O3—C8—C9	123.3 (3)	N1—N2—C1	118.2 (2)
C8—C9—C10	123.6 (2)	C9—N1—N2	122.1 (2)
O1—C10—C9	122.2 (3)		
O3—C8—C9—N1	−168.4 (3)	C1—C6—N3—O5	171.1 (3)
N1—C9—C10—O1	19.7 (5)	C1—N2—N1—C9	−179.8 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···O4	0.83 (4)	2.01 (4)	2.613 (4)	129 (3)
N2—H1···O1	0.83 (4)	2.06 (4)	2.655 (3)	128 (3)
C5—H5···O3^{i}	0.93	2.57	3.227 (4)	128
C12—H12*B*···O5^{ii}	0.96	2.69	3.482 (6)	141

Symmetry codes: (i) $x+2, y-1, z$; (ii) $x-2, y+1, z$.

The H atom bonded to N2 was refined freely. All other H atoms were refined using a riding model, with C—H = 0.93–0.97 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}$(methyl C)].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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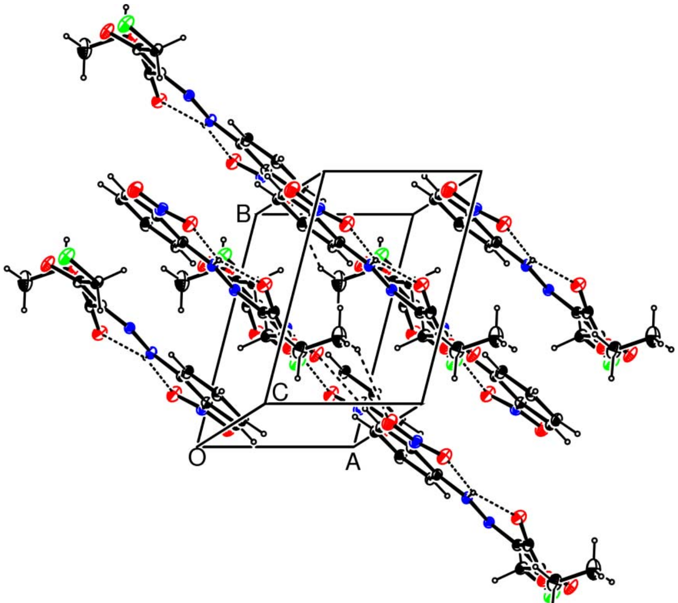

Figure 3
The crystal packing, viewed along the *c* axis. Hydrogen bonds are drawn as dashed lines.

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