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Ethyl 4-chloro-3-oxo-2-(phenylhydrazono)-butyrate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.092
Data-to-parameter ratio = 15.1

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

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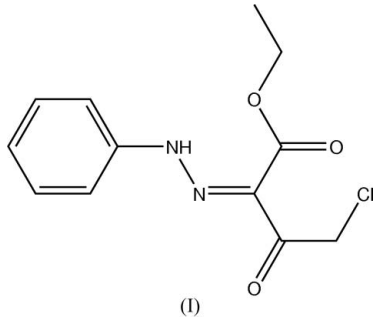
The title compound, $C_{12}H_{13}ClN_2O_3$, adopts a keto–hydrazo tautomeric form stabilized by an intramolecular N—H···O hydrogen bond. The configuration around the C=N bond is *trans*. The dihedral angle between the aromatic ring and the aliphatic chain is 5.52 (9)°. Symmetry-related molecules are linked *via* C—H···O hydrogen bonds to form chains along the *b* axis.

Comment

As part of our project to study the crystal structures of a series of phenylhydrazones and their stereochemistry, the crystal structure of the title compound, (I), has been determined. These compounds can exist either in the normal hydrazone form (Ph—NH—N=C<) or in the azo form (Ph—N=NH—CH<) and have been extensively investigated by various workers, using both chemical and a range of instrumental methods (Prasad & Sahay, 1993). 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).



(I)

Our investigations show that, in the solid state, the molecular structure of (I) adopts a keto–hydrazo tautomeric form with intramolecular hydrogen bonding (Fig. 1). This structure is also indicated by the N1—N2, C1—N1 and N2—C7 bond lengths (Table 1). The corresponding bond lengths in ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate, which exists in the keto–hydrazo tautomeric form, are 1.316 (3), 1.396 (3) and 1.302 (3) Å, respectively (Odabaşoğlu *et al.*, 2005*a*). An H atom is located on N1 rather than on O1, thus confirming a preference for the keto–hydrazo tautomer in the solid state. There is a moderately strong intramolecular N1—H1···O1 hydrogen bond, which is a common feature of similar systems {N—H···O = 2.06 (4) Å in ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005*a*); N—H···O = 2.02 (2) Å in ethyl 4-chloro-2-[(4-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005*b*); N—H···O = 1.97 Å in 4-chloro-2-(4-oxopent-2-en-2-yl-

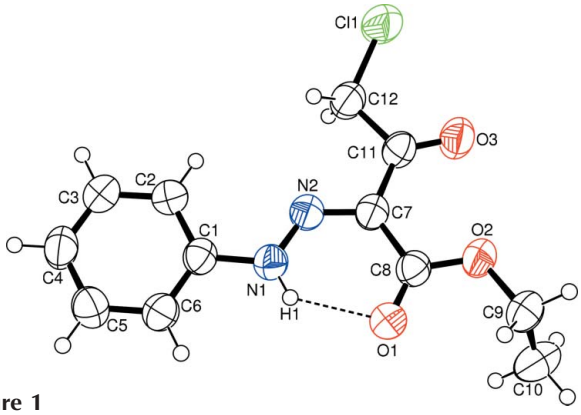


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is shown as a dashed line.

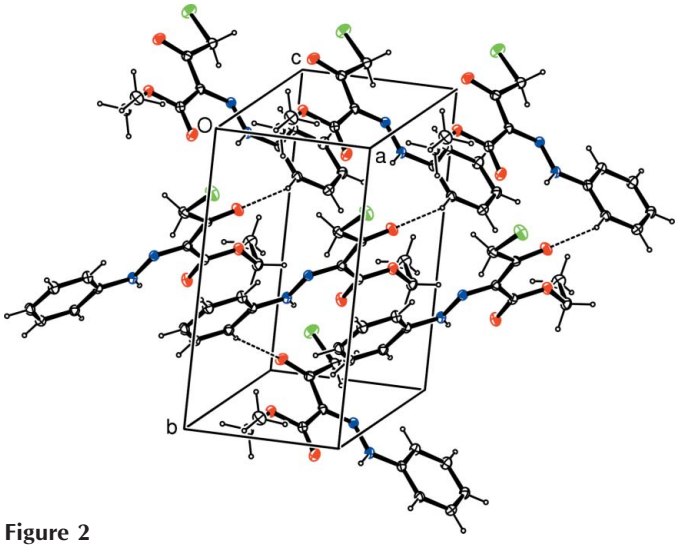


Figure 2
A view of the packing of (I). Hydrogen bonds are drawn as dashed lines.

amino)phenol (Arıcı *et al.*, 1999)}. The molecule adopts a *Z* configuration with respect to the N1—N2 bond. The N1—N2 single bond of 1.300 (2) Å is much shorter than that observed in 1,2-bis-[1-(3-pyridyl)-3-methyltriazen-3-yl]ethane (1.43 Å; Vaughan *et al.*, 2004).

The dihedral angle between the planes of the aromatic C1–C6 ring and the C8/C7/C11/C12/O3 aliphatic chain is 5.52 (9)°. The dihedral angle between the H1/N1/N2/C7/C8/O1 ring formed through intramolecular hydrogen bonding and the O1/C8/C7/C11/C12/O3/Cl1 plane is 3.19 (2)°.

In the crystal structure, molecules of (I) are linked through C6—H6···O3^{i} hydrogen bonds (symmetry code is given in Table 2), forming chains along the *b* axis (Fig. 2).

Experimental

Compound (I) was prepared as the 4-chloro-2-[(4-nitrophenyl)-hydrazono]-3-oxobutyric acid ethyl ester (Odabaşoğlu *et al.*, 2005*a*), using aniline and ethyl 4-chloroacetoacetate as starting materials (yield 87%; m.p. 362–364 K). The compound was recrystallized from glacial acetic acid.

Crystal data

$C_{12}H_{13}ClN_2O_3$
M_r = 268.69
Monoclinic, $P2_1/c$
a = 5.6856 (8) Å
b = 10.9674 (10) Å
c = 20.704 (3) Å
β = 92.306 (12)°
V = 1290.0 (3) Å^3
Z = 4
D_x = 1.384 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7493 reflections
θ = 1.9–27.1°
μ = 0.30 mm^{-1}
T = 296 (2) K
Plate, yellow
0.52 × 0.42 × 0.13 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.860, T_{max} = 0.962
7849 measured reflections
2516 independent reflections
1424 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.0°
$h = -6 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 0.82
2516 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.407 (2)	C9—O2	1.463 (2)
C7—N2	1.314 (2)	C11—O3	1.208 (2)
C8—O1	1.214 (2)	C12—Cl1	1.759 (2)
C8—O2	1.320 (2)	N1—N2	1.300 (2)
C6—C1—N1	118.7 (2)	O1—C8—C7	121.7 (2)
C2—C1—N1	121.4 (2)	O3—C11—C7	124.2 (2)
N2—C7—C11	112.7 (2)	C11—C12—Cl1	111.9 (1)
N2—C7—C8	122.6 (2)	N2—N1—C1	119.4 (2)
C11—C7—C8	124.6 (2)	N1—N2—C7	123.8 (2)
O1—C8—O2	123.4 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O3^{i}	0.93	2.43	3.282 (3)	152
N1—H1···O1	0.83 (2)	1.99 (2)	2.630 (2)	133 (2)

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

The H atom bonded to N1 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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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