

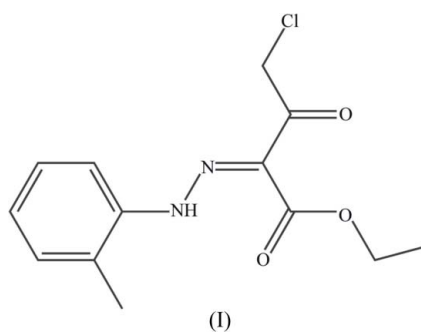
Gökhan Alpaslan,^a Özgür
Özdamar,^b Mustafa
Odabaşoğlu,^b Cem Cüneyt
Ersanlı^{c*} and Ahmet Erdönmez^a^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey, ^bDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Kurupelit-Samsun, Turkey, and ^cDepartment of Physics, Sinop Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-57000 Sinop, Turkey

Correspondence e-mail: ccersan@omu.edu.tr

Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.055
wR factor = 0.158
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(Z)-Ethyl 4-chloro-3-oxo-2-(2-*o*-tolylhydrazono)butanoate**The title compound, $\text{C}_{13}\text{H}_{15}\text{ClN}_2\text{O}_3$, adopts a keto-hydrazo tautomeric form stabilized by an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. The configuration around the $\text{N}-\text{N}$ bond is *trans*. The dihedral angle between the aromatic ring and the plane of the $\text{C}-\text{C}-\text{C}(=\text{O})-\text{C}$ aliphatic chain is $6.07 (8)^\circ$.Received 10 March 2006
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Comment

1,3-Diketones are used in the synthesis of many organic compounds, such as diazepines (Khudina *et al.*, 2004), pyrazoles, pyrimidines 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 (Nathan & Silver, 1997). In addition, the chemistry of hydrazones has been intensively investigated in recent years, owing to their coordinating capability, pharmacological activity and antibacterial and antifungal properties, and their use in analytical chemistry as highly selective extractants (Domiano *et al.*, 1984; Li *et al.*, 1988; Sakamoto *et al.*, 1993). As part of our project studying the crystal structures of a series of phenylhydrazones and their stereochemistry, the crystal structure of the title compound, (I), has been determined.The molecular structure and atom-labelling scheme are shown in Fig. 1. The dihedral angle between the aromatic $\text{C}1-\text{C}6$ ring (*A*) and the plane of the $\text{C}9/\text{C}8/\text{C}12/\text{C}13/\text{O}3$ aliphatic chain is $6.07 (8)^\circ$. The dihedral angle between ring *A* and the plane of the ring formed through intramolecular hydrogen bonding ($\text{H}1/\text{N}1/\text{N}2/\text{C}8/\text{C}9/\text{O}1$) is $4.54 (7)^\circ$; that between ring *A* and the $\text{C}13/\text{C}12/\text{C}8/\text{C}9/\text{O}1/\text{O}3/\text{Cl}1$ plane is $1.17 (8)^\circ$. The whole molecule is roughly planar, the largest deviation from the mean plane being $1.077 (3) \text{ \AA}$ for atom $\text{C}11$.The bond lengths and angles in (I) show normal values and are comparable with those observed in ethyl 4-chloro-3-oxo-2-(phenylhydrazono)butyrate, (II) (Alpaslan *et al.*, 2005a) and (*E*)-ethyl 4-chloro-3-[2-(2-fluorophenyl)hydrazono]butan-

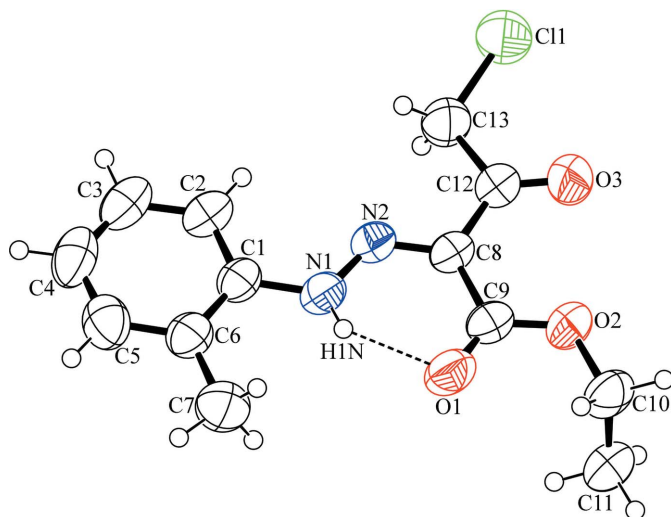


Figure 1

The molecular structure of (I), with the atom-numbering scheme, showing the intramolecular N—H...O hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

oate, (III) (Alpaslan *et al.*, 2005*b*). In (I), the imino group adopts a (*Z*) configuration. The bond lengths (Table 1) show that there is significant elongation of the N1—N2 bond and contraction of the C1—N1 bond in comparison 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 1.272 (2)–1.303 (3) Å (Galić *et al.*, 2000; Baughman *et al.*, 2004; Ersanlı, Albayrak, Odabaşoğlu, & Erdönmez, 2004; Ersanlı, Odabaşoğlu *et al.*, 2004; Petek *et al.*, 2005; Butcher *et al.*, 2005).

Atom H1N was located on atom N1, confirming a preference for the keto–hydrazone tautomer in the solid state. There is a strong intramolecular N—H...O hydrogen bond in (I) (Table 2), which is a common feature of similar systems (Ersanlı *et al.*, 2003; Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez, 2004; Alpaslan *et al.*, 2005*a,b*).

The N1—N2 single bond of 1.297 (3) Å is shorter than that observed in 1,2-bis-[1-(3-pyridyl)3-methyltriazene-3-yl]ethane [1.326 (3) Å; Vaughan *et al.*, 2004]. This shortening in the hydrazone group is consistent with the resonance structures, which give the N1—N2 bond some double-bond character.

Experimental

A mixture of *o*-methylaniline (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 (50 ml) 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-chloroacetate (10 mmol) solution in ethanol (25 ml) was gradually added to a cooled solution of *o*-methylbenzenediazonium 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 absolute ethanol to obtain well shaped crystals of (I) (yield 90%, m.p. 397–399 K).

Crystal data

C₁₃H₁₅ClN₂O₃
M_r = 282.72
 Monoclinic, *P*2₁/*c*
a = 4.7495 (3) Å
b = 14.4685 (11) Å
c = 20.2429 (16) Å
 β = 93.584 (6)°
V = 1388.33 (18) Å³

Z = 4
D_x = 1.353 Mg m⁻³
 Mo K α radiation
 μ = 0.28 mm⁻¹
T = 296 (2) K
 Needle, yellow
 0.60 × 0.14 × 0.13 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.876, *T_{max}* = 0.976

12661 measured reflections
 2404 independent reflections
 1665 reflections with *I* > 2 σ (*I*)
R_{int} = 0.141
 θ_{max} = 25.0°

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.055
wR(*F*²) = 0.158
S = 1.04
 2404 reflections
 177 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.084P)^2 + 0.0492P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.24 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.31 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1—N1	1.405 (3)	C9—O1	1.205 (3)
C8—N2	1.309 (3)	C9—O2	1.311 (3)
C12—O3	1.199 (3)	C10—O2	1.466 (3)
C13—C11	1.764 (3)	N1—N2	1.297 (3)
C6—C1—N1	118.1 (2)	O1—C9—O2	123.8 (2)
C2—C1—N1	120.6 (2)	O1—C9—C8	121.4 (2)
N2—C8—C12	113.6 (2)	O2—C9—C8	114.8 (2)
N2—C8—C9	122.6 (2)	O2—C10—C11	111.7 (2)
O3—C12—C8	124.6 (2)	N2—N1—C1	121.4 (2)
O3—C12—C13	120.9 (2)	N1—N2—C8	122.6 (2)
C12—C13—C11	111.4 (2)	C9—O2—C10	116.4 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O1	0.81 (4)	1.94 (4)	2.599 (3)	139 (3)

The high value of *R_{int}* indicates that the overall quality of the data may be poor due to the crystal quality. The H atom bonded to N1 was refined freely. All other H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97 Å and *U_{iso}*(H) = 1.2 *U_{eq}*(C), or 1.5 *U_{eq}*(C) for methyl H atoms.

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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