

Gökhan Alpaslan,<sup>a</sup> Özgür Özdamar,<sup>b</sup> Mustafa Odabaşoğlu,<sup>b</sup> Cem Cüneyt Ersanlı,<sup>a</sup> Ahmet Erdönmez<sup>a</sup> and Nazan Ocak İskeleli<sup>a\*</sup>

<sup>a</sup>Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey, and <sup>b</sup>Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey

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

#### Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.046  
 $wR$  factor = 0.128  
Data-to-parameter ratio = 17.3

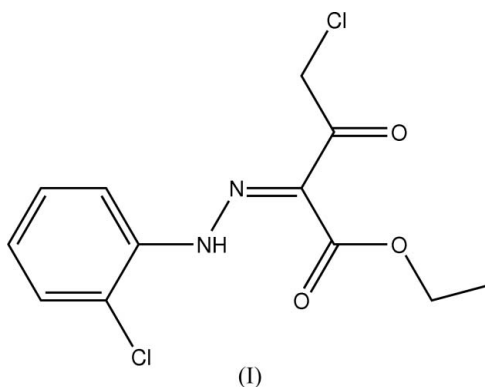
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## (Z)-Ethyl 4-chloro-2-[2-(2-chlorophenyl)hydrazono]-3-oxobutanoate

The title compound,  $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_3$ , adopts a keto–hydrazone tautomeric form stabilized by an intramolecular hydrogen bond. The molecule can be considered as consisting of two connected fragments, *viz.* a chlorophenylhydrazone group, with a *Z* configuration, and an oxobutanoate group. The molecule is roughly planar, the dihedral angle between the benzene ring and the plane including the aliphatic chain being  $4.7(2)^\circ$ .

#### 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. The chemistry of hydrazones has been intensively investigated in recent years, owing to their coordinating capability, pharmacological activity, and antibacterial and antifungal properties, and to their use in analytical chemistry as highly selective extractants (Domiano *et al.*, 1984; Sakamoto *et al.*, 1993; Li *et al.*, 1988). These compounds can exist either in the normal hydrazone form ( $\text{Ph}-\text{NH}-\text{N}=\text{C}<$ ) or in the azo form ( $\text{Ph}-\text{N}=\text{NH}-\text{CH}<$ ) and have been extensively investigated by both chemical and instrumental methods (Prasad & Sahay, 1993).

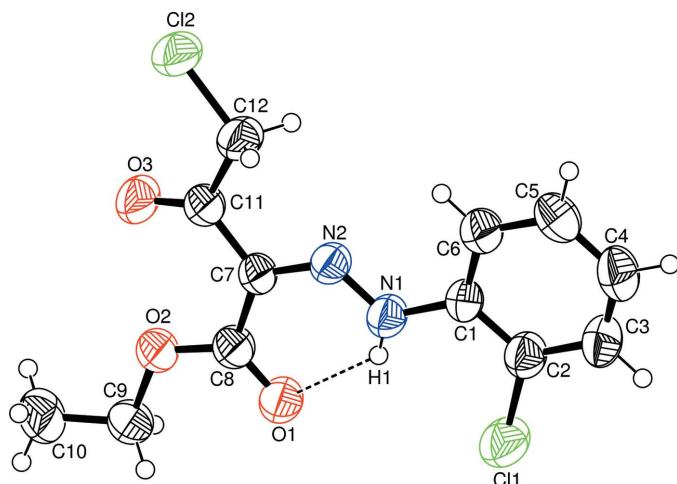


The crystal structure determination of the title compound, (I), was carried out to determine the strength of the hydrogen-bonding capabilities of the aliphatic chain and hydrazone ( $\text{HN}-\text{N}=\text{C}$ ) groups, as well as to establish the molecular arrangement; the aim also was to compare the geometry of the aliphatic chain and hydrazone groups with those found in ethyl 4-chloro-3-oxo-2-(phenylhydrazono)butyrate, (II) (Alpaslan *et al.*, 2005a), (*E*)-ethyl 4-chloro-3-[2-(2-fluorophenyl)hydrazono]butanoate, (III) (Alpaslan *et al.*, 2005b), and (*Z*)-ethyl 4-chloro-2-[2-(2-methoxyphenyl)hydrazono]-3-oxobutanoate, (IV) (Alpaslan *et al.*, 2005c).

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**Figure 1**

A molecular view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

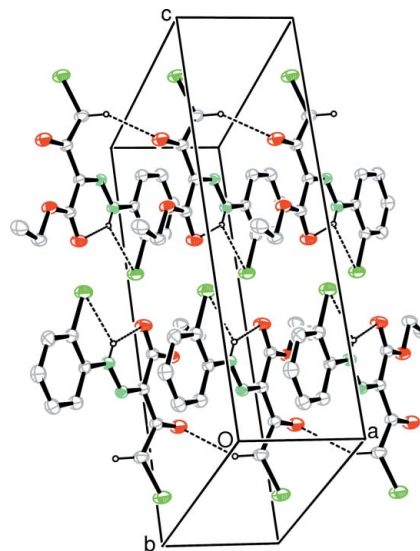
Compound (I) consists of an aromatic ring and an aliphatic chain linked through a hydrazone group (Fig. 1). The molecule adopts a *trans* conformation about the N1–N2 bond, as evidenced by the C1–N1–N2–C7 torsion angle of 178.2 (3)°. The molecule is roughly planar, the dihedral angle between the phenyl ring and the mean plane defined by the C7–C12/O1–O3/C12 aliphatic chain being 4.7 (2)°.

The present X-ray investigation shows that (I) prefers the keto–hydrazo tautomeric form rather than the phenylhydrazo tautomeric form. The results obtained in this study indicate that there are slight differences when comparing the geometry of (I) with the geometries of other aliphatic chain and phenylhydrazone groups, such as those in (II), (III) and (IV) (Table 2).

A moderately strong N1–H1···O1 intramolecular hydrogen bond (Fig. 1 and Table 1) is observed in the molecular structure. It is a common feature for related systems {N–H···O = 2.06 (4) Å in ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005a); N–H···O = 2.02 (2) Å in ethyl 4-chloro-2-[(4-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005b)}. In addition, atom C12 is involved in an intermolecular hydrogen-bond interaction which stabilizes the molecular packing (Table 1 and Fig. 2).

## Experimental

A mixture of *o*-chloroaniline (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. An ethyl 4-chloroacetoacetate (10 mmol) solution in ethanol was gradually added to a cooled solution of the *o*-chlorobenzenediazonium chloride, prepared as described above. The resulting mixture was stirred at 273–278 K



**Figure 2**

Part of the crystal packing of (I). Hydrogen bonds are drawn as dashed lines. For clarity, H atoms not involved in hydrogen bonding have been omitted.

for 60 min in an ice bath and the pH was lowered to 5 with dilute HCl. The product was recrystallized from glacial acetic acid to obtain well shaped crystals of (I) (yield 92%, m.p. 426–429 K).

### Crystal data

$C_{12}H_{12}Cl_2N_2O_3$	$Z = 2$
$M_r = 303.14$	$D_x = 1.472 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.466$ (5) Å	Cell parameters from 10737 reflections
$b = 9.248$ (5) Å	$\theta = 2.3\text{--}27.1^\circ$
$c = 17.078$ (5) Å	$\mu = 0.48 \text{ mm}^{-1}$
$\alpha = 95.000$ (5)°	$T = 296$ (2) K
$\beta = 94.336$ (5)°	Prism, colourless
$\gamma = 102.054$ (5)°	$0.48 \times 0.21 \times 0.14 \text{ mm}$
$V = 684.0$ (9) Å <sup>3</sup>	

### Data collection

Stoe IPDS-II diffractometer	$R_{\text{int}} = 0.091$
$\omega$ scans	$\theta_{\text{max}} = 27.2^\circ$
Absorption correction: none	$h = -5 \rightarrow 5$
12555 measured reflections	$k = -11 \rightarrow 11$
2986 independent reflections	$l = -21 \rightarrow 21$
1545 reflections with $I > 2\sigma(I)$	

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.059P)^2]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2986 reflections	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
173 parameters	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1–H1···O1	0.86	1.95	2.608 (3)	132
C12–H12B···O3 <sup>i</sup>	0.97	2.56	3.426 (5)	148

Symmetry code: (i)  $x + 1, y, z$ .

**Table 2**

Comparison of geometric parameters (Å, °) in the phenylhydrazone group and aliphatic chain of (I) with those in the related compounds (II), (III) and (IV) (see *Comment*).

	(I)	(II)	(III)	(IV)
N1–N2	1.300 (3)	1.300 (2)	1.306 (2)	1.300 (2)
C1–N1	1.405 (3)	1.407 (2)	1.400 (2)	1.408 (2)
C7–N2	1.313 (3)	1.314 (2)	1.308 (2)	1.311 (2)
C8–O1	1.219 (3)	1.214 (2)	1.216 (2)	1.215 (2)
C8–O2	1.315 (3)	1.320 (2)	1.308 (2)	1.321 (2)
C12–C11	1.765 (3)	1.759 (2)	1.760 (2)	1.766 (2)
C1–N1–N2	120.0 (2)	119.4 (2)	119.7 (1)	118.9 (2)
C7–N2–N1	122.5 (2)	123.8 (2)	122.1 (1)	123.0 (2)
C1–N1–N2–C7	178.1 (3)	176.9 (2)	178.7 (2)	174.2 (2)

All H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C–H = 0.93–0.97 Å and N–H = 0.86 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$  (for C<sub>phenyl</sub>, CH<sub>2</sub> and NH) and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  (for CH<sub>3</sub>).

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-III* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

- Alpaslan, G., Özdamar, Ö., Odabaşoğlu, M., Ersanlı, C. C., Büyükgüngör, O. & Erdönmez, A. (2005a). *Acta Cryst.* **E61**, o2428–o2430.
- Alpaslan, G., Özdamar, Ö., Odabaşoğlu, M., Ersanlı, C. C., Büyükgüngör, O. & Erdönmez, A. (2005b). *Acta Cryst.* **E61**, o2823–o2825.
- Alpaslan, G., Özdamar, Ö., Odabaşoğlu, M., Ersanlı, C. C., Büyükgüngör, O. & Erdönmez, A. (2005c). *Acta Cryst.* **E61**, o3442–o3444.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP-III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Domiano, P., Pelizzi, C. & Predieri, G. (1984). *Polyhedron*, **3**, 281–286.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Li, X. R., Sun, Z. M. & Chang, J. C. (1988). *Synth. React. Inorg. Met.-Org. Chem.* **18**, 657–665.
- Odabaşoğlu, M., Özdamar, Ö. & Büyükgüngör, O. (2005a). *Acta Cryst.* **E61**, o2065–o2067.
- Odabaşoğlu, M., Özdamar, Ö. & Büyükgüngör, O. (2005b). *Acta Cryst.* **E61**, o2068–o2070.
- Prasad, N. & Sahay, A. (1993). *Asian J. Chem. Rev.* **4**, 23–32.
- Sakamoto, H., Goto, H., Yokoshima, M., Dobashi, M., Ishikawa, J., Doi, K. & Otomo, M. (1993). *Bull. Chem. Soc. Jpn.* **66**, 2907–2914.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.