

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  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
R factor = 0.040  
wR factor = 0.117  
Data-to-parameter ratio = 14.7

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

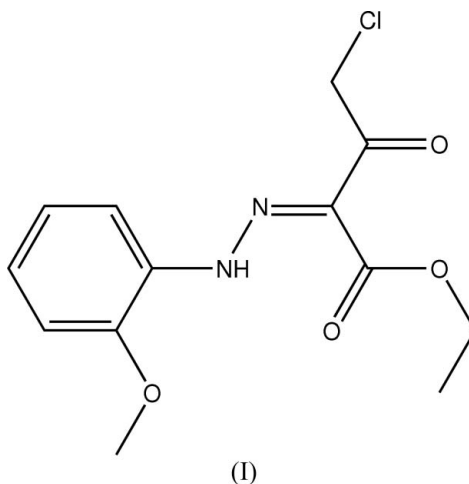
**(Z)-Ethyl 4-chloro-2-[2-(2-methoxyphenyl)-hydrazono]-3-oxobutanoate**

The title compound,  $\text{C}_{13}\text{H}_{15}\text{ClN}_2\text{O}_4$ , adopts a keto–hydrazo tautomeric form stabilized by intramolecular N–H···O hydrogen bonds. The phenylhydrazone fragment is planar within  $\pm 0.028 (2) \text{ \AA}$ . The dihedral angle between the phenylhydrazone and oxobutanoate planes is  $8.15 (9)^\circ$ . Symmetry-related molecules are linked *via* C–H···O hydrogen bonds to form chains along [101].

Received 14 September 2005  
Accepted 21 September 2005  
Online 28 September 2005

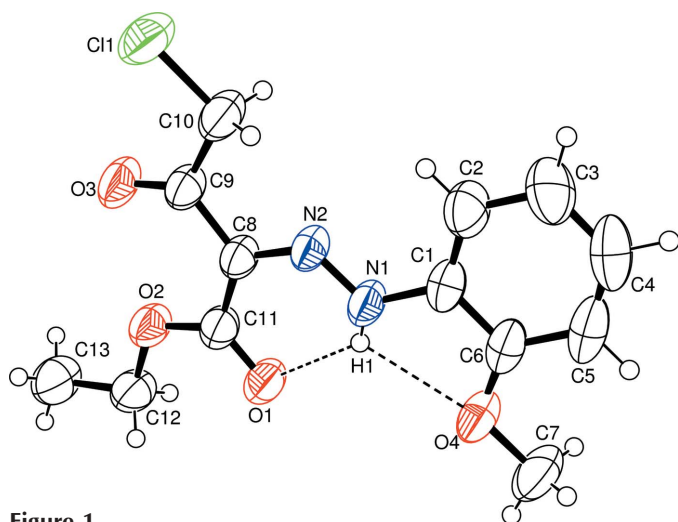
**Comment**

Various hydrazone compounds possess strong bactericidal, herbicidal, insecticidal and fungicidal properties (Sahni *et al.*, 1977). Some phenylhydrazone derivatives have been shown to be potentially DNA-damaging and are mutagenic agents (Okabe *et al.*, 1993). In addition, hydrazones have analytical applications (Heit & Ryan, 1966; Jensen & Pflaum, 1967; Dey *et al.*, 1985). Hydrazones have interesting ligational properties as a result of the presence of several potential coordination sites (Dutta & Hossain, 1985), and both transition and non-transition metal complexes of these ligands have been synthesized previously (Dey *et al.*, 1992).

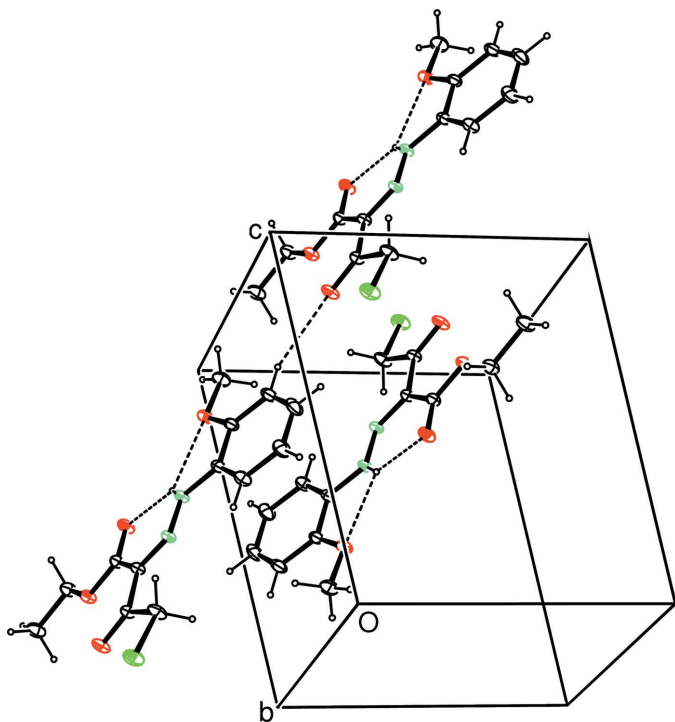


As part of our ongoing research on phenylhydrazone derivatives, the title compound, (I), has been synthesized and its crystal structure is reported here. Previously we reported the structures of ethyl 4-chloro-3-oxo-2-(phenylhydrazone)butyrate (Alpaslan *et al.*, 2005a), (*E*)-ethyl 4-chloro-3-[2-(2-fluorophenyl)hydrazono]butanoate (Alpaslan *et al.*, 2005b), ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005a) and ethyl 4-chloro-2-[(4-nitrophenyl)hydrazono]-3-oxobutyrate (Odabaşoğlu *et al.*, 2005b).

Our investigations show that, in the solid state, the molecular structure of (I) adopts the keto–hydrazo tautomeric



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



**Figure 2**  
Part of the crystal packing of (I). Hydrogen bonds are drawn as dashed lines.

form with intramolecular hydrogen bonds (Fig. 1). The phenylhydrazone fragment is planar within  $\pm 0.028$  (2) Å, and atoms O4 and C7 deviate from that plane by 0.014 (3) and  $-0.165$  (4) Å, respectively. The oxobutanoate fragment (O1–O3/C8–C13) is planar (r.m.s. deviation 0.020 Å). The dihedral angle between the phenylhydrazone and O1–O3/C8–C13 planes is  $8.15$  (9)°.

It is remarkable that the *Z* isomer of the methoxyphenylhydrazone derivative was formed preferentially over the *E* isomer, since the latter would almost certainly feature an N–H...O=C intramolecular hydrogen bond. In (I), the imine

group adopts a *Z* configuration, with bond lengths C1–N1 =  $1.408$  (2) Å, C8–N2 =  $1.311$  (2) Å and N1–N2 =  $1.300$  (2) Å. These data show that there is significant elongation of the N1–N2 bond and contraction of the C1–C2 bond in comparison with azo compounds. For example, the N=N and C–N bonds in azobenzene are  $1.255$  (2) Å and  $1.432$  (2) Å, respectively (Patai, 1975), while the C=N double bonds in imine compounds are in the range  $1.270$  (5)– $1.303$  (3) Å (Ersanlı, Odabaşoğlu, *et al.*, 2004; Baughman *et al.*, 2004; Ersanlı, Albayrak *et al.*, 2004; Odabaşoğlu *et al.*, 2005; Şahin *et al.*, 2005; Butcher *et al.*, 2005). There is a moderately strong intramolecular N1–H1...O1 hydrogen bond, which is a common feature of similar systems {N–H...O =  $1.99$  (2) Å in ethyl 4-chloro-3-oxo-2-(phenylhydrazono)butyrate (Alpaslan *et al.*, 2005a); N–H...O =  $1.96$  (2) Å in (*E*)-ethyl 4-chloro-3-[2-(2-fluorophenyl)hydrazono]butanoate (Alpaslan *et al.*, 2005b)}. The carbonyl groups are on opposite sides of the C9–C8–C11 chain and their bond distances of  $1.203$  (2) and  $1.215$  (2) 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).

In the crystal structure, C5–H5...O3<sup>i</sup> intermolecular hydrogen bonds link the molecules into a chain along [101] (Fig. 2); symmetry code (i) is given in Table 2.

## Experimental

A mixture of *o*-methoxyaniline (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*-methoxybenzenediazonium chloride, prepared as described above. The resulting mixture was stirred at 273–278 K 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 86%, m.p. 423–424 K).

### Crystal data

C<sub>13</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>4</sub>  
 $M_r = 298.72$   
 Triclinic,  $P\bar{1}$   
 $a = 8.605$  (5) Å  
 $b = 8.981$  (5) Å  
 $c = 9.974$  (5) Å  
 $\alpha = 107.615$  (5)°  
 $\beta = 103.543$  (5)°  
 $\gamma = 94.952$  (5)°  
 $V = 703.9$  (7) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.409$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8830 reflections  
 $\theta = 2.4$ – $27.2$ °  
 $\mu = 0.29$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 Prism, yellow  
 $0.49 \times 0.36 \times 0.14$  mm

### Data collection

Stoe IPDS-II diffractometer  
 $\omega$  scans  
 Absorption correction: integration  
 (*X-RED32*; Stoe & Cie, 2002)  
 $T_{\min} = 0.885$ ,  $T_{\max} = 0.964$   
 10993 measured reflections  
 2741 independent reflections

1906 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 26.0$ °  
 $h = -10 \rightarrow 10$   
 $k = -11 \rightarrow 11$   
 $l = -12 \rightarrow 12$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.117$   
 $S = 1.03$   
 2741 reflections  
 187 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.0281P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C6—O4	1.368 (3)	C11—O1	1.215 (2)
C7—O4	1.419 (3)	C11—O2	1.321 (2)
C9—O3	1.203 (2)	C12—O2	1.451 (2)
N2—C8—C9	112.68 (16)	O1—C11—O2	123.04 (18)
C11—C8—C9	124.8 (2)	O2—C11—C8	115.15 (15)
O3—C9—C8	124.6 (2)	N2—N1—C1	118.9 (2)
C8—C9—C10	114.38 (15)	N1—N2—C8	122.97 (16)
N1—C1—C6—O4	−2.2 (2)	C1—N1—N2—C8	174.2 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 $\cdots$ O3 <sup>i</sup>	0.93	2.56	3.413 (3)	153
N1—H1 $\cdots$ O1	0.79 (2)	2.02 (2)	2.602 (2)	131 (2)
N1—H1 $\cdots$ O4	0.79 (2)	2.31 (2)	2.635 (2)	106 (2)

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

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  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}) [1.5U_{\text{eq}}(\text{methyl C})]$ .

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, 1990); 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).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under grant No. F279 of the University Research Fund).

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.
- Baughman, R. G., Martin, K. L., Singh, R. K. & Stoffer, J. O. (2004). *Acta Cryst.* **C60**, o103–o106.
- Butcher, R. J., Basu Baul, T. S., Singh, K. S. & Smith, F. E. (2005). *Acta Cryst.* **E61**, o1007–o1009.
- Chen, B., Fronczek, F. R. & Maverick, A. W. (2004). *Acta Cryst.* **C60**, m147–m149.
- Dey, K., Mandal, K. & Bandyopadhyay, D. (1992). *Indian J. Chem. Sect. A*, **31**, 937–942.
- Dey, K., Ray, S. B., Bhattacharya, P. K., Gangopadhyay, A., Bhasin, K. K. & Verma, R. D. (1985). *J. Indian Chem. Soc.* **62**, 809–814.
- Dutta, R. L. & Hossain, M. (1985). *J. Sci. Ind. Res.* **44**, 635–674.
- Ersanlı, C. C., Albayrak, Ç., Odabaşoğlu, M. & Erdönmez, A. (2004). *Acta Cryst.* **E60**, o389–o391.
- Ersanlı, C. C., Odabaşoğlu, M., Albayrak, Ç. & Erdönmez, A. (2004). *Acta Cryst.* **E60**, o264–o266.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Heit, M. L. & Ryan, D. E. (1966). *Anal. Chim. Acta*, **34**, 407–411.
- Jensen, R. E. & Pflaum, R. T. (1967). *Anal. Chim. Acta*, **37**, 397–400.
- Loudon, M. G. (2002). *Organic Chemistry*, 4th ed., p. 837. Oxford University Press.
- Odabaşoğlu, M., Albayrak, Ç. & Büyükgüngör, O. (2005). *Acta Cryst.* **E61**, o425–o426.
- Odabaşoğlu, M., Büyükgüngör, O., Turgut, G., Karadağ, A., Bulak, E. & Lönnecke, P. (2003). *J. Mol. Struct.* **648**, 133–138.
- Odabaşoğlu, M., Özdamar, Ö. & Büyükgüngör, O. (2005a). *Acta Cryst.* **E61**, o2065–o2067.
- Odabaşoğlu, M., Özdamar, Ö. & Büyükgüngör, O. (2005b). *Acta Cryst.* **E61**, o2068–o2070.
- Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* **C49**, 1678–1680.
- Patai, S. (1975). *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, p. 43. London: John Wiley & Sons.
- Şahin, O., Büyükgüngör, O., Albayrak, Ç. & Odabaşoğlu, M. (2005). *Acta Cryst.* **E61**, o1579–o1581.
- Sahni, S. K., Sangal, S. K., Gupta, S. P. & Rana, V. B. (1977). *J. Inorg. Nucl. Chem.* **39**, 1098–1100.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.