

## Ethyl (Z)-2-chloro-2-(2-phenylhydrazin-1-ylidene)acetate

Abdullah M. Asiri,<sup>a</sup> Mohie E. M. Zayed<sup>a</sup> and Seik Weng Ng<sup>b\*</sup>

<sup>a</sup>Chemistry Department, Faculty of Science, King Abdul Aziz University, PO Box 80203, Jeddah 21589, Saudi Arabia, and <sup>b</sup>Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

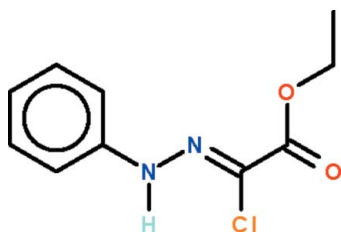
Received 11 August 2010; accepted 13 August 2010

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.076; data-to-parameter ratio = 17.1.

The title compound,  $\text{C}_{10}\text{H}_{11}\text{ClN}_2\text{O}_2$ , features an almost planar  $\text{C}_{\text{ar}}-\text{N}(\text{H})-\text{N}=\text{C}(\text{Cl})$  unit [torsion angle =  $0.8$  (1)° whose phenyl substituent is almost coplanar with it [dihedral angle =  $2.8$  (2)°]; this unit is slightly twisted with respect to the carboxyl  $-\text{CO}_2$  fragment [dihedral angle =  $10.3$  (2)°]. In the crystal, the amino group acts as a hydrogen-bond donor to the carbonyl O atom of an adjacent molecule; the hydrogen bond generates a helical chain that runs along the  $b$  axis of the monoclinic unit cell.

### Related literature

For a review of the reactions of hydrazonyl halides with heterocyclic thiones for heteroannulation, the synthesis of spiroheterocycles and heterocyclic ring formation, see: Shawali & Farghaly (2008). For related crystal structures, see: Xu (2006); Yin *et al.* (2006).



### Experimental

#### Crystal data

$\text{C}_{10}\text{H}_{11}\text{ClN}_2\text{O}_2$   
 $M_r = 226.66$   
 Monoclinic,  $P2_1/c$   
 $a = 10.5091$  (7) Å  
 $b = 11.1813$  (8) Å  
 $c = 10.1190$  (7) Å  
 $\beta = 118.148$  (1)°  
 $V = 1048.41$  (13) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.35$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.30 \times 0.30 \times 0.10$  mm

#### Data collection

Bruker SMART APEX diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.904$ ,  $T_{\text{max}} = 0.966$   
 6532 measured reflections  
 2399 independent reflections  
 2191 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.076$   
 $S = 1.03$   
 2399 reflections  
 140 parameters  
 1 restraint  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}^i$	0.85 (1)	2.18 (1)	2.969 (1)	153 (2)

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

The authors thank King Abdul Aziz University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2054).

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**supplementary materials**

*Acta Cryst.* (2010). E66, o2374 [ doi:10.1107/S1600536810032587 ]

## Ethyl (Z)-2-chloro-2-(2-phenylhydrazin-1-ylidene)acetate

A. M. Asiri, M. E. M. Zayed and S. W. Ng

### Comment

Ethyl 2-chloro(phenylhydrazono)acetate belongs to the class of of hydrazonyl halides that undergo heteroannulation, and are used for the synthesis of spiroheterocycles and other heterocyclic compounds. The utility in some aspects of heterocyclic chemistry has recently been reviewed (Shawali & Farghaly (2008). The central structural feature is an planar  $C_{aryl}-NH-N=C$  unit, as noted in the crystal structures of other substituted derivatives (Xu, 2006; Yin *et al.*, 2006). The parent compound (Scheme I) shows this characteristic linkage, whose torsion angle is  $0.8(1)^\circ$ . The carbon-nitrogen double bond is of a *Z*-configuration (Fig. 1). Such a configuration allows the amino site to form a hydrogen bond to the double-bond carbonyl oxygen atom of an adjacent molecule, this hydrogen bond giving rise to a helical chain that runs along the *b*-axis of the unit cell (Fig. 2).

### Experimental

The synthesis works with either 3-chloropentane-2,4-dione or ethyl 2-chloro-3-oxobutanoate. To a solution of either 3-chloropentane-2,4-dione (1.34 g, 10 mmol) or ethyl 2-chloro-3-oxobutanoate (1.64 g, 10 mmol) in ethanol (100 ml) was added sodium acetate trihydrate (1.3 g, 10 mmol). The mixture was chilled to 273 K. To the mixture was added a cold solution of benzenediazonium chloride, prepared by diazotizing aniline (0.93 g, 10 mmol) dissolved in 6*M* hydrochloric acid (6 ml) with a solution of sodium nitrite (0.7 g, 10 mmol) dissolved in water (10 ml). The diazonium salt was added over a period of 20 min. The reaction mixture was stirred for another 15 min. and then left for 3 h in a refrigerator. The resulting solid was collected and washed with water. The crude product was recrystallized from ethanol to give the hydrazone in 80% yield; m.p. 352–353 K.

### Refinement

Carbon-bound H-atoms were placed in calculated positions [ $C-H$  0.95 to 0.99 Å,  $U(H)$  1.2 to 1.5  $U_{eq}(C)$ ] and were included in the refinement in the riding model approximation. The amino H-atom was located in a difference Fourier map, and was refined with a distance restraint [ $N-H$  0.86±0.01 Å]; its temperature factor was freely refined.

### Figures

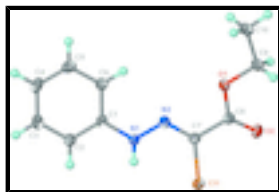


Fig. 1. Displacement ellipsoid plot of  $C_{10}H_{11}ClN_2O_2$  at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

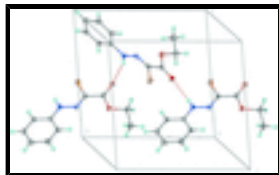


Fig. 2. Part of the hydrogen-bonded helical chain structure (red dashed lines) which runs along the *b*-axis.

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Hall symbol: -P 2ybc

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$c = 10.1190$  (7) Å

$\beta = 118.148$  (1)°

$V = 1048.41$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 472$

$D_x = 1.436$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4259 reflections

$\theta = 2.3$ – $28.3$ °

$\mu = 0.35$  mm<sup>-1</sup>

$T = 100$  K

Irregular, yellow

$0.30 \times 0.30 \times 0.10$  mm

### Data collection

Bruker SMART APEX  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.904$ ,  $T_{\max} = 0.966$

6532 measured reflections

2399 independent reflections

2191 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 2.2$ °

$h = -13 \rightarrow 11$

$k = -14 \rightarrow 12$

$l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.076$

$S = 1.03$

2399 reflections

140 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.389P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.52913 (3)	0.54445 (2)	0.33899 (3)	0.02076 (10)
O1	0.67383 (8)	0.38123 (7)	0.09626 (9)	0.01737 (18)
O2	0.49929 (9)	0.33068 (7)	0.15554 (9)	0.01943 (19)
N1	0.70432 (10)	0.70808 (8)	0.26261 (10)	0.0153 (2)
H1	0.6608 (17)	0.7284 (15)	0.3121 (17)	0.032 (4)*
N2	0.68722 (10)	0.59913 (8)	0.20434 (10)	0.01443 (19)
C1	0.78999 (11)	0.79127 (10)	0.23651 (11)	0.0143 (2)
C2	0.81229 (12)	0.90363 (10)	0.30391 (12)	0.0171 (2)
H2	0.7691	0.9232	0.3651	0.020*
C3	0.89810 (12)	0.98666 (11)	0.28081 (13)	0.0201 (2)
H3	0.9140	1.0629	0.3273	0.024*
C4	0.96101 (13)	0.95973 (11)	0.19073 (14)	0.0208 (2)
H4	1.0194	1.0170	0.1753	0.025*
C5	0.93736 (12)	0.84780 (11)	0.12342 (13)	0.0201 (2)
H5	0.9796	0.8289	0.0612	0.024*
C6	0.85275 (12)	0.76310 (10)	0.14599 (12)	0.0167 (2)
H6	0.8378	0.6866	0.1001	0.020*
C7	0.61141 (12)	0.52090 (10)	0.22737 (12)	0.0152 (2)
C8	0.58682 (11)	0.40102 (10)	0.15624 (12)	0.0147 (2)
C9	0.66715 (12)	0.26082 (10)	0.03770 (13)	0.0176 (2)
H9A	0.5698	0.2446	-0.0461	0.021*
H9B	0.6887	0.2006	0.1172	0.021*
C10	0.77830 (12)	0.25572 (12)	-0.01594 (13)	0.0213 (3)
H10A	0.7777	0.1760	-0.0566	0.032*
H10B	0.8740	0.2719	0.0681	0.032*
H10C	0.7557	0.3159	-0.0943	0.032*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.02594 (16)	0.01667 (16)	0.02897 (16)	-0.00155 (10)	0.02060 (13)	-0.00199 (10)
O1	0.0184 (4)	0.0141 (4)	0.0232 (4)	-0.0018 (3)	0.0128 (3)	-0.0032 (3)
O2	0.0200 (4)	0.0155 (4)	0.0260 (4)	-0.0020 (3)	0.0136 (3)	0.0007 (3)
N1	0.0167 (4)	0.0138 (5)	0.0185 (4)	-0.0005 (4)	0.0109 (4)	-0.0015 (3)
N2	0.0133 (4)	0.0130 (5)	0.0153 (4)	0.0013 (3)	0.0053 (3)	0.0007 (3)
C1	0.0109 (5)	0.0151 (5)	0.0148 (5)	0.0005 (4)	0.0043 (4)	0.0024 (4)
C2	0.0165 (5)	0.0163 (6)	0.0187 (5)	0.0016 (4)	0.0087 (4)	0.0002 (4)
C3	0.0187 (5)	0.0144 (5)	0.0249 (6)	-0.0006 (4)	0.0084 (5)	0.0001 (4)
C4	0.0164 (5)	0.0202 (6)	0.0247 (6)	-0.0026 (4)	0.0090 (5)	0.0044 (4)
C5	0.0172 (5)	0.0250 (6)	0.0201 (5)	0.0002 (5)	0.0105 (4)	0.0017 (4)
C6	0.0163 (5)	0.0169 (5)	0.0170 (5)	-0.0002 (4)	0.0078 (4)	-0.0007 (4)
C7	0.0144 (5)	0.0162 (5)	0.0166 (5)	0.0020 (4)	0.0087 (4)	0.0011 (4)
C8	0.0139 (5)	0.0149 (5)	0.0146 (5)	0.0018 (4)	0.0061 (4)	0.0025 (4)
C9	0.0184 (5)	0.0151 (5)	0.0200 (5)	0.0000 (4)	0.0098 (4)	-0.0022 (4)

# supplementary materials

C10            0.0189 (6)            0.0241 (6)            0.0221 (6)            -0.0015 (5)            0.0107 (5)            -0.0062 (5)

## Geometric parameters (Å, °)

C11—C7	1.7361 (11)	C3—H3	0.9500
O1—C8	1.3331 (13)	C4—C5	1.3900 (17)
O1—C9	1.4593 (13)	C4—H4	0.9500
O2—C8	1.2076 (14)	C5—C6	1.3897 (16)
N1—N2	1.3282 (13)	C5—H5	0.9500
N1—C1	1.4035 (14)	C6—H6	0.9500
N1—H1	0.853 (13)	C7—C8	1.4853 (15)
N2—C7	1.2765 (14)	C9—C10	1.5035 (15)
C1—C2	1.3957 (16)	C9—H9A	0.9900
C1—C6	1.3939 (15)	C9—H9B	0.9900
C2—C3	1.3888 (16)	C10—H10A	0.9800
C2—H2	0.9500	C10—H10B	0.9800
C3—C4	1.3883 (17)	C10—H10C	0.9800
C8—O1—C9	115.22 (8)	C5—C6—H6	120.3
N2—N1—C1	119.25 (9)	C1—C6—H6	120.3
N2—N1—H1	120.4 (11)	N2—C7—C8	120.72 (10)
C1—N1—H1	120.3 (11)	N2—C7—C11	124.07 (9)
C7—N2—N1	120.85 (9)	C8—C7—C11	115.21 (8)
C2—C1—C6	120.14 (10)	O2—C8—O1	124.99 (10)
C2—C1—N1	118.64 (10)	O2—C8—C7	123.26 (10)
C6—C1—N1	121.22 (10)	O1—C8—C7	111.74 (9)
C3—C2—C1	119.48 (10)	O1—C9—C10	106.55 (9)
C3—C2—H2	120.3	O1—C9—H9A	110.4
C1—C2—H2	120.3	C10—C9—H9A	110.4
C4—C3—C2	120.91 (11)	O1—C9—H9B	110.4
C4—C3—H3	119.5	C10—C9—H9B	110.4
C2—C3—H3	119.5	H9A—C9—H9B	108.6
C5—C4—C3	119.11 (11)	C9—C10—H10A	109.5
C5—C4—H4	120.4	C9—C10—H10B	109.5
C3—C4—H4	120.4	H10A—C10—H10B	109.5
C4—C5—C6	120.89 (11)	C9—C10—H10C	109.5
C4—C5—H5	119.6	H10A—C10—H10C	109.5
C6—C5—H5	119.6	H10B—C10—H10C	109.5
C5—C6—C1	119.46 (11)		
C1—N1—N2—C7	179.17 (10)	N1—C1—C6—C5	-179.74 (10)
N2—N1—C1—C2	-177.17 (9)	N1—N2—C7—C8	177.11 (9)
N2—N1—C1—C6	2.49 (15)	N1—N2—C7—C11	-2.23 (15)
C6—C1—C2—C3	-0.40 (16)	C9—O1—C8—O2	-5.24 (15)
N1—C1—C2—C3	179.26 (10)	C9—O1—C8—C7	173.93 (9)
C1—C2—C3—C4	0.50 (17)	N2—C7—C8—O2	-168.44 (10)
C2—C3—C4—C5	-0.11 (17)	C11—C7—C8—O2	10.96 (14)
C3—C4—C5—C6	-0.38 (17)	N2—C7—C8—O1	12.38 (14)
C4—C5—C6—C1	0.47 (17)	C11—C7—C8—O1	-168.22 (7)
C2—C1—C6—C5	-0.08 (16)	C8—O1—C9—C10	-176.85 (9)

*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—H1···O2 <sup>i</sup>	0.85 (1)	2.18 (1)	2.969 (1)	153 (2)

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

Fig. 1

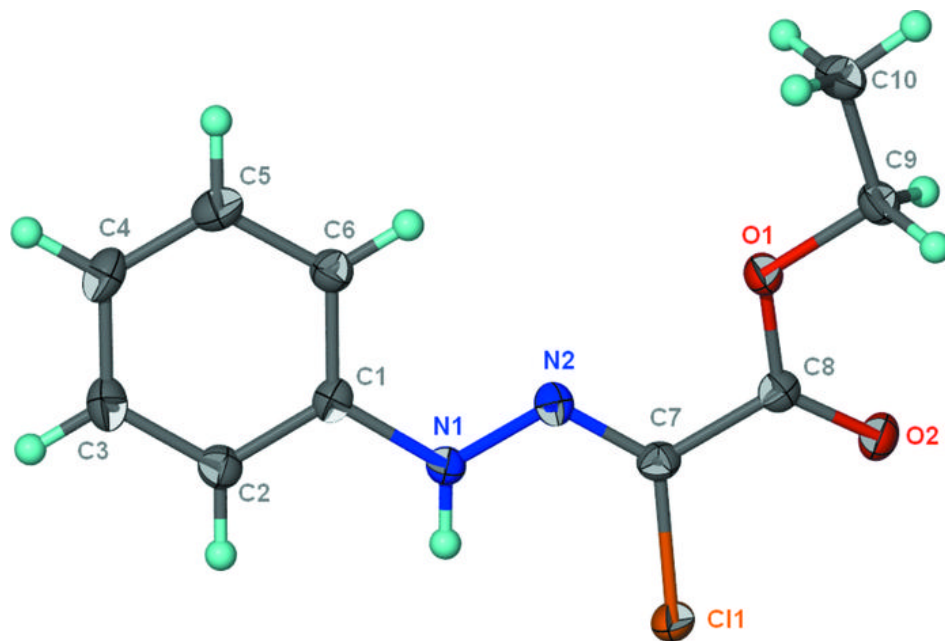




Fig. 2

