organic compounds

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

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The title compound, $C_{12}H_{12}Cl_2N_2O_3$, crystallizes as a non-merohedral twin with a twinning ratio of 0.51:0.49. The molecule adopts a keto–hydrazo tautomeric form stabilized by an intramolecular N—H···O hydrogen bond. The configuration around the N—N bond is *trans*.

Related literature

For related literature, see: Bernstein *et al.* (1995); Odabaşoğlu *et al.* (2005).
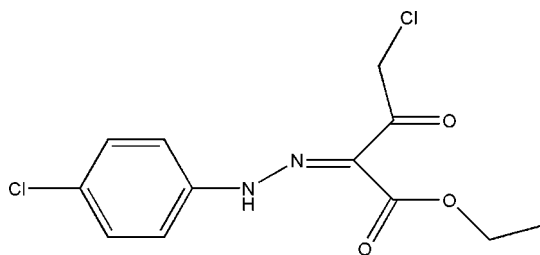
Experimental

Crystal data

$C_{12}H_{12}Cl_2N_2O_3$
M_r = 303.14

Triclinic, $P\bar{1}$
a = 8.6454 (10) Å
b = 9.7251 (11) Å
c = 9.9939 (11) Å
α = 116.001 (8)°
β = 108.721 (8)°
γ = 96.453 (9)°
V = 682.91 (16) Å^3

Z = 2
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 296 (2) K
$0.68 \times 0.49 \times 0.18$ mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.765, T_{max} = 0.916

5532 measured reflections
1325 independent reflections
991 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.138
S = 1.04
1325 reflections
146 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.89 (6)	1.96 (6)	2.608 (4)	129 (6)

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).

References

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Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.

supporting information

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

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S1. 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 overall view and atom-labelling of the molecule of (I) are displayed in Fig.1. Bond lenghts and angles are presented in Table 1 and hydrogen- bonding parametres are given in Table 2. The molecule is approximately planar with dihedral angle between the aromatic C1—C6 ring and the plane of the C7—C12/O1—O3/Cl1 aliphatic chain being 19.71 (12)°. Intramolecular N—H⋯O hydrogen bond generate S(6) ring motif (Bernstein *et al.*, 1995).

S2. Experimental

The title compound was prepared as described by (Odabaşoğlu *et al.*, 2005), using *p*-chloroaniline and ethyl 4-chloro-acetoacetate as starting materials (yield 92%, m.p. 415–417 K). Crystals of (I) suitable for *x*-ray analysis were obtained by slow evaporation of an absolute acetic acid solution at room temperature.

S3. Refinement

The crystal was non-merohedral twin with a twinning ratio of 0.51:0.49 and the reflection data were measured for the two twin domains, scaled and combined together, but overlapping reflections could not be satisfactorily measured and were discarded, leading to a data completeness of only slightly over 49%. The dataset under investigation had 5614 identified reflections associated with component 1 only, 5636 reflections with component 2 only and 1674 are belonging to both components. 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 $U_{iso}(H) = 1.2\ U_{eq}(C)\ [1.5U_{eq}(\text{methyl C})]$. The *SHELXS* EADP restrain applied to benzene ring to increase the Data/Parameter Ratio
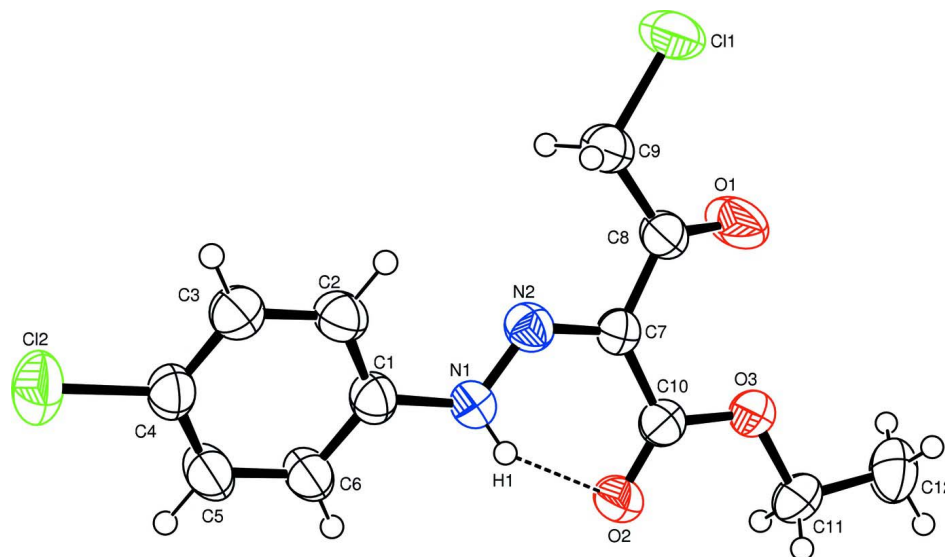
Figure 1

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.

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

Crystal data

$C_{12}H_{12}Cl_2N_2O_3$	$Z = 2$
$M_r = 303.14$	$F(000) = 312$
Triclinic, $P\overline{1}$	$D_x = 1.474$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.6454$ (10) Å	Cell parameters from 9294 reflections
$b = 9.7251$ (11) Å	$\theta = 2.4$–27.3°
$c = 9.9939$ (11) Å	$\mu = 0.48$ mm^{-1}
$\alpha = 116.001$ (8)°	$T = 296$ K
$\beta = 108.721$ (8)°	Prism, red
$\gamma = 96.453$ (9)°	$0.68 \times 0.49 \times 0.18$ mm
$V = 682.91$ (16) Å^3	

Data collection

STOE IPDS-II diffractometer	5532 measured reflections
Radiation source: fine-focus sealed tube	1325 independent reflections
Graphite monochromator	991 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.068$
rotation method scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.6°$
Absorption correction: integration	$h = -10 \rightarrow 10$
(*X-RED32*; Stoe & Cie, 2002)	$k = -11 \rightarrow 11$
$T_{min} = 0.765$, $T_{max} = 0.916$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.138$	
$S = 1.04$	H atoms treated by a mixture of independent and constrained refinement
1325 reflections	
146 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.2407P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.26$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5661 (5)	0.3299 (6)	−0.0883 (6)	0.0501 (4)
C2	0.7250 (5)	0.4411 (6)	−0.0047 (6)	0.0501 (4)
H2	0.7943	0.4673	0.1012	0.060*
C3	0.7804 (5)	0.5136 (5)	−0.0808 (5)	0.0501 (4)
H3	0.8872	0.5896	−0.0255	0.060*
C4	0.6775 (5)	0.4732 (6)	−0.2378 (6)	0.0501 (4)
C5	0.5195 (5)	0.3614 (6)	−0.3217 (6)	0.0501 (4)
H5	0.4507	0.3333	−0.4283	0.060*
C6	0.4649 (5)	0.2915 (5)	−0.2442 (5)	0.0501 (4)
H6	0.3572	0.2169	−0.2990	0.060*
C7	0.5520 (5)	0.1834 (5)	0.1806 (6)	0.0427 (10)
C8	0.6923 (5)	0.1826 (6)	0.3131 (6)	0.0461 (10)
C9	0.8672 (5)	0.2758 (6)	0.3529 (6)	0.0501 (12)
H9A	0.8680	0.3841	0.3775	0.060*
H9B	0.8935	0.2265	0.2583	0.060*
C10	0.3677 (5)	0.0997 (5)	0.1201 (5)	0.0426 (10)
C11	0.1601 (6)	−0.0318 (7)	0.1644 (7)	0.0551 (14)
H11A	0.1154	−0.1244	0.0552	0.066*
H11B	0.0913	0.0402	0.1634	0.066*
C12	0.1543 (7)	−0.0832 (7)	0.2848 (7)	0.0682 (14)
H12A	0.0381	−0.1366	0.2548	0.102*
H12B	0.1990	0.0093	0.3924	0.102*
H12C	0.2220	−0.1551	0.2842	0.102*
Cl1	1.02658 (14)	0.28272 (16)	0.52211 (16)	0.0687 (4)

Cl2	0.74774 (17)	0.56273 (16)	−0.33405 (18)	0.0700 (4)
N1	0.5022 (5)	0.2540 (5)	−0.0167 (5)	0.0441 (8)
N2	0.6056 (4)	0.2539 (4)	0.1110 (4)	0.0433 (7)
O1	0.6713 (4)	0.1079 (6)	0.3773 (5)	0.0874 (13)
O2	0.2590 (3)	0.0861 (4)	−0.0001 (4)	0.0541 (8)
O3	0.3374 (4)	0.0489 (4)	0.2148 (4)	0.0528 (9)
H1	0.392 (8)	0.198 (8)	−0.068 (10)	0.09 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C2	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C3	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C4	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C5	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C6	0.0478 (11)	0.0566 (10)	0.0507 (10)	0.0105 (7)	0.0182 (7)	0.0336 (9)
C7	0.041 (3)	0.044 (2)	0.043 (2)	0.0080 (17)	0.0166 (18)	0.024 (2)
C8	0.042 (3)	0.053 (3)	0.045 (2)	0.0086 (18)	0.0133 (18)	0.030 (2)
C9	0.038 (3)	0.065 (3)	0.045 (3)	0.0064 (19)	0.0092 (17)	0.034 (3)
C10	0.042 (3)	0.044 (2)	0.040 (2)	0.0079 (17)	0.0165 (18)	0.020 (2)
C11	0.038 (3)	0.070 (3)	0.057 (3)	0.001 (2)	0.018 (2)	0.036 (3)
C12	0.073 (4)	0.073 (3)	0.068 (3)	0.008 (2)	0.035 (3)	0.042 (3)
Cl1	0.0491 (8)	0.0800 (9)	0.0655 (8)	0.0080 (5)	0.0017 (5)	0.0454 (7)
Cl2	0.0865 (10)	0.0747 (8)	0.0828 (9)	0.0238 (6)	0.0491 (7)	0.0572 (8)
N1	0.038 (2)	0.053 (2)	0.0418 (19)	0.0072 (15)	0.0128 (15)	0.0287 (17)
N2	0.046 (2)	0.0459 (19)	0.0429 (19)	0.0138 (13)	0.0169 (13)	0.0269 (16)
O1	0.055 (2)	0.123 (3)	0.093 (3)	−0.0056 (17)	0.0025 (16)	0.089 (3)
O2	0.0368 (16)	0.076 (2)	0.0524 (18)	0.0078 (13)	0.0133 (12)	0.0409 (17)
O3	0.041 (2)	0.070 (2)	0.058 (2)	0.0090 (15)	0.0194 (15)	0.043 (2)

Geometric parameters (Å, º)

C1—C6	1.369 (6)	C8—C9	1.502 (6)
C1—C2	1.375 (6)	C9—Cl1	1.774 (4)
C1—N1	1.410 (5)	C9—H9A	0.9700
C2—C3	1.392 (5)	C9—H9B	0.9700
C2—H2	0.9300	C10—O2	1.204 (5)
C3—C4	1.375 (6)	C10—O3	1.322 (5)
C3—H3	0.9300	C11—O3	1.451 (5)
C4—C5	1.372 (6)	C11—C12	1.504 (6)
C4—Cl2	1.744 (4)	C11—H11A	0.9700
C5—C6	1.382 (5)	C11—H11B	0.9700
C5—H5	0.9300	C12—H12A	0.9600
C6—H6	0.9300	C12—H12B	0.9600
C7—N2	1.312 (5)	C12—H12C	0.9600
C7—C8	1.485 (6)	N1—N2	1.302 (5)
C7—C10	1.492 (6)	N1—H1	0.89 (6)

C8—O1	1.194 (5)		
C6—C1—C2	120.2 (4)	C8—C9—H9A	109.3
C6—C1—N1	118.3 (4)	Cl1—C9—H9A	109.3
C2—C1—N1	121.5 (4)	C8—C9—H9B	109.3
C1—C2—C3	119.0 (4)	Cl1—C9—H9B	109.3
C1—C2—H2	120.5	H9A—C9—H9B	107.9
C3—C2—H2	120.5	O2—C10—O3	124.5 (4)
C4—C3—C2	120.1 (4)	O2—C10—C7	122.3 (3)
C4—C3—H3	119.9	O3—C10—C7	113.1 (4)
C2—C3—H3	119.9	O3—C11—C12	107.6 (4)
C5—C4—C3	120.9 (4)	O3—C11—H11A	110.2
C5—C4—Cl2	119.0 (3)	C12—C11—H11A	110.2
C3—C4—Cl2	120.1 (3)	O3—C11—H11B	110.2
C4—C5—C6	118.5 (4)	C12—C11—H11B	110.2
C4—C5—H5	120.8	H11A—C11—H11B	108.5
C6—C5—H5	120.8	C11—C12—H12A	109.5
C1—C6—C5	121.3 (4)	C11—C12—H12B	109.5
C1—C6—H6	119.3	H12A—C12—H12B	109.5
C5—C6—H6	119.3	C11—C12—H12C	109.5
N2—C7—C8	113.7 (4)	H12A—C12—H12C	109.5
N2—C7—C10	122.2 (4)	H12B—C12—H12C	109.5
C8—C7—C10	123.8 (3)	N2—N1—C1	120.4 (4)
O1—C8—C7	123.8 (4)	N2—N1—H1	122 (5)
O1—C8—C9	122.1 (4)	C1—N1—H1	118 (5)
C7—C8—C9	114.0 (3)	N1—N2—C7	122.4 (4)
C8—C9—Cl1	111.7 (3)	C10—O3—C11	116.1 (3)
C6—C1—C2—C3	0.2 (8)	O1—C8—C9—Cl1	−8.4 (7)
N1—C1—C2—C3	−179.2 (4)	C7—C8—C9—Cl1	175.5 (4)
C1—C2—C3—C4	−0.5 (7)	N2—C7—C10—O2	3.4 (8)
C2—C3—C4—C5	0.0 (7)	C8—C7—C10—O2	−170.9 (5)
C2—C3—C4—Cl2	−179.4 (4)	N2—C7—C10—O3	−174.3 (4)
C3—C4—C5—C6	0.8 (8)	C8—C7—C10—O3	11.5 (7)
Cl2—C4—C5—C6	−179.8 (3)	C6—C1—N1—N2	162.5 (4)
C2—C1—C6—C5	0.6 (8)	C2—C1—N1—N2	−18.2 (8)
N1—C1—C6—C5	180.0 (4)	C1—N1—N2—C7	−179.3 (4)
C4—C5—C6—C1	−1.1 (8)	C8—C7—N2—N1	173.9 (4)
N2—C7—C8—O1	−170.5 (5)	C10—C7—N2—N1	−0.9 (7)
C10—C7—C8—O1	4.2 (8)	O2—C10—O3—C11	1.6 (7)
N2—C7—C8—C9	5.5 (6)	C7—C10—O3—C11	179.2 (4)
C10—C7—C8—C9	−179.8 (4)	C12—C11—O3—C10	178.6 (5)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.89 (6)	1.96 (6)	2.608 (4)	129 (6)