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Ethyl 3-oxo-2-(2-phenylhydrazinylidene)-butanoate: a re-determination

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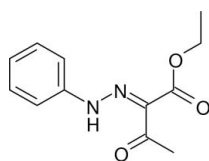
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.052; wR factor = 0.185; data-to-parameter ratio = 12.1.

The previous crystallographic studies [Wang *et al.* (2005). *Huaxue Yanjiu* **16**, 29–32; Wang *et al.* (2007). *Youji Huaxue*, **27**, 524] of the title compound, $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3$, gave only the unit-cell dimensions and an R factor with no other details available: the full structure is presented here. The ethoxy group is disordered over two orientations with refined occupancies of 0.642 (15):0.358 (15). The nine C atoms and two N atoms of the 1-phenyl-2-(propan-2-ylidene)hydrazine segment of the molecule are close to being coplanar, with a maximum deviation of 0.0779 (14) Å for the phenylamino N atom and an intramolecular N–H \cdots O hydrogen bond generates an $S(6)$ ring. In the crystal, pairs of C–H \cdots O hydrogen bonds link molecules into inversion dimers, generating $R_2^2(16)$ loops.

Related literature

For previous reports of the structure of the title compound, see: Wang *et al.* (2005, 2007). For further synthetic details, see: Fernandes *et al.* (1975). For graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_3$
 $M_r = 234.25$
Monoclinic, $P2_1/c$
 $a = 8.4375$ (9) Å
 $b = 17.551$ (2) Å
 $c = 8.242$ (1) Å
 $\beta = 91.24$ (1)°
 $V = 1220.2$ (2) Å³
 $Z = 4$
Cu $K\alpha$ radiation
 $\mu = 0.77$ mm⁻¹
 $T = 293$ K
 $0.2 \times 0.16 \times 0.12$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2393 measured reflections
2243 independent reflections
1715 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
3 standard reflections every 60 min
intensity decay: 0.0%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.185$
 $S = 1.07$
2243 reflections
186 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.86	1.92	2.571 (2)	131
$\text{C2}-\text{H2}\cdots\text{O1}^i$	0.93	2.53	3.430 (3)	163

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5790).

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supporting information

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Ethyl 3-oxo-2-(2-phenylhydrazinylidene)butanoate: a re-determination

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S1. Comment

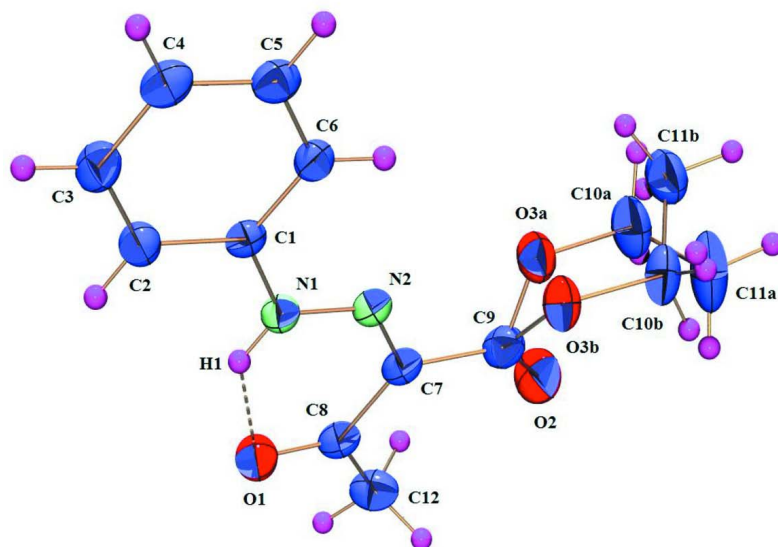
The unit cell of the title compound, (I), was reported by Wang *et al.* (2005, 2007). In the full structure reported here, the ethoxy group is disordered over two orientations with refined occupancies 0.642 (15):0.358 (15). The planes C9—O3A—C10A (plane A) and C9—O3B—C10B (plane B) of the two disordered ethoxy groups are inclined at an angle of 38.3 (17)°. The bonds C10A—C11A and C10B—C11B are bent in opposite directions with atom C11A and C11B deviating from planes A & B by 1.33 (1)Å and -1.41 (2)Å, respectively. The torsion angles C9—O3A—C10A—C11A and C9—O3B—C10B—C11B are 80.3 (6) and -89.0 (12)°, respectively. An intramolecular N—H···O hydrogen bond contributes to the planarity of the C1···C9, N1, N2, 1-phenyl-2-(propan-2-ylidene)hydrazine segment of the molecule. In the crystal structure C2—H2···O1 hydrogen bonds link pairs of molecules into centrosymmetric dimers generating R₂²(16) rings (Bernstein *et al.*, 1995).

S2. Experimental

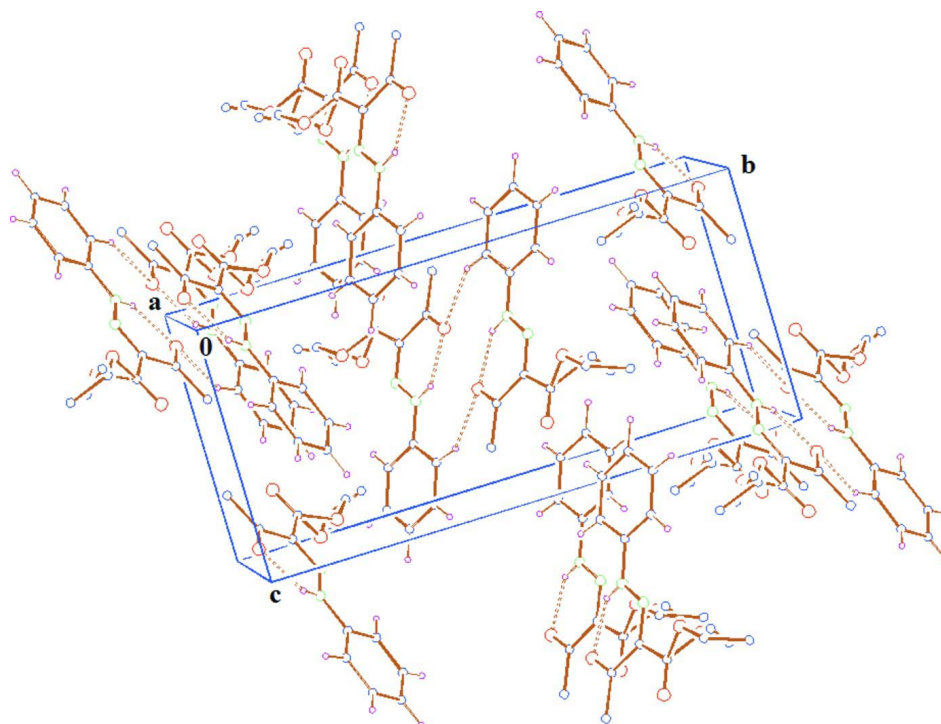
The title compound was prepared by the coupling of diazonium salt of aniline with ethyl acetoacetate (Fernandes *et al.*, 1975). It was recrystallized from methanol by slow evaporation at room temperature to yield colourless blocks of (I).

S3. Refinement

High values of isotropic thermal parameters for atoms O3 and C10 and unacceptable bond lengths for O3—C10 and C10—C11 of the ethoxy group indicated possible disorder. A difference electron density map excluding the atoms O3, C10 and C11 showed that the ethoxy group to be disordered over two sites. The ratio of the occupancy factors of the two disorder components refined to 0.642 (15):0.358 (15). All H-atoms were positioned geometrically and refined using a riding model with d(C-H) = 0.93Å, U_{iso} = 1.2U_{eq} (C) for aromatic 0.97Å, U_{iso} = 1.2U_{eq} (C) for CH₂, 0.86Å, U_{iso} = 1.2U_{eq} (N) for NH, and 0.96Å, U_{iso} = 1.5U_{eq} (C) for CH₃ atoms.

**Figure 1**

The structure of (I) with 30% probability displacement ellipsoids for non-hydrogen atoms showing the disordered ethoxy group O3—C10—C11.

**Figure 2**

Crystal packing of (I) viewed down the *a* axis.

Ethyl 3-oxo-2-(2-phenylhydrazinylidene)butanoate

Crystal data

C₁₂H₁₄N₂O₃ $M_r = 234.25$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 8.4375$ (9) Å $b = 17.551$ (2) Å $c = 8.242$ (1) Å $\beta = 91.24$ (1)° $V = 1220.2$ (2) Å³ $Z = 4$ $F(000) = 496$ $D_x = 1.275$ Mg m⁻³Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å

Cell parameters from 25 reflections

 $\theta = 25.8$ – 35.5 ° $\mu = 0.77$ mm⁻¹ $T = 293$ K

Block, colourless

 $0.2 \times 0.16 \times 0.12$ mm

Data collection

Enraf–Nonius CAD-4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω - 2θ scans

2393 measured reflections

2243 independent reflections

1715 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.022$ $\theta_{\text{max}} = 69.8$ °, $\theta_{\text{min}} = 5.0$ ° $h = -10$ → 10 $k = 0$ → 21 $l = 0$ → 9

3 standard reflections every 60 min

intensity decay: 0.0%

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.185$ $S = 1.07$

2243 reflections

186 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.1173P)^2 + 0.0072P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³Extinction correction: *SHELXL97* (Sheldrick,2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.072 (5)

Special details

Geometry. All su's are estimated using the full covariance matrix. The cell su's are taken into account individually in the estimation of su's in distances, angles and torsion angles; correlations between su's in cell parameters are only used when they are defined by crystal symmetry.

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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O3A	0.5943 (5)	0.3242 (3)	0.4120 (7)	0.0880 (14)	0.642 (15)
C10A	0.7449 (8)	0.2909 (5)	0.3648 (8)	0.104 (2)	0.642 (15)
H10A	0.7582	0.2984	0.2493	0.125*	0.642 (15)

H10B	0.7425	0.2365	0.3851	0.125*	0.642 (15)
C11A	0.8803 (11)	0.3242 (4)	0.4529 (7)	0.117 (2)	0.642 (15)
H11A	0.8555	0.3295	0.5655	0.176*	0.642 (15)
H11B	0.9035	0.3734	0.4084	0.176*	0.642 (15)
H11C	0.9709	0.2916	0.4426	0.176*	0.642 (15)
O3B	0.6366 (10)	0.3601 (9)	0.4633 (10)	0.095 (3)	0.358 (15)
C10B	0.792 (2)	0.3348 (9)	0.416 (2)	0.126 (4)	0.358 (15)
H10C	0.8323	0.3678	0.3320	0.151*	0.358 (15)
H10D	0.8649	0.3363	0.5084	0.151*	0.358 (15)
C11B	0.7762 (19)	0.2558 (11)	0.354 (2)	0.168 (7)	0.358 (15)
H11D	0.7167	0.2560	0.2538	0.252*	0.358 (15)
H11E	0.7222	0.2252	0.4324	0.252*	0.358 (15)
H11F	0.8796	0.2349	0.3371	0.252*	0.358 (15)
O1	0.1739 (2)	0.49615 (9)	0.38454 (16)	0.0898 (5)	
O2	0.6193 (2)	0.41989 (13)	0.2324 (2)	0.1178 (7)	
N1	0.23998 (17)	0.41137 (8)	0.63121 (16)	0.0619 (4)	
H1	0.1711	0.4412	0.5862	0.074*	
N2	0.36686 (18)	0.39265 (8)	0.55505 (17)	0.0621 (4)	
C1	0.2155 (2)	0.38255 (9)	0.78858 (19)	0.0585 (5)	
C2	0.0821 (2)	0.40648 (12)	0.8691 (2)	0.0727 (5)	
H2	0.0112	0.4404	0.8199	0.087*	
C3	0.0557 (3)	0.37944 (14)	1.0233 (3)	0.0833 (6)	
H3	-0.0327	0.3958	1.0790	0.100*	
C4	0.1590 (3)	0.32856 (12)	1.0954 (2)	0.0803 (6)	
H4	0.1396	0.3101	1.1989	0.096*	
C5	0.2912 (3)	0.30493 (11)	1.0145 (2)	0.0742 (6)	
H5	0.3613	0.2707	1.0638	0.089*	
C6	0.3204 (2)	0.33190 (10)	0.8599 (2)	0.0647 (5)	
H6	0.4097	0.3160	0.8051	0.078*	
C7	0.4007 (2)	0.42190 (11)	0.4118 (2)	0.0647 (5)	
C8	0.3017 (2)	0.47900 (11)	0.3269 (2)	0.0700 (5)	
C9	0.5507 (3)	0.39304 (14)	0.3460 (3)	0.0820 (6)	
C12	0.3544 (3)	0.51477 (14)	0.1731 (3)	0.0881 (7)	
H12A	0.2856	0.5565	0.1454	0.132*	
H12B	0.3507	0.4777	0.0875	0.132*	
H12C	0.4610	0.5331	0.1873	0.132*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3A	0.0801 (18)	0.079 (2)	0.106 (3)	0.0054 (16)	0.0292 (17)	0.0026 (18)
C10A	0.107 (4)	0.093 (4)	0.115 (4)	0.023 (3)	0.040 (3)	-0.008 (3)
C11A	0.087 (4)	0.142 (5)	0.122 (4)	0.029 (3)	0.018 (3)	0.003 (3)
O3B	0.081 (3)	0.111 (7)	0.095 (4)	0.020 (4)	0.020 (3)	0.005 (4)
C10B	0.085 (9)	0.139 (10)	0.154 (10)	0.025 (7)	0.033 (7)	-0.010 (8)
C11B	0.137 (10)	0.129 (12)	0.241 (16)	0.046 (9)	0.066 (9)	-0.030 (10)
O1	0.1019 (11)	0.1033 (11)	0.0645 (8)	0.0229 (8)	0.0097 (7)	0.0206 (7)
O2	0.1127 (14)	0.1545 (18)	0.0879 (12)	0.0112 (11)	0.0391 (10)	0.0288 (11)

N1	0.0694 (9)	0.0669 (9)	0.0495 (8)	0.0048 (6)	0.0022 (6)	0.0060 (6)
N2	0.0684 (9)	0.0645 (8)	0.0535 (8)	-0.0050 (6)	0.0021 (6)	-0.0015 (6)
C1	0.0697 (10)	0.0578 (9)	0.0479 (9)	-0.0059 (7)	-0.0021 (7)	0.0010 (7)
C2	0.0725 (11)	0.0827 (12)	0.0631 (10)	0.0069 (9)	0.0064 (8)	0.0105 (9)
C3	0.0880 (13)	0.0957 (14)	0.0669 (12)	0.0012 (11)	0.0180 (10)	0.0088 (10)
C4	0.1020 (15)	0.0811 (13)	0.0579 (10)	-0.0139 (10)	0.0066 (10)	0.0127 (9)
C5	0.0991 (14)	0.0629 (11)	0.0601 (10)	-0.0009 (9)	-0.0064 (9)	0.0089 (8)
C6	0.0786 (11)	0.0583 (9)	0.0572 (10)	0.0041 (7)	-0.0002 (8)	-0.0005 (7)
C7	0.0736 (11)	0.0695 (10)	0.0511 (9)	-0.0098 (8)	0.0023 (7)	-0.0005 (7)
C8	0.0816 (12)	0.0753 (11)	0.0529 (9)	-0.0100 (9)	-0.0013 (8)	0.0033 (8)
C9	0.0801 (13)	0.1015 (16)	0.0648 (11)	-0.0064 (11)	0.0107 (10)	-0.0009 (10)
C12	0.0926 (15)	0.1040 (16)	0.0677 (12)	-0.0173 (12)	-0.0002 (10)	0.0252 (11)

Geometric parameters (Å, °)

O3A—C9	1.373 (4)	N1—H1	0.8600
O3A—C10A	1.459 (8)	N2—C7	1.324 (2)
C10A—C11A	1.462 (12)	C1—C2	1.384 (3)
C10A—H10A	0.9700	C1—C6	1.377 (2)
C10A—H10B	0.9700	C2—C3	1.379 (3)
C11A—H11A	0.9600	C2—H2	0.9300
C11A—H11B	0.9600	C3—C4	1.374 (3)
C11A—H11C	0.9600	C3—H3	0.9300
O3B—C9	1.328 (7)	C4—C5	1.376 (3)
O3B—C10B	1.445 (15)	C4—H4	0.9300
C10B—C11B	1.48 (2)	C5—C6	1.387 (3)
C10B—H10C	0.9700	C5—H5	0.9300
C10B—H10D	0.9700	C6—H6	0.9300
C11B—H11D	0.9600	C7—C8	1.472 (3)
C11B—H11E	0.9600	C7—C9	1.477 (3)
C11B—H11F	0.9600	C8—C12	1.491 (3)
O1—C8	1.225 (2)	C12—H12A	0.9600
O2—C9	1.207 (3)	C12—H12B	0.9600
N1—N2	1.295 (2)	C12—H12C	0.9600
N1—C1	1.412 (2)		
C9—O3A—C10A	118.3 (4)	C4—C3—C2	120.6 (2)
O3A—C10A—C11A	112.6 (9)	C4—C3—H3	119.7
O3A—C10A—H10A	109.1	C2—C3—H3	119.7
C11A—C10A—H10A	109.1	C5—C4—C3	119.96 (18)
O3A—C10A—H10B	109.1	C5—C4—H4	120.0
C11A—C10A—H10B	109.1	C3—C4—H4	120.0
H10A—C10A—H10B	107.8	C4—C5—C6	120.32 (18)
C9—O3B—C10B	114.9 (9)	C4—C5—H5	119.8
C11B—C10B—O3B	107.8 (17)	C6—C5—H5	119.8
C11B—C10B—H10C	110.1	C1—C6—C5	119.16 (18)
O3B—C10B—H10C	110.1	C1—C6—H6	120.4
C11B—C10B—H10D	110.1	C5—C6—H6	120.4

O3B—C10B—H10D	110.1	N2—C7—C8	123.80 (17)
H10C—C10B—H10D	108.5	N2—C7—C9	113.43 (17)
C10B—C11B—H11D	109.5	C8—C7—C9	122.76 (17)
C10B—C11B—H11E	109.5	O1—C8—C7	118.59 (16)
H11D—C11B—H11E	109.5	O1—C8—C12	120.48 (19)
C10B—C11B—H11F	109.5	C7—C8—C12	120.92 (19)
H11D—C11B—H11F	109.5	O2—C9—O3B	118.1 (4)
H11E—C11B—H11F	109.5	O2—C9—O3A	121.5 (3)
N2—N1—C1	119.56 (14)	O3B—C9—O3A	36.0 (5)
N2—N1—H1	120.2	O2—C9—C7	125.4 (2)
C1—N1—H1	120.2	O3B—C9—C7	109.9 (3)
N1—N2—C7	122.04 (15)	O3A—C9—C7	112.4 (2)
C2—C1—C6	120.85 (16)	C8—C12—H12A	109.5
C2—C1—N1	117.94 (15)	C8—C12—H12B	109.5
C6—C1—N1	121.21 (16)	H12A—C12—H12B	109.5
C1—C2—C3	119.12 (18)	C8—C12—H12C	109.5
C1—C2—H2	120.4	H12A—C12—H12C	109.5
C3—C2—H2	120.4	H12B—C12—H12C	109.5
C9—O3A—C10A—C11A	80.3 (6)	C9—C7—C8—O1	175.22 (18)
C9—O3B—C10B—C11B	-89.0 (12)	N2—C7—C8—C12	174.34 (17)
C1—N1—N2—C7	-175.53 (14)	C9—C7—C8—C12	-4.1 (3)
N2—N1—C1—C2	177.16 (15)	C10B—O3B—C9—O2	-22.3 (18)
N2—N1—C1—C6	-3.1 (3)	C10B—O3B—C9—O3A	83.5 (14)
C6—C1—C2—C3	0.6 (3)	C10B—O3B—C9—C7	-175.5 (12)
N1—C1—C2—C3	-179.73 (18)	C10A—O3A—C9—O2	12.4 (9)
C1—C2—C3—C4	-0.9 (4)	C10A—O3A—C9—O3B	-83.2 (8)
C2—C3—C4—C5	0.8 (4)	C10A—O3A—C9—C7	-176.6 (6)
C3—C4—C5—C6	-0.4 (3)	N2—C7—C9—O2	-167.1 (2)
C2—C1—C6—C5	-0.1 (3)	C8—C7—C9—O2	11.5 (3)
N1—C1—C6—C5	-179.79 (16)	N2—C7—C9—O3B	-16.3 (8)
C4—C5—C6—C1	0.0 (3)	C8—C7—C9—O3B	162.3 (8)
N1—N2—C7—C8	1.4 (3)	N2—C7—C9—O3A	22.3 (4)
N1—N2—C7—C9	179.99 (16)	C8—C7—C9—O3A	-159.1 (4)
N2—C7—C8—O1	-6.3 (3)		

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...O1	0.86	1.92	2.571 (2)	131
C2—H2...O1 ⁱ	0.93	2.53	3.430 (3)	163

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