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2-Bromo-*N*′-[(*Z*)-2-bromobenzylidene]-5-methoxybenzohydrazide

Hongqi Li,[a]* B. K. Sarojini,[b] B. Narayana,[c] H. S. Yathirajan[d] and William T. A. Harrison[e]

[a]Key Laboratory of Science & Technology of Eco-Textiles, Ministry of Education, College of Chemistry, Chemical Engineering & Biotechnology, Donghua University, Shanghai 201620, People's Republic of China, [b]Department of Chemistry, P. A. College of Engineering, Mangalore 574 153, India, [c]Department of Studies in Chemistry, Mangalore University, Mangalagangotri 574 199, India, [d]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and [e]Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: hongqili@dhu.edu.cn

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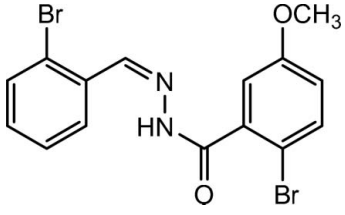
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.047; wR factor = 0.122; data-to-parameter ratio = 18.0.

In the title compound, $C_{15}H_{12}Br_2N_2O_2$, the molecule adopts an *E* conformation about the C=N double bond and a *transoid* conformation about the central N—N bond, with a C(=O)—N—N—C(H) dihedral angle of 169.4 (4)°. In the crystal, molecules are linked by N—H···O hydrogen bonds, leading to *C*(4) chains. The packing also features slipped π–π stacking interactions, with a centroid–centroid separation of 3.838 (3) Å and a slippage of 1.19 Å.

Related literature

For related structures and background, see: Narayana *et al.* (2007); Butcher *et al.* (2007).



Experimental

Crystal data

$C_{15}H_{12}Br_2N_2O_2$
M_r = 412.09
Monoclinic, $P2_1/c$
a = 14.768 (5) Å
b = 12.753 (4) Å
c = 8.227 (3) Å
β = 96.114 (4)°
V = 1540.6 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.27 mm^{-1}
T = 296 K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.301, T_{max} = 0.419
(expected range = 0.251–0.349)
9369 measured reflections
3515 independent reflections
1902 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.122
S = 0.96
3515 reflections
195 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.87 (4)	2.07 (4)	2.906 (4)	160 (4)

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

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

HSY thanks the University of Mysore for research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2231).

References

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Narayana, B., Siddaraju, B. P., Raju, C. R., Yathirajan, H. S. & Bolte, M. (2007). *Acta Cryst.* E**63**, o3522.
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supporting information

Acta Cryst. (2009). E**65**, o1750 [doi:10.1107/S1600536809024921]

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S1. Comment

As part of our ongoing studies of substituted benzohydrazides (Narayana *et al.*, 2007; Butcher *et al.*, 2007) we now describe the synthesis and crystal structure of the title compound, (I) (Fig. 1).

The dihedral angle between the mean planes of the A (C1–C6) and B (C10–C15) rings is 18.6 (3)°. Atom C7 is dispalaced from the A plane by 0.064 (9)Å. The molecule is significantly twisted about the N1—N2 bond.

In the crystal, an intermolecular N—H···O interaction occurs (Table 2), leading to C(4) chains (Fig. 2) of molecules propagating in [001]. The shortest intermolecular aromatic ring centroid–centroid separation is 3.638 (3)Å, indicative of weak π-π stacking.

S2. Experimental

A mixture of 2-bromobenzaldehyde (1.85 g, 0.01 mol) and 2-bromo-5-methoxybenzo-hydrazide (2.45 g, 0.01mol) in 15 ml of ethanol containing 2 drops of 4 M hydrochloric acid was refluxed for 3 hours. On cooling, the solid separated was filtered and recrystallized from ethyl alcohol to yield colourless blocks of (I) (m.p: 440-442 K). Analysis (%) for $C_{15}H_{12}Br_2N_2O_2$: calculated (found): C 43.73 (43.66), H 2.94 (2.91), N 6.80 (6.76).

S3. Refinement

The N-bound H atom was located in a difference map and its position was freely refined. All the other H atoms were placed in idealized locations (C—H = 0.93–0.98 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(methyl C). The methyl group was allowed to rotate, but not to tip, to best fit the electron density.

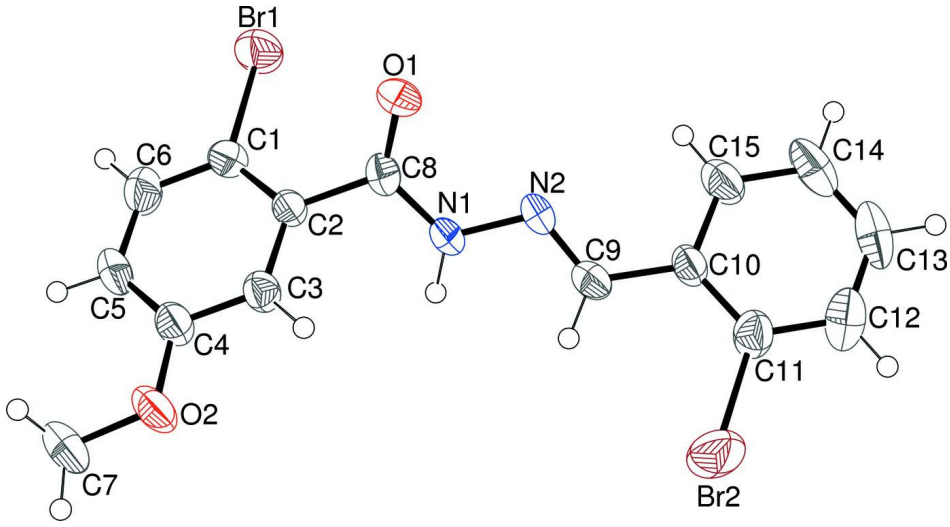

Figure 1

A view of (I) with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

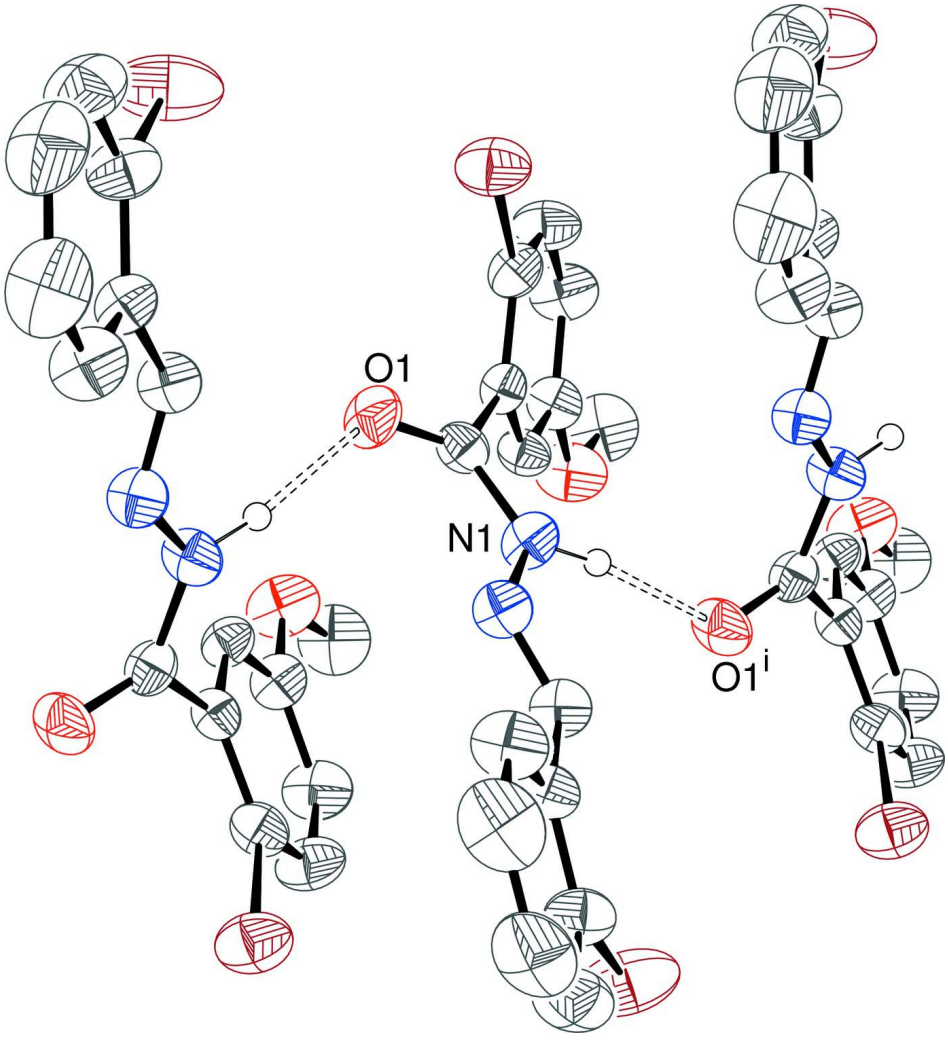

Figure 2

A fragment of an [001] C(4) chain of molcules in the crystal of (I). Symmetry code as in Table 2.

2-Bromo-N′-[(Z)-2-bromobenzylidene]-5-methoxybenzohydrazide

Crystal data

$C_{15}H_{12}Br_2N_2O_2$
$M_r = 412.09$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 14.768$ (5) Å
$b = 12.753$ (4) Å
$c = 8.227$ (3) Å
$\beta = 96.114$ (4)°
$V = 1540.6$ (9) Å^3
$Z = 4$

$F(000) = 808$
$D_x = 1.777$ Mg m^{-3}
Melting point = 440–442 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1776 reflections
$\theta = 2.8$–22.8°
$\mu = 5.27$ mm^{-1}
$T = 296$ K
Block, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.301, T_{max} = 0.419
9369 measured reflections
3515 independent reflections
1902 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.5°, θ_{min} = 2.1°
h = −19→14
k = −12→16
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.122
S = 0.96
3515 reflections
195 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0145 (10)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.1558 (3)	0.0150 (3)	0.5766 (5)	0.0405 (11)
C2	0.1498 (3)	0.1213 (3)	0.5376 (5)	0.0322 (9)
C3	0.0842 (3)	0.1808 (3)	0.6039 (5)	0.0367 (10)
H3	0.0794	0.2520	0.5796	0.044*
C4	0.0256 (3)	0.1365 (3)	0.7055 (5)	0.0415 (11)
C5	0.0317 (3)	0.0314 (4)	0.7407 (6)	0.0536 (13)
H5	−0.0084	0.0006	0.8065	0.064*
C6	0.0973 (3)	−0.0282 (4)	0.6780 (6)	0.0522 (12)
H6	0.1024	−0.0990	0.7045	0.063*
C7	−0.0958 (3)	0.1633 (4)	0.8725 (6)	0.0655 (15)
H7A	−0.1332	0.1093	0.8189	0.098*
H7B	−0.1339	0.2188	0.9054	0.098*
H7C	−0.0608	0.1347	0.9672	0.098*
C8	0.2084 (3)	0.1719 (3)	0.4227 (5)	0.0356 (10)
C9	0.3247 (3)	0.4087 (4)	0.4401 (5)	0.0406 (10)

H9	0.2985	0.4355	0.5293	0.049*
C10	0.3904 (3)	0.4723 (3)	0.3608 (5)	0.0374 (10)
C11	0.3967 (3)	0.5806 (4)	0.3780 (6)	0.0477 (11)
C12	0.4617 (4)	0.6382 (4)	0.3079 (7)	0.0646 (15)
H12	0.4641	0.7107	0.3198	0.077*
C13	0.5223 (4)	0.5874 (5)	0.2207 (7)	0.0712 (17)
H13	0.5668	0.6254	0.1742	0.085*
C14	0.5179 (4)	0.4814 (5)	0.2017 (7)	0.0708 (16)
H14	0.5590	0.4475	0.1415	0.085*
C15	0.4530 (3)	0.4241 (4)	0.2707 (6)	0.0527 (13)
H15	0.4510	0.3517	0.2568	0.063*
Br1	0.24530 (3)	−0.07259 (4)	0.49919 (6)	0.0578 (2)
Br2	0.31365 (4)	0.65524 (4)	0.49486 (9)	0.0861 (3)
O1	0.2174 (2)	0.1358 (2)	0.2869 (3)	0.0489 (8)
O2	−0.0358 (2)	0.2037 (3)	0.7627 (4)	0.0579 (9)
N1	0.2468 (2)	0.2623 (3)	0.4809 (4)	0.0400 (9)
H1	0.239 (3)	0.277 (3)	0.582 (5)	0.048*
N2	0.3036 (2)	0.3173 (3)	0.3872 (4)	0.0391 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.038 (3)	0.042 (3)	0.042 (3)	−0.002 (2)	0.011 (2)	−0.007 (2)
C2	0.030 (2)	0.037 (2)	0.030 (2)	−0.0044 (18)	0.0070 (18)	−0.0026 (18)
C3	0.038 (2)	0.036 (2)	0.038 (2)	0.0012 (19)	0.0104 (19)	0.0061 (19)
C4	0.036 (2)	0.046 (3)	0.044 (3)	0.000 (2)	0.012 (2)	0.003 (2)
C5	0.056 (3)	0.051 (3)	0.060 (3)	−0.010 (2)	0.034 (3)	0.004 (3)
C6	0.056 (3)	0.038 (3)	0.066 (3)	−0.005 (2)	0.020 (3)	0.008 (2)
C7	0.051 (3)	0.080 (4)	0.071 (4)	−0.002 (3)	0.035 (3)	0.000 (3)
C8	0.035 (2)	0.037 (3)	0.035 (2)	−0.0032 (19)	0.0082 (19)	0.007 (2)
C9	0.037 (2)	0.044 (3)	0.043 (3)	0.003 (2)	0.017 (2)	−0.001 (2)
C10	0.033 (2)	0.039 (3)	0.042 (2)	0.0010 (19)	0.0143 (19)	0.006 (2)
C11	0.037 (2)	0.043 (3)	0.064 (3)	−0.002 (2)	0.011 (2)	0.006 (2)
C12	0.057 (3)	0.056 (3)	0.080 (4)	−0.014 (3)	0.006 (3)	0.019 (3)
C13	0.055 (3)	0.091 (5)	0.070 (4)	−0.022 (3)	0.020 (3)	0.026 (3)
C14	0.051 (3)	0.100 (5)	0.068 (4)	0.001 (3)	0.035 (3)	0.012 (3)
C15	0.048 (3)	0.056 (3)	0.058 (3)	0.005 (2)	0.027 (2)	0.004 (2)
Br1	0.0569 (4)	0.0486 (3)	0.0713 (4)	0.0116 (2)	0.0227 (3)	−0.0006 (2)
Br2	0.0675 (4)	0.0502 (4)	0.1467 (7)	0.0080 (3)	0.0393 (4)	−0.0194 (4)
O1	0.066 (2)	0.050 (2)	0.0337 (17)	−0.0067 (16)	0.0203 (15)	−0.0084 (15)
O2	0.0502 (19)	0.059 (2)	0.071 (2)	0.0080 (17)	0.0370 (17)	0.0058 (18)
N1	0.044 (2)	0.045 (2)	0.035 (2)	−0.0083 (17)	0.0204 (18)	−0.0031 (18)
N2	0.039 (2)	0.044 (2)	0.038 (2)	−0.0050 (17)	0.0188 (16)	0.0016 (17)

Geometric parameters (Å, º)

C1—C6	1.378 (6)	C8—N1	1.350 (5)
C1—C2	1.394 (6)	C9—N2	1.272 (5)

C1—Br1	1.892 (4)	C9—C10	1.469 (6)
C2—C3	1.387 (5)	C9—H9	0.9300
C2—C8	1.495 (5)	C10—C15	1.388 (6)
C3—C4	1.386 (5)	C10—C11	1.390 (6)
C3—H3	0.9300	C11—C12	1.382 (6)
C4—O2	1.367 (5)	C11—Br2	1.894 (5)
C4—C5	1.373 (6)	C12—C13	1.369 (8)
C5—C6	1.375 (6)	C12—H12	0.9300
C5—H5	0.9300	C13—C14	1.361 (8)
C6—H6	0.9300	C13—H13	0.9300
C7—O2	1.427 (5)	C14—C15	1.375 (7)
C7—H7A	0.9600	C14—H14	0.9300
C7—H7B	0.9600	C15—H15	0.9300
C7—H7C	0.9600	N1—N2	1.388 (4)
C8—O1	1.229 (5)	N1—H1	0.87 (4)

C6—C1—C2	120.0 (4)	N2—C9—C10	120.3 (4)
C6—C1—Br1	118.2 (3)	N2—C9—H9	119.9
C2—C1—Br1	121.8 (3)	C10—C9—H9	119.9
C3—C2—C1	118.2 (3)	C15—C10—C11	116.9 (4)
C3—C2—C8	119.2 (4)	C15—C10—C9	120.1 (4)
C1—C2—C8	122.6 (3)	C11—C10—C9	122.9 (4)
C4—C3—C2	121.4 (4)	C12—C11—C10	121.9 (4)
C4—C3—H3	119.3	C12—C11—Br2	117.4 (4)
C2—C3—H3	119.3	C10—C11—Br2	120.7 (3)
O2—C4—C5	124.8 (4)	C13—C12—C11	119.2 (5)
O2—C4—C3	115.6 (4)	C13—C12—H12	120.4
C5—C4—C3	119.6 (4)	C11—C12—H12	120.4
C4—C5—C6	119.6 (4)	C14—C13—C12	120.3 (5)
C4—C5—H5	120.2	C14—C13—H13	119.9
C6—C5—H5	120.2	C12—C13—H13	119.9
C5—C6—C1	121.2 (4)	C13—C14—C15	120.5 (5)
C5—C6—H6	119.4	C13—C14—H14	119.7
C1—C6—H6	119.4	C15—C14—H14	119.7
O2—C7—H7A	109.5	C14—C15—C10	121.2 (5)
O2—C7—H7B	109.5	C14—C15—H15	119.4
H7A—C7—H7B	109.5	C10—C15—H15	119.4
O2—C7—H7C	109.5	C4—O2—C7	118.1 (4)
H7A—C7—H7C	109.5	C8—N1—N2	119.4 (3)
H7B—C7—H7C	109.5	C8—N1—H1	115 (3)
O1—C8—N1	124.1 (4)	N2—N1—H1	125 (3)
O1—C8—C2	122.7 (4)	C9—N2—N1	114.5 (3)
N1—C8—C2	113.2 (4)		

C6—C1—C2—C3	0.2 (6)	N2—C9—C10—C11	160.4 (4)
Br1—C1—C2—C3	−177.8 (3)	C15—C10—C11—C12	0.5 (7)
C6—C1—C2—C8	−177.3 (4)	C9—C10—C11—C12	177.2 (4)
Br1—C1—C2—C8	4.7 (6)	C15—C10—C11—Br2	178.8 (3)

C1—C2—C3—C4	−0.3 (6)	C9—C10—C11—Br2	−4.4 (6)
C8—C2—C3—C4	177.2 (4)	C10—C11—C12—C13	−0.8 (8)
C2—C3—C4—O2	180.0 (4)	Br2—C11—C12—C13	−179.2 (4)
C2—C3—C4—C5	−0.6 (7)	C11—C12—C13—C14	0.8 (8)
O2—C4—C5—C6	−179.0 (4)	C12—C13—C14—C15	−0.5 (9)
C3—C4—C5—C6	1.7 (7)	C13—C14—C15—C10	0.2 (8)
C4—C5—C6—C1	−1.8 (8)	C11—C10—C15—C14	−0.2 (7)
C2—C1—C6—C5	0.9 (7)	C9—C10—C15—C14	−177.0 (5)
Br1—C1—C6—C5	179.0 (4)	C5—C4—O2—C7	2.8 (7)
C3—C2—C8—O1	−127.5 (4)	C3—C4—O2—C7	−177.8 (4)
C1—C2—C8—O1	50.0 (6)	O1—C8—N1—N2	−2.9 (6)
C3—C2—C8—N1	50.2 (5)	C2—C8—N1—N2	179.5 (3)
C1—C2—C8—N1	−132.4 (4)	C10—C9—N2—N1	174.9 (4)
N2—C9—C10—C15	−23.0 (7)	C8—N1—N2—C9	169.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.87 (4)	2.07 (4)	2.906 (4)	160 (4)

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