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(2E)-N-(3,5-Dibromo-4-methoxyphenyl)-2-(hydroxyimino)acetamideSimon J. Garden,^{a‡} Angelo C. Pinto,^a Fernanda R. da Cunha,^a Silvia P. Fontes,^a A. S. Lima^a and Edward R. T. Tiekink^{b*}

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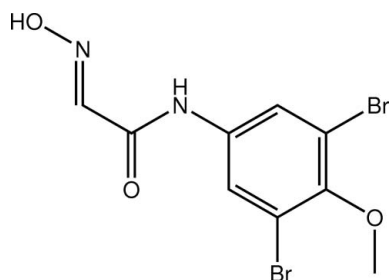
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.028; wR factor = 0.090; data-to-parameter ratio = 17.7.

The title compound, $\text{C}_9\text{H}_8\text{Br}_2\text{N}_2\text{O}_3$, is planar (r.m.s. deviation = 0.030 Å) with the exception of the terminal methyl group which lies out of the plane [1.219 (3) Å]. The conformation about the $\text{C}=\text{N}$ double bond [1.268 (3) Å] is *E*. An intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond occurs. Linear supramolecular chains along the b axis mediated by $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions feature in the crystal structure. These chains are also stabilized by weak $\text{C}-\text{H}\cdots\text{N}$ contacts.

Related literature

For the preparation of isonitrosoacetanilides from aniline derivatives, see: Garden *et al.* (1997). For the use of isonitrosoacetanilides as precursors of pharmacologically important heterocyclic compounds, see: da Silva *et al.* (2001); Garden *et al.* (2002); Matheus *et al.* (2007); Maronas *et al.* (2008). For related structures, see: Briansó *et al.* (1974); Plana *et al.* (1976).



Experimental

Crystal data

$\text{C}_9\text{H}_8\text{Br}_2\text{N}_2\text{O}_3$
 $M_r = 351.98$

Monoclinic, $P2_1/n$
 $a = 10.3841$ (2) Å

$b = 8.8535$ (1) Å
 $c = 13.0164$ (3) Å
 $\beta = 106.356$ (1)°
 $V = 1148.24$ (4) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 7.05$ mm⁻¹
 $T = 120$ K
 $0.20 \times 0.10 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.715$, $T_{\max} = 1.000$

14309 measured reflections
2643 independent reflections
2306 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.090$
 $S = 1.16$
2643 reflections
149 parameters

1 restraint
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.86$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1n}\cdots\text{N2}$	0.88	2.30	2.702 (3)	108
$\text{O2}-\text{H2o}\cdots\text{O1}^{\text{i}}$	0.84	1.83	2.672 (3)	175
$\text{C2}-\text{H2}\cdots\text{N2}^{\text{ii}}$	0.95	2.51	3.345 (3)	146

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{5}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{5}{2}$.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England, and the valuable assistance of the staff there is gratefully acknowledged. SJG thanks CNPq and FAPERJ for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2689).

References

- Brandenburg, K. (2006). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Briansó, J. L., Miravittles, C., Plana, F. & Font-Altaba, M. (1974). *Estud. Geol. (Madrid)*, **30**, 423–428.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Garden, S. J., da Silva, R. B. & Pinto, A. C. (2002). *Tetrahedron*, **58**, 8399–8412.
Garden, S. J., Torres, J. C., Ferreira, A. A., Silva, R. B. & Pinto, A. C. (1997). *Tetrahedron Lett.* **38**, 1501–1504.
Hooft, R. W. W. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
Maronas, P. A., Sudo, R. T., Correa, M. B., Pinto, A. C., Garden, S. J., Trachez, M. M. & Zapata-Sudo, G. (2008). *Clin. Exp. Pharmacol. Physiol.* **35**, 1091–1096.
Matheus, M. E., Violante, F. D., Garden, S. J., Pinto, A. C. & Fernandes, P. D. (2007). *Eur. J. Pharmacol.* **556**, 200–206.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Plana, F., Briansó, J. L., Miravittles, C., Solans, X., Font-Altaba, M., Dideberg, O., Declercq, J. P. & Germain, G. (1976). *Acta Cryst.* **B32**, 2660–2664.

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Sheldrick, G. M. (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Silva, J. F. M. da, Garden, S. J. & Pinto, A. C. (2001). *J. Braz. Chem. Soc.* **12**, 273–324.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

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(2*E*)-*N*-(3,5-Dibromo-4-methoxyphenyl)-2-(hydroxyimino)acetamide

Simon J. Garden, Angelo C. Pinto, Fernanda R. da Cunha, Silvia P. Fontes, A. S. Lima and Edward R. T. Tiekink

S1. Comment

Isonitrosoacetanilides, readily available from aniline derivatives (Garden *et al.*, 1997), have found use as precursors of pharmacologically important heterocyclic compounds (da Silva *et al.*, 2001; Garden *et al.*, 2002; Matheus *et al.*, 2007; Maronas *et al.*, 2008).

The molecular structure of (I), Fig. 1, is essentially planar with the exception of the terminal methyl group. Thus, the r.m.s. deviation of all non-hydrogen atoms, excluding the methyl-C9 atom, is 0.030 Å; the C9 atom lies 1.219 (3) Å out of the plane. The conformation about the C2=N2 double bond [1.268 (3) Å] is *E*. The observed planarity is partially stabilised by an intramolecular N–H⋯N hydrogen bond (Table 1). There two other methoxy substituted 2-(hydroxyimino)-*N*-arylacetamide structures available for comparison, *i.e.* *o*-OMe (Plana *et al.*, 1976) and *p*-OMe (Briansó *et al.*, 1974) derivatives. The geometric parameters in these match closely those in (I). The major difference in the three structures relate to the non-planarity of (I) compared to the planarity in the literature structures. The proximity of the OMe group to two bromido substituents in (I) is the likely explanation for the deviation from planarity in (I). The crystal packing is dominated by O–H⋯O hydrogen bonding interactions that lead to the formation of a supramolecular linear chain along the *b* axis, Fig. 2 and Table 1. These chains are also stabilised by weak C–H⋯N contacts, Table 1.

S2. Experimental

The compound was prepared as previously reported from 3,5-dibromo-4-methoxyaniline, hydroxylamine.hydrogen sulfate in aqueous ethanol, containing sodium sulfate and CCl₃CH(OH)₂ (Garden *et al.*, 1997). The sample for the crystallographic study was recrystallised from EtOH, m.p. 463 K.

S3. Refinement

The O-, N- and C-bound H atoms were geometrically placed (O–H = 0.84 Å, N–H = 0.88 Å and C–H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2-1.5U_{eq}(\text{parent atom})$.

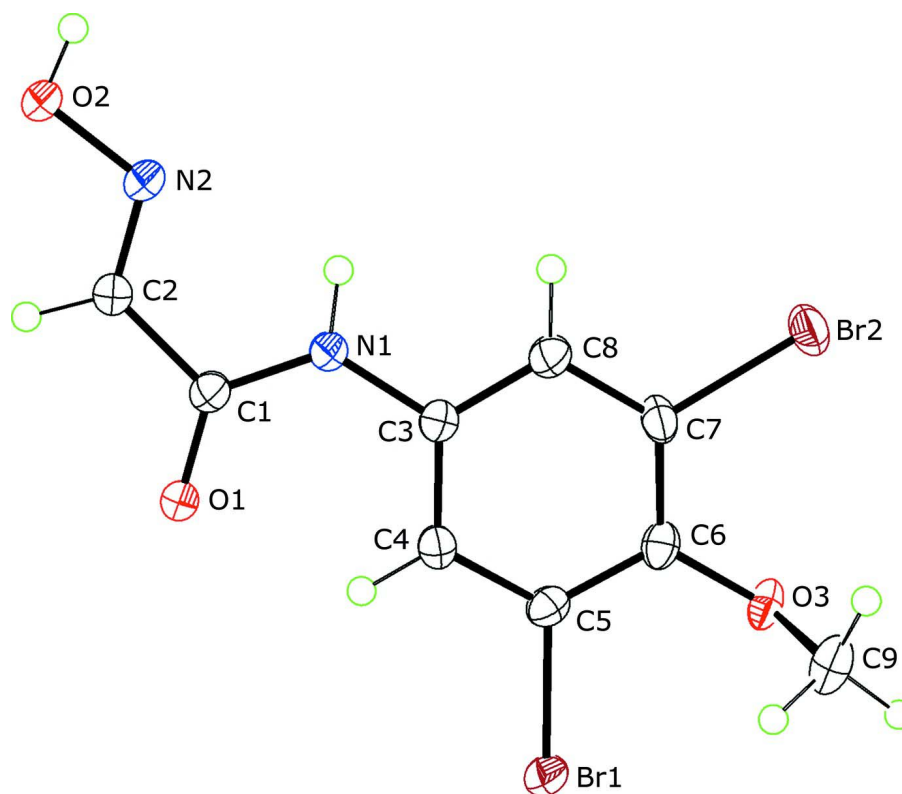


Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

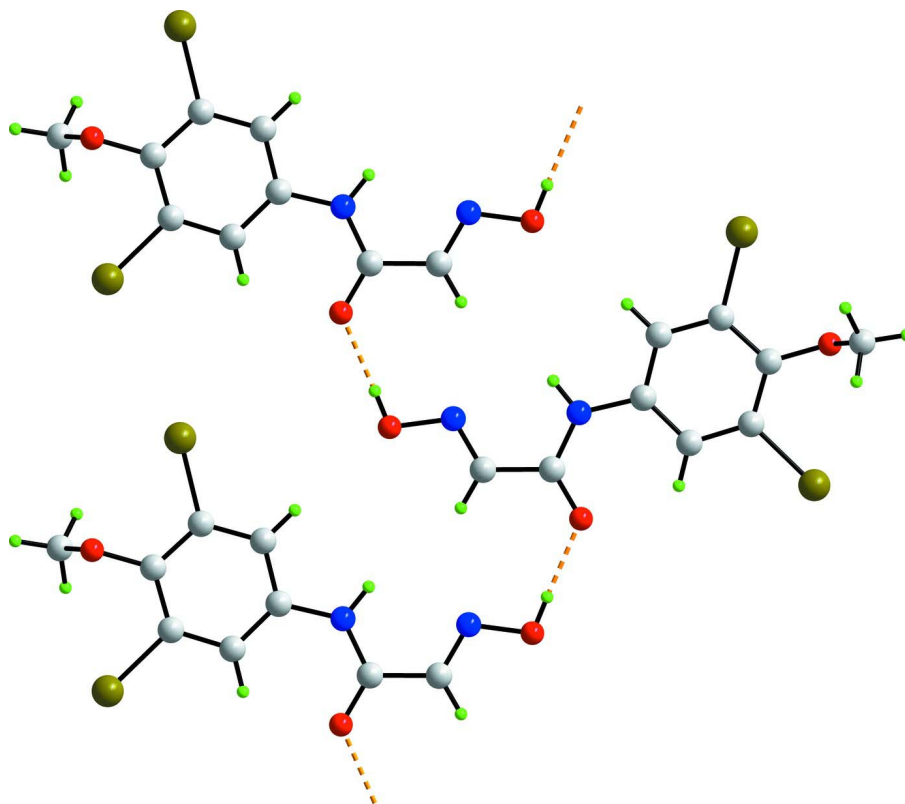


Figure 2

A view of a supramolecular array in (I) aligned along the *b* axis. The O–H···O hydrogen bonding interactions are shown as orange dashed lines. Colour code: Br, olive; O, red; N, blue; C, grey; and H, green.

(2*E*)-*N*-(3,5-Dibromo-4-methoxyphenyl)-2-(hydroxyimino)acetamide

Crystal data

$C_9H_8Br_2N_2O_3$

$M_r = 351.98$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.3841 (2) \text{ \AA}$

$b = 8.8535 (1) \text{ \AA}$

$c = 13.0164 (3) \text{ \AA}$

$\beta = 106.356 (1)^\circ$

$V = 1148.24 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 680$

$D_x = 2.036 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2760 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 7.05 \text{ mm}^{-1}$

$T = 120 \text{ K}$

Plate, colourless

$0.20 \times 0.10 \times 0.01 \text{ mm}$

Data collection

Nonius KappaCCD area-detector
diffractometer

Radiation source: Enraf Nonius FR591 rotating
anode

10 cm confocal mirrors monochromator

Detector resolution: $9.091 \text{ pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)

$T_{\min} = 0.715$, $T_{\max} = 1.000$

14309 measured reflections

2643 independent reflections

2306 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 10$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.090$
 $S = 1.16$
 2643 reflections
 149 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.0437P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.77 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.86 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.51024 (3)	0.51328 (3)	0.64286 (2)	0.03073 (12)
Br2	0.57429 (3)	1.12760 (3)	0.76735 (2)	0.03212 (12)
O1	0.6650 (2)	0.4317 (2)	1.04372 (14)	0.0253 (4)
O2	0.7998 (2)	0.6540 (2)	1.37265 (15)	0.0268 (4)
H2O	0.8150	0.7416	1.3979	0.040*
O3	0.50326 (19)	0.8555 (2)	0.61613 (15)	0.0248 (4)
N2	0.7577 (2)	0.6746 (2)	1.26323 (17)	0.0228 (5)
N1	0.6742 (2)	0.6890 (2)	1.04718 (16)	0.0234 (5)
H1N	0.6916	0.7664	1.0914	0.028*
C1	0.6888 (3)	0.5517 (3)	1.0935 (2)	0.0216 (5)
C2	0.7347 (3)	0.5508 (3)	1.2123 (2)	0.0235 (5)
H2	0.7469	0.4577	1.2501	0.028*
C3	0.6344 (3)	0.7255 (3)	0.9367 (2)	0.0217 (5)
C4	0.5979 (3)	0.6159 (3)	0.8574 (2)	0.0221 (5)
H4	0.5995	0.5118	0.8755	0.027*
C5	0.5590 (3)	0.6618 (3)	0.7514 (2)	0.0218 (5)
C6	0.5517 (2)	0.8133 (3)	0.7211 (2)	0.0221 (5)
C7	0.5887 (3)	0.9197 (3)	0.8032 (2)	0.0238 (5)
C8	0.6305 (3)	0.8778 (3)	0.9101 (2)	0.0242 (6)
H8	0.6562	0.9524	0.9645	0.029*
C9	0.6056 (3)	0.8606 (4)	0.5605 (2)	0.0332 (6)
H9A	0.6683	0.9431	0.5894	0.050*
H9B	0.5635	0.8776	0.4840	0.050*
H9C	0.6544	0.7645	0.5704	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0466 (2)	0.02593 (18)	0.01798 (18)	-0.00608 (11)	0.00633 (13)	-0.00244 (9)
Br2	0.0420 (2)	0.01905 (17)	0.0298 (2)	-0.00089 (10)	0.00100 (13)	0.00607 (10)
O1	0.0388 (11)	0.0189 (9)	0.0175 (9)	-0.0002 (8)	0.0067 (8)	0.0009 (7)
O2	0.0400 (11)	0.0222 (9)	0.0154 (9)	-0.0022 (8)	0.0033 (8)	0.0001 (7)
O3	0.0255 (9)	0.0305 (10)	0.0166 (9)	-0.0010 (7)	0.0031 (7)	0.0081 (7)
N2	0.0274 (12)	0.0235 (11)	0.0159 (11)	-0.0009 (8)	0.0033 (8)	0.0000 (8)
N1	0.0321 (12)	0.0184 (10)	0.0165 (11)	-0.0005 (9)	0.0015 (9)	0.0004 (8)
C1	0.0235 (12)	0.0220 (12)	0.0181 (13)	-0.0011 (10)	0.0042 (10)	0.0000 (10)
C2	0.0307 (14)	0.0196 (12)	0.0193 (13)	-0.0001 (10)	0.0054 (10)	0.0011 (10)
C3	0.0243 (12)	0.0209 (12)	0.0190 (13)	0.0013 (10)	0.0046 (10)	0.0015 (9)
C4	0.0246 (13)	0.0197 (12)	0.0215 (14)	0.0008 (9)	0.0056 (10)	0.0028 (9)
C5	0.0214 (12)	0.0250 (12)	0.0184 (13)	-0.0019 (10)	0.0045 (10)	-0.0018 (10)
C6	0.0188 (12)	0.0261 (13)	0.0195 (13)	0.0009 (10)	0.0022 (10)	0.0053 (10)
C7	0.0255 (13)	0.0184 (12)	0.0248 (14)	-0.0010 (10)	0.0028 (10)	0.0060 (10)
C8	0.0267 (13)	0.0244 (13)	0.0189 (13)	-0.0024 (10)	0.0024 (10)	0.0001 (9)
C9	0.0345 (16)	0.0420 (16)	0.0244 (15)	0.0030 (12)	0.0103 (12)	0.0102 (12)

Geometric parameters (\AA , $^\circ$)

Br1—C5	1.892 (3)	C2—H2	0.9500
Br2—C7	1.894 (3)	C3—C4	1.390 (4)
O1—C1	1.233 (3)	C3—C8	1.390 (4)
O2—N2	1.379 (3)	C4—C5	1.385 (3)
O2—H2o	0.8400	C4—H4	0.9500
O3—C6	1.368 (3)	C5—C6	1.394 (4)
O3—C9	1.445 (3)	C6—C7	1.395 (4)
N2—C2	1.268 (3)	C7—C8	1.386 (4)
N1—C1	1.346 (3)	C8—H8	0.9500
N1—C3	1.417 (3)	C9—H9A	0.9800
N1—H1N	0.8800	C9—H9B	0.9800
C1—C2	1.484 (4)	C9—H9C	0.9800
N2—O2—H2o	104.6	C4—C5—C6	122.8 (2)
C6—O3—C9	113.1 (2)	C4—C5—Br1	118.79 (19)
C2—N2—O2	112.6 (2)	C6—C5—Br1	118.39 (19)
C1—N1—C3	128.6 (2)	O3—C6—C5	121.4 (2)
C1—N1—H1N	115.7	O3—C6—C7	121.7 (2)
C3—N1—H1N	115.7	C5—C6—C7	116.8 (2)
O1—C1—N1	124.3 (2)	C8—C7—C6	121.9 (2)
O1—C1—C2	120.1 (2)	C8—C7—Br2	119.2 (2)
N1—C1—C2	115.7 (2)	C6—C7—Br2	118.81 (19)
N2—C2—C1	119.9 (2)	C7—C8—C3	119.3 (2)
N2—C2—H2	120.0	C7—C8—H8	120.4
C1—C2—H2	120.0	C3—C8—H8	120.4
C4—C3—C8	120.6 (2)	O3—C9—H9A	109.5

C4—C3—N1	122.4 (2)	O3—C9—H9B	109.5
C8—C3—N1	117.0 (2)	H9A—C9—H9B	109.5
C5—C4—C3	118.5 (2)	O3—C9—H9C	109.5
C5—C4—H4	120.7	H9A—C9—H9C	109.5
C3—C4—H4	120.7	H9B—C9—H9C	109.5
C3—N1—C1—O1	-2.1 (4)	C4—C5—C6—O3	-175.0 (2)
C3—N1—C1—C2	178.9 (2)	Br1—C5—C6—O3	3.8 (3)
O2—N2—C2—C1	-179.9 (2)	C4—C5—C6—C7	1.3 (4)
O1—C1—C2—N2	-179.2 (3)	Br1—C5—C6—C7	-179.86 (19)
N1—C1—C2—N2	-0.2 (4)	O3—C6—C7—C8	176.2 (2)
C1—N1—C3—C4	2.9 (4)	C5—C6—C7—C8	-0.1 (4)
C1—N1—C3—C8	-178.4 (3)	O3—C6—C7—Br2	-1.3 (4)
C8—C3—C4—C5	0.7 (4)	C5—C6—C7—Br2	-177.56 (18)
N1—C3—C4—C5	179.3 (2)	C6—C7—C8—C3	-0.8 (4)
C3—C4—C5—C6	-1.7 (4)	Br2—C7—C8—C3	176.7 (2)
C3—C4—C5—Br1	179.57 (19)	C4—C3—C8—C7	0.5 (4)
C9—O3—C6—C5	-88.4 (3)	N1—C3—C8—C7	-178.2 (2)
C9—O3—C6—C7	95.4 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1n \cdots N2	0.88	2.30	2.702 (3)	108
O2—H2o \cdots O1 ⁱ	0.84	1.83	2.672 (3)	175
C2—H2 \cdots N2 ⁱⁱ	0.95	2.51	3.345 (3)	146

Symmetry codes: (i) $-x+3/2, y+1/2, -z+5/2$; (ii) $-x+3/2, y-1/2, -z+5/2$.