

Crystal structure of 2-[(*R*)-[1-(4-bromophenyl)ethyl]iminomethyl]-4-(phenyldiazenyl)phenol, a chiral photochromic Schiff base

Ryoji Moriwaki and Takashi Akitsu*

Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. *Correspondence e-mail: akitsu@rs.kagu.tus.ac.jp

Received 5 October 2015; accepted 21 October 2015

Edited by V. V. Chernyshev, Moscow State University, Russia

The title chiral photochromic Schiff base compound, $C_{21}H_{18}BrN_3O$, was synthesized from (*R*)-(+)-1-(4-bromophenyl)ethylamine and the salicylaldehyde of an azobenzene derivative. The molecule corresponds to the phenol–imine tautomer, the C=N and N–C bond distances being 1.285 (3) and 1.470 (3) Å, respectively. The diazenyl group adopts a *trans* form, with an N=N distance of 1.256 (3) Å. The hydroxy group is involved in intramolecular O–H...N hydrogen bonding. In the crystal, C–H... π interactions consolidate the crystal packing of one-dimensional chains, which exhibits short intermolecular Br...C contacts of 3.400 (3) Å.

Keywords: crystal structure; Schiff base; azobenzene; photochromic.

CCDC reference: 1432412

1. Related literature

For applications of (chiral) photochromic Schiff base compounds, see: Akitsu & Einaga (2006*b*); Akitsu *et al.* (2004); Aritake *et al.* (2010); Miura *et al.* (2009). For the crystal structures of related compounds, see: Akitsu & Einaga (2005*a,b*, 2006*a*); Akitsu (2007); Akitsu & Itoh (2010); Aslantas *et al.* (2007); Hadjoudis & Mavridis (2004); Khandar & Rezvani (1999).

2. Experimental

2.1. Crystal data

$C_{21}H_{18}BrN_3O$	$V = 1813.3 (11) \text{ \AA}^3$
$M_r = 408.29$	$Z = 4$
Orthorhombic $P2_12_12$	Mo $K\alpha$ radiation
$a = 7.271 (3) \text{ \AA}$	$\mu = 2.28 \text{ mm}^{-1}$
$b = 41.901 (15) \text{ \AA}$	$T = 113 \text{ K}$
$c = 5.952 (2) \text{ \AA}$	$0.37 \times 0.23 \times 0.08 \text{ mm}$

2.2. Data collection

Bruker APEXII CCD diffractometer	10349 measured reflections
Absorption correction: empirical (using intensity measurements) (<i>SADABS</i> ; Sheldrick, 1996)	4176 independent reflections
$T_{\min} = 0.486$, $T_{\max} = 0.833$	3723 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$
$wR(F^2) = 0.047$	Absolute structure: Flack x determined using 1360 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
$S = 1.01$	Absolute structure parameter: 0.005 (4)
4176 reflections	
237 parameters	
H-atom parameters constrained	
$\Delta\rho_{\max} = 0.57 \text{ e \AA}^{-3}$	

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are centroids of C1–C6 and C7–C11/C13 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1A...N3	0.84	1.84	2.585 (3)	148
C12–H12...Cg1 ⁱ	0.95	2.80	3.399 (3)	122
C10–H10...Cg1 ⁱⁱ	0.95	2.74	3.415 (3)	128
C6–H6...Cg2 ⁱⁱⁱ	0.95	2.75	3.423 (3)	128

Symmetry codes: (i) $-x + 1, -y + 1, z$; (ii) $-x, -y + 1, z + 1$; (iii) $x, y, z + 1$.

Data collection: *APEX2* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: CV5499).

References

- Akitsu, T. (2007). *Polyhedron*, **26**, 2527–2535.
- Akitsu, T. & Einaga, Y. (2005a). *Polyhedron*, **24**, 1869–1877.
- Akitsu, T. & Einaga, Y. (2005b). *Polyhedron*, **24**, 2933–2943.
- Akitsu, T. & Einaga, Y. (2006a). *Polyhedron*, **25**, 1089–1095.
- Akitsu, T. & Einaga, Y. (2006b). *Acta Cryst. E* **62**, o4315–o4317.
- Akitsu, T. & Itoh, T. (2010). *Polyhedron*, **29**, 477–487.
- Akitsu, T., Takeuchi, Y. & Einaga, Y. (2004). *Acta Cryst. C* **60**, o801–o802.
- Aritake, Y., Watanabe, Y. & Akitsu, T. (2010). *Acta Cryst. E* **66**, o749.
- Aslantas, M., Kurtoglu, N., Sahin, E. & Kurtoglu, M. (2007). *Acta Cryst. E* **63**, o3637.
- Bruker (1998). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Hadjoudis, E. & Mavridis, I. M. (2004). *Chem. Soc. Rev.* **33**, 579–588.
- Khandar, A. A. & Rezvani, Z. (1999). *Polyhedron*, **18**, 129–133.
- Miura, Y., Aritake, Y. & Akitsu, T. (2009). *Acta Cryst. E* **65**, o2381.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst. B* **69**, 249–259.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.

supporting information

Acta Cryst. (2015). E71, o886–o887 [https://doi.org/10.1107/S2056989015019866]

Crystal structure of 2-[(*R*)-[1-(4-bromophenyl)ethyl]iminomethyl]-4-(phenyldiazenyl)phenol, a chiral photochromic Schiff base

Ryoji Moriwaki and Takashi Akitsu

S1. Comment

In recent years, there is a growing interest in the organic/inorganic metal complexes and photochromic compounds. For example, *cis-trans* photoisomerization of azobenzene could switch conformation of chiral ligands (Akitsu & Einaga, 2005*a*, 2005*b*), chiral conformation change in a solution induced by a photochromic solute (Akitsu & Einaga, 2006*a*; Akitsu, 2007) and optical anisotropy in polymeric films (Akitsu & Itoh, 2010). Also free Schiff base ligands may act as photochromic, thermochromics, and fluorescence materials (Akitsu *et al.*, 2004; Hadjoudis & Mavridis, 2004; Akitsu & Einaga, 2006*b*). Recently, we have synthesized the title compound (I). Herewith we present its crystal structure.

The molecule of (I) (Fig. I) adopts an *E* configuration with respect to the imine C=N double bond with C13—C12—N3—C14 torsion angle of 178.6 (2)°. Thus, the π -conjugated system around the imine group is essentially planar. All bond lengths and angles in (I) correspond well to those observed in similar Schiff base ligands (Akitsu & Einaga, 2006*b*; Miura *et al.*, 2009; Aritake *et al.*, 2010) and azobenzene derivatives (Aslantas *et al.*, 2007; Khandar & Rezvani, 1999). The C11—O1 bond distance of 1.350 (3) Å suggests that it is the phenol-imine tautomer. The contraction of the C12=N3 bond [1.285 (3) Å] is also in agreement with the phenol-imine tautomer. As for the azobenzene moiety, the azo N=N double bond adopts an *E* configuration with the N=N distance of 1.256 (3) Å. Hydroxyl group is involved in intramolecular O—H...N hydrogen bond (Table 1).

In the crystal, C—H... π interactions (Table 1) consolidate the crystal packing, which exhibits short intermolecular Br1...C20(1/2+x, 1/2-y, 2-z) contact of 3.400 (3) Å.

S2. Experimental

Treatment of aniline (0.951 g, 10.0 mmol) in 15 ml of 6*M* HCl and NaNO₂ (0.690 g, 10 mmol) in 15 ml of H₂O for 30 min at 278 K gave rise to the yellow precursor. Treatment of the precursor and salicylaldehyde (1.22 g 10 mmol) in 30 ml of 10% NaOH aqueous solution for 1 h at 278 K, and the resulting brown precipitates were filtrated and washed with water and ethanol, and dried in a desiccator for several days. Treatment of the brown precipitates (0.226 g, 1.00 mmol) and (*R*)-(+)-1-(4-Bromophenyl)ethylamine (0.200 g, 1.00 mmol) for 2 h at 298 K under a nitrogen atmosphere gave rise to orange compound after evaporation (yield 0.0598 g, 29.3%). This crude orange compound was filtered and recrystallized slow evaporation from acetone to give orange prismatic single crystals. Anal. Calc. for C₂₁H₁₈BrN₃O: C, 61.78; H, 4.44; N, 10.29. Found: C, 61.66; H, 4.67; N, 10.17%. IR (KBr, cm⁻¹): 1585 (N=N), 1632 (C=N). ¹H NMR (300 MHz, DMSO) δ (p.p.m.): 1.60 (d, 3H), 2.50 (m, 2H), 4.80 (dd, 1H), 7.03 (d, 2H), 7.41 (tt, 2H), 7.56 (m, 5H), 7.84 (tt, 2H), 7.95 (dd, 1H), 8.12 (d, 1H), 8.88 (s, 1H).

S3. Refinement

All hydrogen atoms were geometrically positioned and refined as riding.

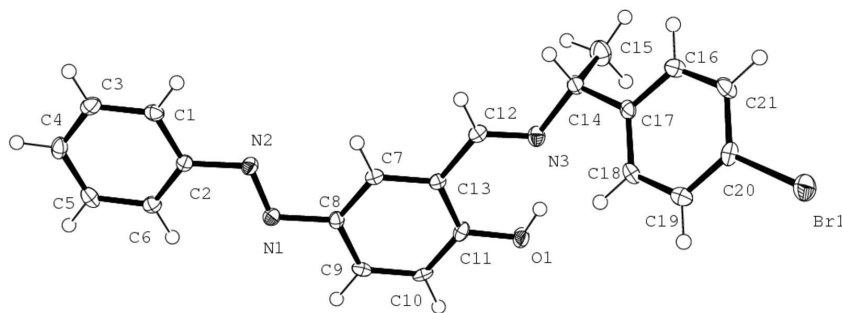


Figure 1

Molecular structure of (I) showing the atomic numbering and 50% probability displacement ellipsoids.

2-[(R)-[1-(4-Bromophenyl)ethyl]iminomethyl]-4-(phenyldiazenyl)phenol

Crystal data

$C_{21}H_{18}BrN_3O$

$M_r = 408.29$

Orthorhombic, $P2_12_12$

$a = 7.271 (3) \text{ \AA}$

$b = 41.901 (15) \text{ \AA}$

$c = 5.952 (2) \text{ \AA}$

$V = 1813.3 (11) \text{ \AA}^3$

$Z = 4$

$F(000) = 832$

$D_x = 1.496 \text{ Mg m}^{-3}$

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

Cell parameters from 10349 reflections

$\theta = 2.8\text{--}27.7^\circ$

$\mu = 2.28 \text{ mm}^{-1}$

$T = 113 \text{ K}$

Needle, orange

$0.37 \times 0.23 \times 0.08 \text{ mm}$

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: $8.333 \text{ pixels mm}^{-1}$

φ and ω scans

Absorption correction: empirical (using intensity measurements)

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.486$, $T_{\max} = 0.833$

10349 measured reflections

4176 independent reflections

3723 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.7^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -8 \rightarrow 9$

$k = -54 \rightarrow 33$

$l = -7 \rightarrow 7$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.047$ $S = 1.01$

4176 reflections

237 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$ Absolute structure: Flack x determined using
1360 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.005 (4)

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.

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	1.09221 (4)	0.26333 (2)	0.94955 (5)	0.02934 (9)
C1	0.2882 (4)	0.55533 (6)	0.2777 (4)	0.0162 (6)
H1	0.347	0.54	0.185	0.019*
C2	0.2286 (3)	0.54700 (5)	0.4928 (4)	0.0132 (6)
C3	0.2610 (4)	0.58613 (6)	0.2004 (5)	0.0191 (6)
H3	0.3033	0.5919	0.0551	0.023*
C4	0.1732 (4)	0.60841 (6)	0.3323 (5)	0.0193 (7)
H4	0.1531	0.6294	0.2766	0.023*
C5	0.1136 (4)	0.60022 (5)	0.5478 (5)	0.0189 (6)
H5	0.0549	0.6157	0.6397	0.023*
C6	0.1400 (3)	0.56948 (5)	0.6277 (4)	0.0153 (6)
H6	0.098	0.5638	0.7733	0.018*
C7	0.3225 (3)	0.45296 (5)	0.6999 (4)	0.0130 (6)
H7	0.3679	0.4579	0.5543	0.016*
C8	0.2539 (4)	0.47727 (5)	0.8343 (4)	0.0133 (6)
C9	0.1948 (3)	0.47027 (5)	1.0517 (5)	0.0147 (5)
H9	0.1538	0.487	1.1473	0.018*
C10	0.1954 (4)	0.43923 (6)	1.1290 (4)	0.0147 (6)
H10	0.1524	0.4347	1.2762	0.018*
C11	0.2586 (3)	0.41462 (5)	0.9931 (4)	0.0152 (6)
C12	0.3926 (4)	0.39625 (5)	0.6274 (4)	0.0142 (5)
H12	0.4383	0.4015	0.4826	0.017*
C13	0.3259 (4)	0.42154 (5)	0.7748 (4)	0.0120 (6)
C14	0.4556 (3)	0.34250 (5)	0.5321 (5)	0.0170 (6)
H14	0.5028	0.3533	0.394	0.02*
C15	0.2920 (4)	0.32168 (6)	0.4678 (5)	0.0273 (7)
H15A	0.2462	0.3106	0.6014	0.041*

H15B	0.3305	0.306	0.3551	0.041*
H15C	0.1941	0.3351	0.4054	0.041*
C16	0.6884 (4)	0.29788 (5)	0.5224 (5)	0.0206 (6)
H16	0.6402	0.2924	0.3791	0.025*
C17	0.6118 (4)	0.32344 (5)	0.6378 (4)	0.0148 (6)
C18	0.6859 (4)	0.33094 (6)	0.8466 (4)	0.0212 (7)
H18	0.637	0.3484	0.9289	0.025*
C19	0.8302 (4)	0.31341 (5)	0.9371 (5)	0.0220 (6)
H19	0.8799	0.3189	1.0796	0.026*
C20	0.9003 (4)	0.28803 (5)	0.8183 (4)	0.0186 (6)
C21	0.8323 (4)	0.28005 (6)	0.6082 (5)	0.0214 (7)
H21	0.8831	0.2628	0.5253	0.026*
N1	0.2355 (3)	0.50990 (4)	0.7656 (4)	0.0149 (5)
N2	0.2565 (3)	0.51440 (4)	0.5585 (4)	0.0150 (5)
N3	0.3906 (3)	0.36692 (4)	0.6905 (3)	0.0169 (5)
O1	0.2552 (3)	0.38445 (4)	1.0728 (3)	0.0200 (4)
H1A	0.2988	0.372	0.9758	0.03*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03065 (17)	0.02551 (13)	0.03187 (16)	0.01116 (13)	−0.00603 (16)	−0.00168 (14)
C1	0.0158 (16)	0.0182 (13)	0.0147 (15)	−0.0033 (11)	−0.0014 (12)	−0.0026 (11)
C2	0.0111 (13)	0.0139 (11)	0.0148 (17)	−0.0035 (9)	−0.0047 (11)	0.0012 (10)
C3	0.0191 (16)	0.0228 (14)	0.0154 (15)	−0.0084 (12)	−0.0061 (13)	0.0028 (11)
C4	0.0186 (16)	0.0148 (13)	0.0246 (17)	−0.0040 (11)	−0.0077 (14)	0.0051 (12)
C5	0.0162 (15)	0.0147 (11)	0.0258 (14)	0.0011 (10)	−0.0031 (16)	−0.0051 (12)
C6	0.0130 (16)	0.0177 (12)	0.0151 (14)	−0.0012 (10)	−0.0021 (11)	−0.0001 (11)
C7	0.0099 (14)	0.0172 (12)	0.0118 (14)	−0.0022 (10)	−0.0003 (11)	0.0005 (11)
C8	0.0117 (15)	0.0122 (12)	0.0161 (15)	0.0003 (10)	−0.0025 (12)	0.0009 (11)
C9	0.0127 (14)	0.0186 (12)	0.0128 (13)	0.0002 (10)	−0.0016 (14)	−0.0050 (12)
C10	0.0140 (15)	0.0229 (13)	0.0071 (13)	−0.0014 (11)	−0.0001 (11)	0.0019 (11)
C11	0.0119 (14)	0.0159 (12)	0.0176 (18)	0.0004 (10)	−0.0017 (11)	0.0051 (10)
C12	0.0106 (14)	0.0176 (12)	0.0145 (13)	0.0000 (11)	−0.0009 (12)	0.0013 (10)
C13	0.0091 (14)	0.0147 (12)	0.0123 (14)	0.0014 (10)	−0.0006 (12)	0.0004 (10)
C14	0.0213 (16)	0.0132 (11)	0.0166 (14)	0.0005 (10)	0.0031 (13)	−0.0004 (11)
C15	0.0249 (17)	0.0213 (13)	0.0357 (18)	−0.0018 (11)	−0.0050 (16)	−0.0010 (14)
C16	0.0267 (16)	0.0190 (13)	0.0162 (16)	−0.0006 (11)	−0.0005 (14)	−0.0027 (11)
C17	0.0183 (15)	0.0101 (11)	0.0159 (13)	−0.0032 (11)	0.0042 (13)	0.0015 (10)
C18	0.0292 (18)	0.0126 (12)	0.0219 (16)	0.0034 (11)	−0.0003 (14)	−0.0041 (11)
C19	0.0277 (16)	0.0200 (12)	0.0182 (14)	0.0008 (11)	−0.0032 (15)	−0.0047 (13)
C20	0.0186 (15)	0.0148 (12)	0.0224 (15)	0.0015 (12)	0.0000 (15)	0.0052 (11)
C21	0.0271 (17)	0.0166 (13)	0.0206 (17)	0.0048 (11)	0.0045 (13)	−0.0051 (11)
N1	0.0144 (13)	0.0154 (11)	0.0149 (13)	−0.0001 (9)	0.0004 (10)	0.0007 (9)
N2	0.0160 (12)	0.0145 (10)	0.0146 (12)	−0.0005 (8)	0.0010 (12)	0.0021 (10)
N3	0.0157 (13)	0.0151 (10)	0.0198 (12)	0.0015 (9)	0.0020 (12)	0.0012 (9)
O1	0.0279 (12)	0.0150 (8)	0.0172 (10)	0.0034 (7)	0.0064 (10)	0.0036 (8)

Geometric parameters (Å, °)

Br1—C20	1.905 (3)	C11—C13	1.419 (4)
C1—C3	1.384 (3)	C12—N3	1.285 (3)
C1—C2	1.396 (3)	C12—C13	1.459 (3)
C1—H1	0.95	C12—H12	0.95
C2—C6	1.395 (3)	C14—N3	1.470 (3)
C2—N2	1.435 (3)	C14—C15	1.524 (3)
C3—C4	1.376 (4)	C14—C17	1.524 (4)
C3—H3	0.95	C14—H14	1.0
C4—C5	1.397 (4)	C15—H15A	0.98
C4—H4	0.95	C15—H15B	0.98
C5—C6	1.386 (3)	C15—H15C	0.98
C5—H5	0.95	C16—C21	1.383 (4)
C6—H6	0.95	C16—C17	1.389 (3)
C7—C8	1.388 (3)	C16—H16	0.95
C7—C13	1.390 (3)	C17—C18	1.390 (4)
C7—H7	0.95	C18—C19	1.389 (4)
C8—C9	1.395 (3)	C18—H18	0.95
C8—N1	1.433 (3)	C19—C20	1.375 (3)
C9—C10	1.380 (3)	C19—H19	0.95
C9—H9	0.95	C20—C21	1.386 (4)
C10—C11	1.389 (3)	C21—H21	0.95
C10—H10	0.95	N1—N2	1.256 (3)
C11—O1	1.350 (3)	O1—H1A	0.84
C3—C1—C2	119.6 (2)	C7—C13—C12	120.1 (2)
C3—C1—H1	120.2	C11—C13—C12	121.1 (2)
C2—C1—H1	120.2	N3—C14—C15	108.0 (2)
C6—C2—C1	120.1 (2)	N3—C14—C17	109.8 (2)
C6—C2—N2	123.5 (2)	C15—C14—C17	112.67 (19)
C1—C2—N2	116.4 (2)	N3—C14—H14	108.8
C4—C3—C1	120.6 (3)	C15—C14—H14	108.8
C4—C3—H3	119.7	C17—C14—H14	108.8
C1—C3—H3	119.7	C14—C15—H15A	109.5
C3—C4—C5	120.1 (2)	C14—C15—H15B	109.5
C3—C4—H4	120.0	H15A—C15—H15B	109.5
C5—C4—H4	120.0	C14—C15—H15C	109.5
C6—C5—C4	120.0 (3)	H15A—C15—H15C	109.5
C6—C5—H5	120.0	H15B—C15—H15C	109.5
C4—C5—H5	120.0	C21—C16—C17	122.5 (3)
C5—C6—C2	119.6 (2)	C21—C16—H16	118.7
C5—C6—H6	120.2	C17—C16—H16	118.7
C2—C6—H6	120.2	C16—C17—C18	117.4 (2)
C8—C7—C13	121.1 (2)	C16—C17—C14	119.9 (2)
C8—C7—H7	119.4	C18—C17—C14	122.6 (2)
C13—C7—H7	119.4	C19—C18—C17	121.3 (2)
C7—C8—C9	119.4 (2)	C19—C18—H18	119.3

C7—C8—N1	124.7 (2)	C17—C18—H18	119.3
C9—C8—N1	115.9 (2)	C20—C19—C18	119.3 (3)
C10—C9—C8	120.4 (2)	C20—C19—H19	120.3
C10—C9—H9	119.8	C18—C19—H19	120.3
C8—C9—H9	119.8	C19—C20—C21	121.2 (3)
C9—C10—C11	120.5 (2)	C19—C20—Br1	118.8 (2)
C9—C10—H10	119.8	C21—C20—Br1	120.02 (19)
C11—C10—H10	119.8	C16—C21—C20	118.2 (2)
O1—C11—C10	119.0 (2)	C16—C21—H21	120.9
O1—C11—C13	121.3 (2)	C20—C21—H21	120.9
C10—C11—C13	119.7 (2)	N2—N1—C8	114.3 (2)
N3—C12—C13	121.0 (2)	N1—N2—C2	113.1 (2)
N3—C12—H12	119.5	C12—N3—C14	118.3 (2)
C13—C12—H12	119.5	C11—O1—H1A	109.5
C7—C13—C11	118.8 (2)		
C3—C1—C2—C6	0.8 (4)	C21—C16—C17—C18	0.3 (4)
C3—C1—C2—N2	178.1 (2)	C21—C16—C17—C14	178.9 (2)
C2—C1—C3—C4	−1.0 (4)	N3—C14—C17—C16	176.7 (2)
C1—C3—C4—C5	1.2 (4)	C15—C14—C17—C16	56.2 (3)
C3—C4—C5—C6	−1.1 (4)	N3—C14—C17—C18	−4.8 (3)
C4—C5—C6—C2	0.9 (4)	C15—C14—C17—C18	−125.3 (3)
C1—C2—C6—C5	−0.8 (4)	C16—C17—C18—C19	−0.5 (4)
N2—C2—C6—C5	−177.9 (2)	C14—C17—C18—C19	−179.0 (2)
C13—C7—C8—C9	2.8 (4)	C17—C18—C19—C20	−0.4 (4)
C13—C7—C8—N1	−176.2 (2)	C18—C19—C20—C21	1.3 (4)
C7—C8—C9—C10	−3.3 (4)	C18—C19—C20—Br1	−177.8 (2)
N1—C8—C9—C10	175.8 (2)	C17—C16—C21—C20	0.6 (4)
C8—C9—C10—C11	1.4 (4)	C19—C20—C21—C16	−1.5 (4)
C9—C10—C11—O1	−179.2 (2)	Br1—C20—C21—C16	177.69 (19)
C9—C10—C11—C13	1.1 (4)	C7—C8—N1—N2	11.8 (4)
C8—C7—C13—C11	−0.3 (4)	C9—C8—N1—N2	−167.2 (2)
C8—C7—C13—C12	177.8 (2)	C8—N1—N2—C2	177.17 (19)
O1—C11—C13—C7	178.7 (2)	C6—C2—N2—N1	−16.5 (3)
C10—C11—C13—C7	−1.6 (4)	C1—C2—N2—N1	166.3 (2)
O1—C11—C13—C12	0.5 (4)	C13—C12—N3—C14	178.6 (2)
C10—C11—C13—C12	−179.8 (2)	C15—C14—N3—C12	−113.7 (3)
N3—C12—C13—C7	−177.4 (2)	C17—C14—N3—C12	123.1 (3)
N3—C12—C13—C11	0.7 (4)		

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>
O1—H1A \cdots N3	0.84	1.84	2.585 (3)	148
C12—H12 \cdots Cg1 ⁱ	0.95	2.80	3.399 (3)	122

C10—H10 \cdots Cg1 ⁱⁱ	0.95	2.74	3.415 (3)	128
C6—H6 \cdots Cg2 ⁱⁱⁱ	0.95	2.75	3.423 (3)	128

Symmetry codes: (i) $-x+1, -y+1, z$; (ii) $-x, -y+1, z+1$; (iii) $x, y, z+1$.