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Crystal structure of (*Z*)-3-benzyloxy-6-[(2-hydroxy-5-methylanilino)methylidene]cyclohexa-2,4-dien-1-one

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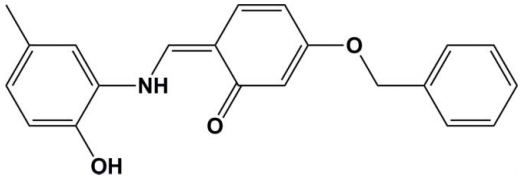
In the title Schiff base compound, $C_{21}H_{19}NO_3$, the conformation about the C=C bond is *Z*. The N—H group and carbonyl O atom form an intramolecular N—H···O hydrogen bond with an *S*(6) ring motif. The benzyloxy ring and the 2-hydroxy-5-methylphenyl ring are inclined to the central six-membered ring by 13.68 (9) and 9.13 (8)°, respectively, and to one another by 21.95 (9)°. In the crystal, molecules are linked by O—H···O hydrogen bonds, forming helical chains along [010].

Keywords: crystal structure; Schiff base; azomethines.

CCDC reference: 1015522

1. Related literature

For some general background on Schiff bases and their various biological activities, see: Arora *et al.* (2002); El-Masry *et al.* (2000); Jarrahpour & Khalili (2006); More *et al.* (2001); Phatak *et al.* (2000). For related structures, see: Akkurt *et al.* (2005, 2008). For pharmaceutical and industrial applications of azomethines, see: Prakash & Adhikari (2011). For the effect of hydrophilicity on drug properties, see: Lin & Lu (1997).



2. Experimental

2.1. Crystal data

$C_{21}H_{19}NO_3$
M_r = 333.37
Monoclinic, $P2_1/c$
a = 12.594 (5) Å
b = 9.303 (5) Å
c = 14.997 (5) Å
β = 96.402 (5)°
V = 1746.1 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.03 × 0.02 × 0.01 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
19603 measured reflections
5148 independent reflections
2672 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.158
S = 1.01
5148 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*n*···O2	0.94 (2)	1.83 (2)	2.609 (2)	138.7 (16)
O1—H1*o*···O2^{i}	0.96 (2)	1.63 (2)	2.590 (2)	176.1 (17)

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

Data collection: *APEX2* (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: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2761).

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supporting information

Acta Cryst. (2014). E**70**, o957–o958 [doi:10.1107/S1600536814016936]

Crystal structure of (*Z*)-3-benzyloxy-6-[(2-hydroxy-5-methylanilino)methylidene]cyclohexa-2,4-dien-1-one

Nadir Ghichi, Ali Benosmane, Ali Benboudiaf and Hocine Merazig

S1. Experimental

A mixture of 2-amino-4-methylphenol (1 mmol) and 4-(benzyloxy)-2-hydroxybenzaldehyde (1 mmol) was heated to form a clear solution. To this a few drops of conc. HCL was added as a catalyst and the mixture was refluxed for 12 h. After cooling the solution to 80°C it was stirred for 45 min the a precipitate formed. It was filtered off and washed with ice cold ethyl acetate to give the pure title Schiff base compound as an orange solid (yield 35%). This crude product was dissolved in ethyl acetate and two spoons of activated charcoal were added. The mixture was filtered over celiteμ000174 and the product was crystallized from ethyl acetate. The compound was very difficult to crystalize and only after several attempts over a period of four months were crystals suitable for X-ray diffraction analysis finally obtained.

S2. Refinement

The OH and NH H atoms, and the methine H atom were located in a difference Fourier map and freely refined. The C-bound H atoms were fixed geometrically and treated as riding atoms: C—H = 0.93 Å (aromatic) and 0.97 Å (methylene) with $U_{iso}(H) = 1.2U_{eq}(C)$.

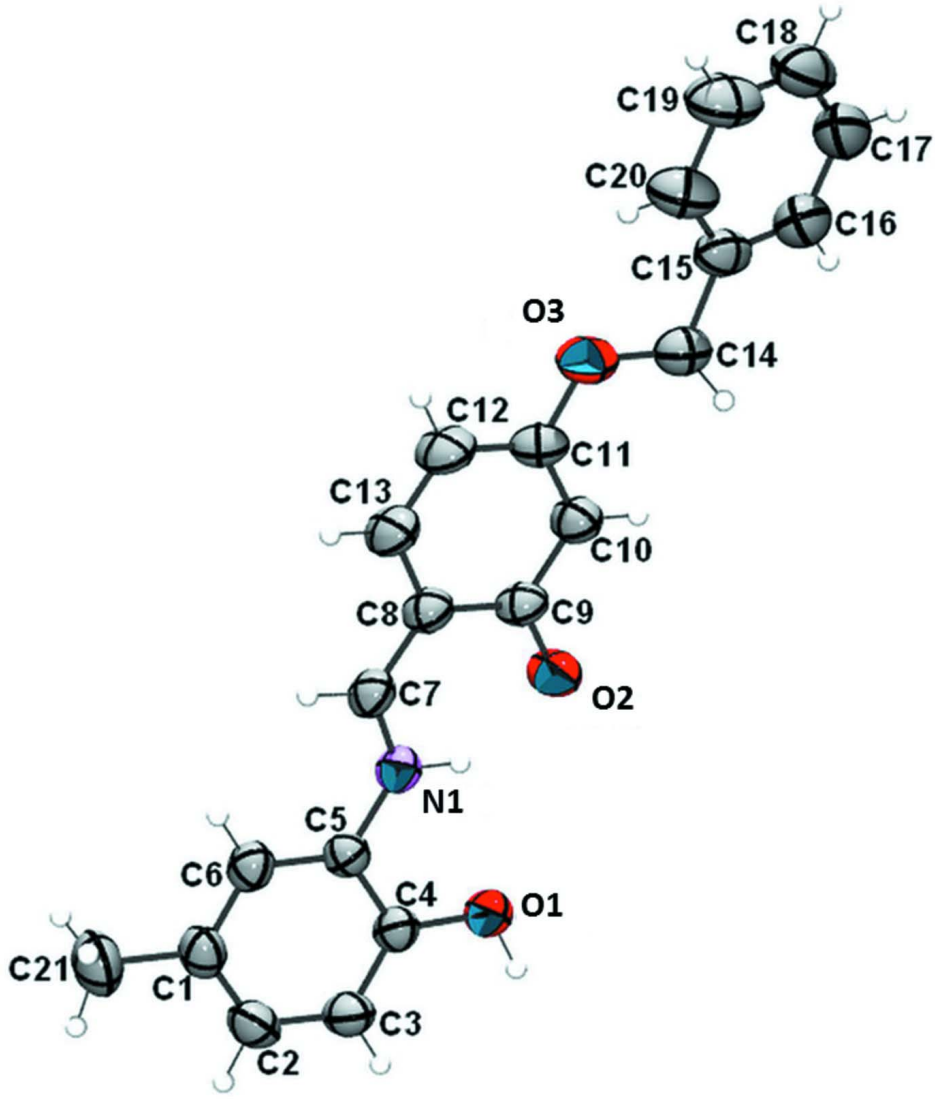

Figure 1

View of the molecular structure of the title molecule, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

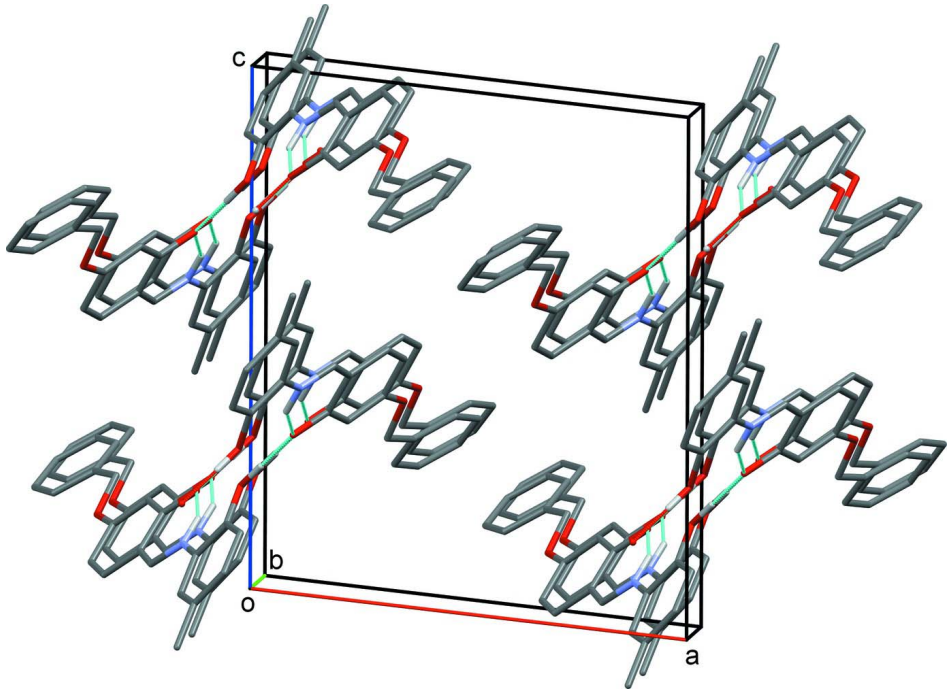

Figure 2

Partial view along the *b* axis of the crystal packing of the title compound, showing the hydrogen bonds as dashed lines (see Table 1 for details).

(*Z*)-3-Benzyloxy-6-[(2-hydroxy-5-methylanilino)methylidene]cyclohexa-2,4-dien-1-one

Crystal data

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$Z = 4$
$F(000) = 704$
$D_x = 1.268$ Mg m^{-3}
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$\mu = 0.09$ mm^{-1}
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Block, orange
0.03 × 0.02 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
19603 measured reflections
5148 independent reflections
2672 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 30.2°$, $\theta_{min} = 2.6°$
$h = -17\rightarrow17$
$k = -13\rightarrow13$
$l = -21\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.158$
$S = 1.01$
5148 reflections
238 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
$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 0.1066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.00597 (9)	0.00730 (11)	0.29239 (8)	0.0607 (4)
O2	0.11904 (9)	0.35839 (11)	0.32139 (8)	0.0632 (4)
O3	0.35952 (9)	0.74624 (12)	0.39999 (9)	0.0686 (4)
N1	0.14153 (10)	0.12579 (13)	0.41887 (9)	0.0466 (4)
C1	0.10315 (13)	−0.23275 (17)	0.52145 (11)	0.0543 (5)
C2	0.03317 (14)	−0.29008 (17)	0.45329 (12)	0.0599 (6)
C3	−0.00117 (13)	−0.21414 (16)	0.37654 (11)	0.0557 (5)
C4	0.03510 (12)	−0.07513 (15)	0.36568 (10)	0.0464 (5)
C5	0.10653 (11)	−0.01575 (15)	0.43336 (10)	0.0435 (4)
C6	0.13925 (12)	−0.09409 (16)	0.51009 (10)	0.0502 (5)
C7	0.21681 (12)	0.19787 (17)	0.46691 (11)	0.0500 (5)
C8	0.24727 (11)	0.33802 (16)	0.44826 (10)	0.0488 (5)
C9	0.19690 (11)	0.41507 (16)	0.37232 (11)	0.0488 (5)
C10	0.23632 (12)	0.55360 (16)	0.35497 (11)	0.0535 (5)
C11	0.31795 (12)	0.61279 (17)	0.41101 (11)	0.0549 (6)
C12	0.36589 (14)	0.53810 (18)	0.48665 (13)	0.0654 (6)
C13	0.33182 (13)	0.40505 (18)	0.50384 (12)	0.0626 (6)
C14	0.31877 (13)	0.82640 (18)	0.32322 (12)	0.0600 (6)
C15	0.37303 (14)	0.96959 (18)	0.32326 (12)	0.0597 (6)
C16	0.32694 (18)	1.0777 (2)	0.26853 (13)	0.0769 (8)
C17	0.3757 (2)	1.2105 (2)	0.26580 (14)	0.0893 (9)
C18	0.4695 (2)	1.2378 (2)	0.31800 (16)	0.0918 (10)
C19	0.51594 (18)	1.1327 (2)	0.37257 (18)	0.0933 (9)
C20	0.46785 (16)	0.9979 (2)	0.37561 (16)	0.0781 (8)
C21	0.13941 (16)	−0.3163 (2)	0.60556 (13)	0.0792 (8)
H1o	−0.0411 (17)	−0.044 (2)	0.2490 (16)	0.101 (7)*
H2	0.00830	−0.38330	0.45937	0.0719*
H1n	0.1091 (14)	0.1794 (19)	0.3701 (13)	0.075 (6)*
H3	−0.04862	−0.25606	0.33208	0.0668*

H6	0.18647	−0.05266	0.55491	0.0603*
H7	0.2525 (13)	0.1493 (17)	0.5192 (12)	0.065 (5)*
H10	0.20650	0.60482	0.30510	0.0642*
H12	0.42068	0.58043	0.52442	0.0785*
H13	0.36443	0.35558	0.55341	0.0750*
H14A	0.24242	0.84004	0.32335	0.0720*
H14B	0.33057	0.77387	0.26933	0.0720*
H16	0.26261	1.06082	0.23328	0.0922*
H17	0.34437	1.28183	0.22815	0.1070*
H18	0.50154	1.32764	0.31634	0.1101*
H19	0.57997	1.15094	0.40792	0.1119*
H20	0.49987	0.92686	0.41309	0.0937*
H21A	0.10696	−0.40980	0.60202	0.1186*
H21B	0.11862	−0.26601	0.65674	0.1186*
H21C	0.21574	−0.32628	0.61143	0.1186*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0764 (8)	0.0485 (6)	0.0514 (7)	−0.0042 (5)	−0.0186 (6)	0.0026 (5)
O2	0.0626 (7)	0.0505 (6)	0.0687 (8)	−0.0121 (5)	−0.0277 (6)	0.0067 (5)
O3	0.0682 (7)	0.0572 (7)	0.0771 (9)	−0.0194 (6)	−0.0061 (6)	−0.0054 (6)
N1	0.0481 (7)	0.0460 (7)	0.0435 (7)	0.0016 (5)	−0.0050 (6)	−0.0001 (6)
C1	0.0591 (10)	0.0511 (9)	0.0523 (9)	0.0110 (7)	0.0047 (8)	0.0065 (7)
C2	0.0691 (10)	0.0415 (8)	0.0684 (11)	0.0006 (7)	0.0041 (9)	0.0038 (8)
C3	0.0612 (10)	0.0449 (8)	0.0580 (10)	−0.0016 (7)	−0.0066 (8)	−0.0057 (7)
C4	0.0490 (8)	0.0436 (8)	0.0448 (8)	0.0055 (6)	−0.0029 (7)	−0.0017 (6)
C5	0.0430 (7)	0.0412 (7)	0.0456 (8)	0.0057 (6)	0.0019 (6)	−0.0023 (6)
C6	0.0502 (9)	0.0533 (9)	0.0457 (9)	0.0052 (7)	−0.0014 (7)	0.0000 (7)
C7	0.0501 (9)	0.0538 (9)	0.0436 (9)	0.0020 (7)	−0.0060 (7)	−0.0022 (7)
C8	0.0449 (8)	0.0508 (8)	0.0487 (9)	−0.0029 (7)	−0.0041 (7)	−0.0059 (7)
C9	0.0426 (8)	0.0482 (8)	0.0529 (9)	−0.0017 (6)	−0.0063 (7)	−0.0075 (7)
C10	0.0517 (9)	0.0491 (8)	0.0569 (10)	−0.0032 (7)	−0.0069 (7)	−0.0011 (7)
C11	0.0484 (9)	0.0501 (9)	0.0650 (11)	−0.0082 (7)	0.0013 (8)	−0.0106 (8)
C12	0.0581 (10)	0.0642 (11)	0.0682 (11)	−0.0130 (8)	−0.0182 (9)	−0.0096 (9)
C13	0.0612 (10)	0.0634 (10)	0.0576 (10)	−0.0062 (8)	−0.0178 (8)	−0.0039 (8)
C14	0.0588 (10)	0.0554 (9)	0.0659 (11)	−0.0070 (8)	0.0075 (9)	−0.0090 (8)
C15	0.0650 (11)	0.0543 (9)	0.0630 (11)	−0.0093 (8)	0.0210 (9)	−0.0150 (8)
C16	0.1016 (15)	0.0646 (12)	0.0650 (12)	−0.0107 (11)	0.0122 (11)	−0.0092 (10)
C17	0.140 (2)	0.0627 (12)	0.0685 (14)	−0.0114 (13)	0.0257 (14)	−0.0049 (10)
C18	0.127 (2)	0.0675 (13)	0.0879 (17)	−0.0338 (13)	0.0433 (15)	−0.0139 (12)
C19	0.0841 (15)	0.0798 (15)	0.1170 (19)	−0.0316 (12)	0.0161 (14)	−0.0185 (14)
C20	0.0707 (12)	0.0616 (11)	0.1026 (16)	−0.0153 (9)	0.0123 (11)	−0.0092 (10)
C21	0.0904 (14)	0.0737 (12)	0.0710 (13)	0.0068 (10)	−0.0014 (11)	0.0239 (10)

Geometric parameters (Å, º)

O1—C4	1.357 (2)	C15—C20	1.379 (3)
O2—C9	1.287 (2)	C15—C16	1.384 (3)
O3—C11	1.365 (2)	C16—C17	1.382 (3)
O3—C14	1.419 (2)	C17—C18	1.366 (4)
O1—H1o	0.96 (2)	C18—C19	1.364 (3)
N1—C5	1.413 (2)	C19—C20	1.396 (3)
N1—C7	1.310 (2)	C2—H2	0.9300
N1—H1n	0.940 (19)	C3—H3	0.9300
C1—C6	1.385 (2)	C6—H6	0.9300
C1—C21	1.508 (3)	C7—H7	0.971 (17)
C1—C2	1.380 (3)	C10—H10	0.9300
C2—C3	1.378 (2)	C12—H12	0.9300
C3—C4	1.387 (2)	C13—H13	0.9300
C4—C5	1.393 (2)	C14—H14A	0.9700
C5—C6	1.385 (2)	C14—H14B	0.9700
C7—C8	1.396 (2)	C16—H16	0.9300
C8—C13	1.421 (2)	C17—H17	0.9300
C8—C9	1.433 (2)	C18—H18	0.9300
C9—C10	1.416 (2)	C19—H19	0.9300
C10—C11	1.369 (2)	C20—H20	0.9300
C11—C12	1.408 (3)	C21—H21A	0.9600
C12—C13	1.344 (2)	C21—H21B	0.9600
C14—C15	1.497 (3)	C21—H21C	0.9600
C11—O3—C14	117.87 (13)	C18—C19—C20	120.3 (2)
C4—O1—H1o	111.1 (13)	C15—C20—C19	120.28 (19)
C5—N1—C7	127.71 (13)	C1—C2—H2	119.00
C5—N1—H1n	119.9 (11)	C3—C2—H2	119.00
C7—N1—H1n	112.4 (11)	C2—C3—H3	120.00
C2—C1—C6	117.40 (15)	C4—C3—H3	120.00
C2—C1—C21	121.94 (15)	C1—C6—H6	119.00
C6—C1—C21	120.67 (15)	C5—C6—H6	119.00
C1—C2—C3	122.37 (15)	N1—C7—H7	116.6 (10)
C2—C3—C4	119.94 (15)	C8—C7—H7	118.9 (10)
C3—C4—C5	118.58 (14)	C9—C10—H10	120.00
O1—C4—C3	124.00 (14)	C11—C10—H10	120.00
O1—C4—C5	117.41 (13)	C11—C12—H12	120.00
N1—C5—C4	116.40 (13)	C13—C12—H12	120.00
N1—C5—C6	123.29 (13)	C8—C13—H13	119.00
C4—C5—C6	120.31 (13)	C12—C13—H13	119.00
C1—C6—C5	121.40 (14)	O3—C14—H14A	110.00
N1—C7—C8	124.48 (15)	O3—C14—H14B	110.00
C9—C8—C13	118.89 (14)	C15—C14—H14A	110.00
C7—C8—C9	121.29 (14)	C15—C14—H14B	110.00
C7—C8—C13	119.80 (14)	H14A—C14—H14B	108.00
O2—C9—C8	120.49 (13)	C15—C16—H16	120.00

O2—C9—C10	121.57 (14)	C17—C16—H16	120.00
C8—C9—C10	117.93 (14)	C16—C17—H17	120.00
C9—C10—C11	120.54 (15)	C18—C17—H17	120.00
C10—C11—C12	121.43 (15)	C17—C18—H18	120.00
O3—C11—C12	114.26 (14)	C19—C18—H18	120.00
O3—C11—C10	124.31 (15)	C18—C19—H19	120.00
C11—C12—C13	119.45 (16)	C20—C19—H19	120.00
C8—C13—C12	121.72 (16)	C15—C20—H20	120.00
O3—C14—C15	110.09 (14)	C19—C20—H20	120.00
C14—C15—C16	119.02 (16)	C1—C21—H21A	109.00
C14—C15—C20	122.43 (16)	C1—C21—H21B	109.00
C16—C15—C20	118.55 (17)	C1—C21—H21C	109.00
C15—C16—C17	120.6 (2)	H21A—C21—H21B	109.00
C16—C17—C18	120.52 (19)	H21A—C21—H21C	109.00
C17—C18—C19	119.73 (19)	H21B—C21—H21C	109.00

C14—O3—C11—C10	−3.0 (2)	C7—C8—C9—C10	−176.46 (14)
C14—O3—C11—C12	177.39 (14)	C13—C8—C9—O2	−178.95 (14)
C11—O3—C14—C15	179.43 (14)	C13—C8—C9—C10	1.8 (2)
C7—N1—C5—C4	−171.50 (15)	C7—C8—C13—C12	177.89 (16)
C7—N1—C5—C6	8.9 (2)	C9—C8—C13—C12	−0.4 (2)
C5—N1—C7—C8	179.88 (14)	O2—C9—C10—C11	178.81 (15)
C6—C1—C2—C3	−0.4 (3)	C8—C9—C10—C11	−1.9 (2)
C21—C1—C2—C3	179.41 (16)	C9—C10—C11—O3	−178.96 (14)
C2—C1—C6—C5	0.0 (2)	C9—C10—C11—C12	0.7 (2)
C21—C1—C6—C5	−179.84 (15)	O3—C11—C12—C13	−179.54 (15)
C1—C2—C3—C4	0.3 (3)	C10—C11—C12—C13	0.8 (3)
C2—C3—C4—O1	179.74 (15)	C11—C12—C13—C8	−0.9 (3)
C2—C3—C4—C5	0.3 (2)	O3—C14—C15—C16	−163.21 (16)
O1—C4—C5—N1	0.2 (2)	O3—C14—C15—C20	17.1 (2)
O1—C4—C5—C6	179.81 (14)	C14—C15—C16—C17	−178.97 (18)
C3—C4—C5—N1	179.66 (14)	C20—C15—C16—C17	0.7 (3)
C3—C4—C5—C6	−0.7 (2)	C14—C15—C20—C19	179.30 (19)
N1—C5—C6—C1	−179.83 (14)	C16—C15—C20—C19	−0.4 (3)
C4—C5—C6—C1	0.6 (2)	C15—C16—C17—C18	−0.9 (3)
N1—C7—C8—C9	−0.4 (2)	C16—C17—C18—C19	0.7 (4)
N1—C7—C8—C13	−178.58 (15)	C17—C18—C19—C20	−0.3 (4)
C7—C8—C9—O2	2.8 (2)	C18—C19—C20—C15	0.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*n*···O2	0.94 (2)	1.83 (2)	2.609 (2)	138.7 (16)
O1—H1*o*···O2^{i}	0.96 (2)	1.63 (2)	2.590 (2)	176.1 (17)

Symmetry code: (i) −*x*, *y*−1/2, −*z*+1/2.