organic compounds

2-(4H-1,3-Benzoxazin-2-yl)phenol

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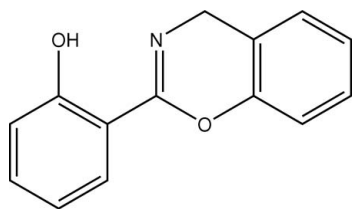
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The title compound, $C_{14}H_{11}NO_2$, features an essentially planar molecule, the r.m.s. deviation for the 17 non-H atoms being 0.035 Å. This conformation is stabilized by an intramolecular O—H···N hydrogen bond that results in the formation of an $S(6)$ ring. In the crystal structure, methylene–hydroxy C—H···O contacts result in a supramolecular chain aligned along the b axis.

Related literature

For general background to the synthesis, see: Hunter & Sims (1972a,b); Corey, & Kühnle (1997); Larter et al. (1998); Chou et al. (2004); Fernandes et al. (2007). For the reactions of 2-hydroxybenzaldehyde derivatives, see; Kitan et al. (1990); Kanakarajan et al. (1975); Meier et al. (1979); Beer et al. (1948).

Experimental

Crystal data

$C_{14}H_{11}NO_2$	a = 14.1148 (8) Å
M_r = 225.24	b = 5.1725 (2) Å
Monoclinic, $P2/n$	c = 15.8813 (8) Å
β = 115.032 (2)°	μ = 0.10 mm^{-1}
V = 1050.57 (9) Å^3	T = 120 K
Z = 4	0.55 × 0.08 × 0.08 mm
Mo $K\alpha$ radiation	

Data collection

Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer	10487 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1841 independent reflections
T_{min} = 0.949, T_{max} = 0.992	1479 reflections with $I > 2\sigma(I)$
	R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048	1 restraint
$wR(F^2)$ = 0.122	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
1841 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}
158 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N1	0.84	1.78	2.5586 (16)	154
C14—H14A···O1^i	0.99	2.45	3.3551 (19)	151

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

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: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2009).

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supporting information

2-(4*H*-1,3-Benzoxazin-2-yl)phenol

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S1. Comment

Reactions of various arene-aldehydes, ArCHO, *e.g.* Ar = Ph, thien-2-yl and pyridin2-yl, with ammonia, under basic conditions, have provided rac-2,4,5-Ar$_3$-4,5-dihydro-1*H*-imidazoles, **1** (Hunter & Sims, 1972*a*, b; Corey, & Kühnle, 1997; Larter *et al.*, 1998; Chou *et al.*, 2004), see Fig. 3, either as the kinetic product, the *cis*-isomer, or the thermodynamic product, the *trans*-isomer. We reported similar products from these aldehydes using the mixture of NH$_4$Cl and NEt$_3$ as the ammonia source in MeOH (Fernandes *et al.*, 2007). In contrast, we have found that 2-hydroxy-benzaldehyde, under these conditions produced (**2**: *R* = H).

The reaction of 2-hydroxybenzaldehyde with ammonia had previously been studied as a function of solvent (Kitan *et al.*, 1990). Thus in C$_6$H$_6$, hexane or Et$_2$O, 2-HOC$_6$H$_4$CHNH was formed. In H$_2$O, dioxan, MeOH or EtOH solution 2-HOC$_6$H$_4$CH(NCHC$_6$H$_4$OH-2)$_2$ (**3**), was the product, while in MeOH with NH$_4$OAc and NH$_4$HCO$_3$, both **3** and **4** were formed. Earlier, it had been reported that 2-hydroxybenzaldehyde, NH$_4$OAc and HOAc in refluxing C$_6$H$_6$ produced **4** (Kanakarajan *et al.*, 1975). Interestingly, (**2**: *R* = H) has been shown to arise from the acid-catalysed decomposition of **4**, alternatively obtained as the *cyclo*-condensation product of 2-hydroxybenzaldehyde with HONH$_2$ (Meier *et al.*, 1979).

While the NMR spectra, in particular the two hydrogen singlet in the ^{1}H NMR spectrum, suggested the compound (**2**: *R* = H) confirmation from the X-ray structure determination was considered to be of value, particularly since treatment of 6-nitro-2-hydroxybenzaldehyde with NH$_4$OAc in acetic acid had been reported to give **5** (Beer *et al.*, 1948). However, no spectral details had been provided for **5**. In the light of our findings, the structure of **5** could be modified to (**2**: *R* = NO$_2$). The change from **5** to (**2**: *R* = NO$_2$) merely involves a prototropic rearrangement. Herein, the crystal and molecular structure of (I) [= **2**: *R* = H in Fig. 1] is described.

The molecular structure of (I), Fig. 2, is essentially planar with the RMS for the 17 non-hydrogen atoms being 0.035 Å. The maximum deviation is 0.049 (1) Å for the N1 atom. This conformation is stabilized by an intramolecular O–H···N hydrogen bond that completes an S(6) ring synthon. The most prominent interactions in the crystal structure are of the type C–H···O, Table 1, which lead to supramolecular chains along the *b* direction, Fig. 3.

S2. Experimental

A solution of 2-hydroxybenzaldehyde (3.7 g, 0.03 mol), ammonium chloride (3 g, 0.06 mol) and triethylamine (8.1 ml, 0.06 mol) in MeOH (30 ml) was refluxed for 8 h. The solvent was removed *in vacuo*, the residue was extracted into CHCl$_3$, washed with water (2 *x* 1 5 ml), dried over magnesium chloride, and rotary evaporated. The pale coloured residue was recrystallized from EtOH to give colourless crystals. Anal. Calc. for C$_{14}$H$_{11}$NO$_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.32; H, 4.80; N, 6.01%. ^{1}H NMR (Me$_2$CO-d6, 400 MHz): δ 13.02 (*s*, 1H), 7.96 (*dd*, J = 1.6, 8.0 Hz, 1H), 7.41–7.37 (*dt*, J = 1.7, 8.0 Hz, 1H), 7.33–7.28 (*m*, 1H), 7.20–7.14 (*m*, 3H), 6.91 (*m*, 2H), 4.82 (*s*, 2H) p.p.m. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 134.1, 129.4, 128.1, 127.3, 126.3, 119.1, 118.0, 116.6, 44.1 p.p.m.; quaternary-C not detected.

S3. Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxyl-H was located from a difference map and refined with O–H = 0.840±0.001 Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

1

2

4

5
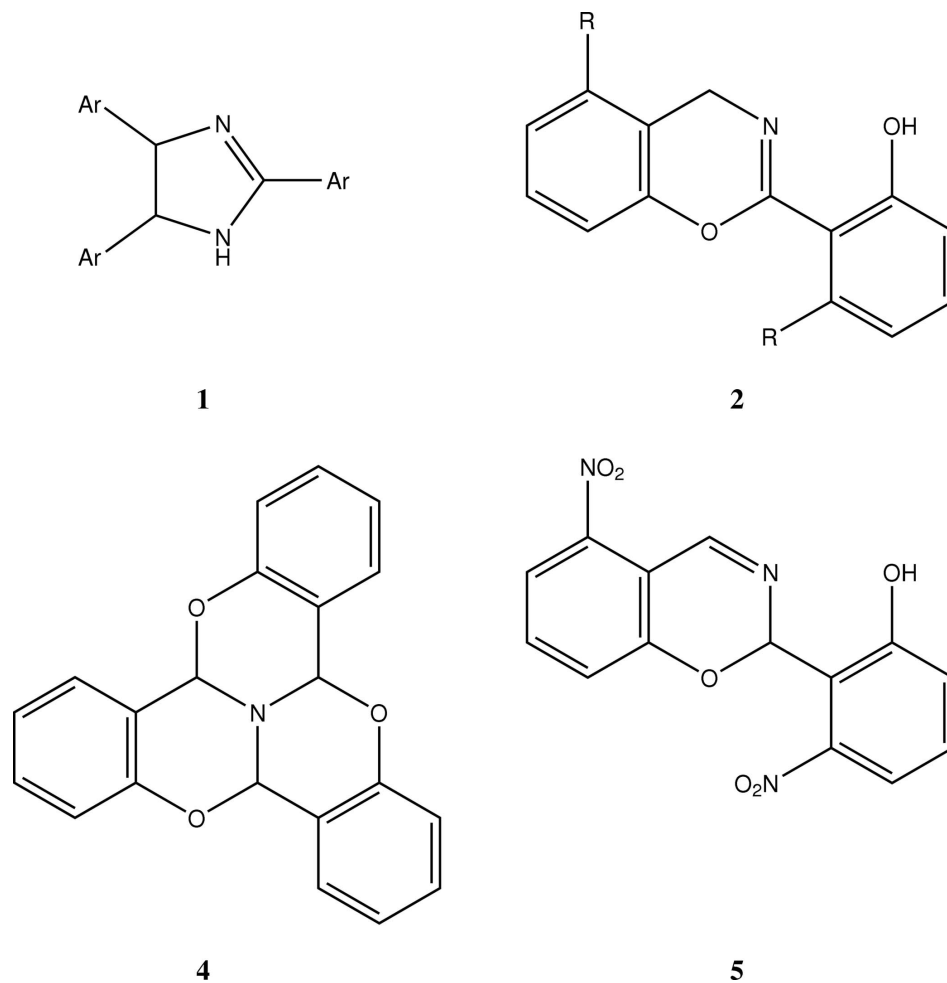
Figure 1

Reaction products.
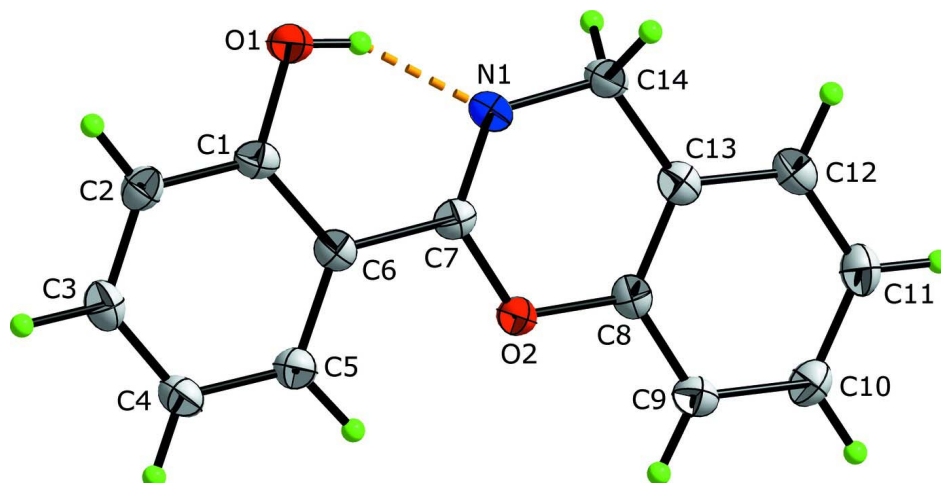
Figure 2

Molecular structure of (I) showing the intramolecular O–H···N hydrogen bonding (orange dashed lines), the atom-labelling scheme, and displacement ellipsoids at the 50% probability level.
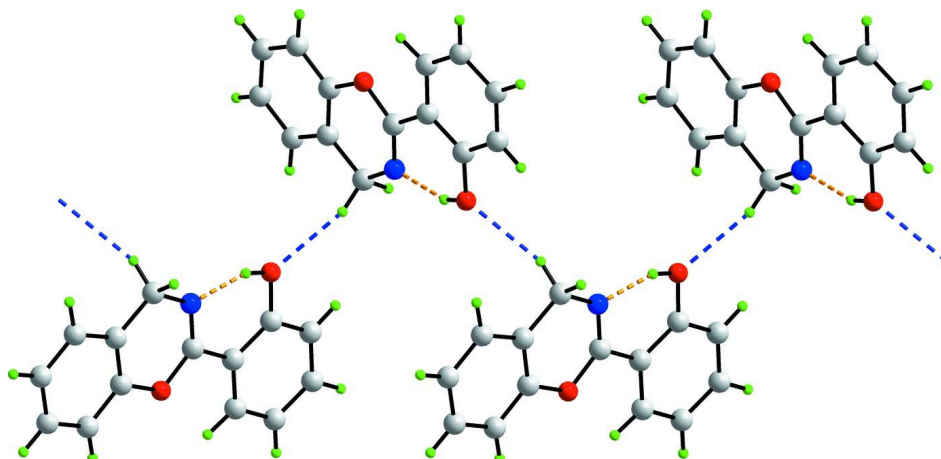
Figure 3

Supramolecular chain formation along the *b* axis mediated by C–H···O contacts (bue dashed lines) in the structure of (I).

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Crystal data

$C_{14}H_{11}NO_2$	$F(000) = 472$
$M_r = 225.24$	$D_x = 1.424$ Mg m^{-3}
Monoclinic, $P2/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yac	Cell parameters from 10058 reflections
$a = 14.1148$ (8) Å	$\theta = 2.9$–$27.5°$
$b = 5.1725$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 15.8813$ (8) Å	$T = 120$ K
$\beta = 115.032$ (2)°	Needle, orange
$V = 1050.57$ (9) Å^3	$0.55 \times 0.08 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker–Nonius 95mm CCD camera on κ-goniostat diffractometer	$T_{min} = 0.949$, $T_{max} = 0.992$
	10487 measured reflections
	1841 independent reflections
Radiation source: Bruker-Nonius FR591 rotating anode	1479 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.066$
10 cm confocal mirrors monochromator	$\theta_{max} = 25.0°$, $\theta_{min} = 3.2°$
Detector resolution: 9.091 pixels mm^{-1}	$h = -16\rightarrow16$
φ and ω scans	$k = -6\rightarrow6$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$l = -18\rightarrow18$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.1735P]$
$wR(F^2) = 0.122$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1841 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
158 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
1 restraint	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.031 (5)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.87956 (9)	−0.1882 (2)	0.76593 (8)	0.0294 (3)
H1O	0.8351	−0.0735	0.7382	0.044*
O2	0.84545 (9)	0.3337 (2)	0.55121 (7)	0.0251 (3)
N1	0.78226 (10)	0.1846 (2)	0.65809 (9)	0.0225 (3)
C1	0.94605 (12)	−0.1824 (3)	0.72470 (10)	0.0224 (4)
C2	1.02672 (13)	−0.3622 (3)	0.75286 (11)	0.0255 (4)
H2	1.0334	−0.4852	0.7995	0.031*
C3	1.09719 (13)	−0.3631 (3)	0.71350 (11)	0.0280 (4)
H3	1.1518	−0.4875	0.7329	0.034*
C4	1.08874 (13)	−0.1831 (3)	0.64558 (11)	0.0285 (4)
H4	1.1375	−0.1839	0.6188	0.034*
C5	1.00909 (12)	−0.0038 (3)	0.61741 (11)	0.0255 (4)
H5	1.0039	0.1199	0.5714	0.031*

C6	0.93574 (12)	−0.0004 (3)	0.65525 (10)	0.0210 (4)
C7	0.84764 (12)	0.1812 (3)	0.62239 (10)	0.0214 (4)
C8	0.76543 (12)	0.5157 (3)	0.51535 (10)	0.0218 (4)
C9	0.76759 (13)	0.6767 (3)	0.44659 (11)	0.0253 (4)
H9	0.8216	0.6614	0.4262	0.030*
C10	0.68991 (13)	0.8601 (3)	0.40814 (11)	0.0271 (4)
H10	0.6900	0.9711	0.3605	0.033*
C11	0.61167 (13)	0.8827 (3)	0.43898 (11)	0.0277 (4)
H11	0.5585	1.0094	0.4127	0.033*
C12	0.61155 (12)	0.7197 (3)	0.50813 (11)	0.0257 (4)
H12	0.5580	0.7361	0.5291	0.031*
C13	0.68845 (12)	0.5327 (3)	0.54724 (10)	0.0222 (4)
C14	0.69092 (13)	0.3531 (3)	0.62239 (11)	0.0252 (4)
H14A	0.6898	0.4570	0.6743	0.030*
H14B	0.6271	0.2450	0.5977	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0263 (7)	0.0350 (7)	0.0318 (7)	0.0037 (5)	0.0169 (6)	0.0083 (5)
O2	0.0243 (7)	0.0280 (6)	0.0264 (6)	0.0058 (5)	0.0141 (5)	0.0068 (4)
N1	0.0196 (7)	0.0265 (8)	0.0224 (7)	0.0004 (5)	0.0097 (6)	−0.0018 (5)
C1	0.0207 (9)	0.0248 (8)	0.0220 (8)	−0.0044 (6)	0.0093 (7)	−0.0042 (6)
C2	0.0253 (9)	0.0244 (8)	0.0241 (8)	−0.0006 (7)	0.0077 (7)	0.0015 (6)
C3	0.0234 (9)	0.0277 (9)	0.0305 (9)	0.0036 (7)	0.0090 (8)	−0.0017 (7)
C4	0.0244 (9)	0.0330 (10)	0.0318 (9)	0.0031 (7)	0.0157 (8)	−0.0004 (7)
C5	0.0252 (9)	0.0273 (9)	0.0260 (8)	−0.0004 (7)	0.0128 (7)	0.0008 (6)
C6	0.0182 (8)	0.0228 (8)	0.0200 (8)	−0.0023 (6)	0.0063 (7)	−0.0034 (6)
C7	0.0220 (9)	0.0216 (8)	0.0197 (8)	−0.0037 (6)	0.0079 (7)	−0.0024 (6)
C8	0.0191 (8)	0.0217 (8)	0.0219 (8)	−0.0001 (6)	0.0062 (7)	−0.0029 (6)
C9	0.0240 (9)	0.0277 (9)	0.0257 (8)	−0.0027 (7)	0.0120 (7)	−0.0016 (6)
C10	0.0298 (10)	0.0250 (9)	0.0239 (8)	−0.0014 (7)	0.0088 (7)	0.0016 (6)
C11	0.0265 (9)	0.0258 (9)	0.0265 (9)	0.0034 (7)	0.0070 (7)	−0.0011 (6)
C12	0.0222 (9)	0.0285 (9)	0.0256 (9)	0.0011 (7)	0.0094 (7)	−0.0042 (6)
C13	0.0217 (9)	0.0242 (8)	0.0190 (8)	−0.0022 (6)	0.0069 (7)	−0.0050 (6)
C14	0.0233 (9)	0.0297 (9)	0.0257 (8)	0.0018 (7)	0.0133 (7)	0.0000 (6)

Geometric parameters (Å, º)

O1—C1	1.3530 (19)	C5—H5	0.9500
O1—H1O	0.8403	C6—C7	1.467 (2)
O2—C7	1.3680 (18)	C8—C13	1.382 (2)
O2—C8	1.3937 (19)	C8—C9	1.384 (2)
N1—C7	1.271 (2)	C9—C10	1.381 (2)
N1—C14	1.458 (2)	C9—H9	0.9500
C1—C2	1.389 (2)	C10—C11	1.390 (2)
C1—C6	1.410 (2)	C10—H10	0.9500
C2—C3	1.381 (2)	C11—C12	1.385 (2)

C2—H2	0.9500	C11—H11	0.9500
C3—C4	1.391 (2)	C12—C13	1.389 (2)
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.378 (2)	C13—C14	1.501 (2)
C4—H4	0.9500	C14—H14A	0.9900
C5—C6	1.400 (2)	C14—H14B	0.9900
C1—O1—H1O	104.4	C13—C8—C9	122.28 (15)
C7—O2—C8	117.29 (12)	C13—C8—O2	121.33 (13)
C7—N1—C14	121.61 (13)	C9—C8—O2	116.39 (13)
O1—C1—C2	118.12 (14)	C10—C9—C8	118.93 (15)
O1—C1—C6	122.02 (14)	C10—C9—H9	120.5
C2—C1—C6	119.86 (14)	C8—C9—H9	120.5
C3—C2—C1	120.39 (15)	C9—C10—C11	120.16 (14)
C3—C2—H2	119.8	C9—C10—H10	119.9
C1—C2—H2	119.8	C11—C10—H10	119.9
C2—C3—C4	120.46 (15)	C12—C11—C10	119.75 (15)
C2—C3—H3	119.8	C12—C11—H11	120.1
C4—C3—H3	119.8	C10—C11—H11	120.1
C5—C4—C3	119.52 (15)	C11—C12—C13	121.03 (15)
C5—C4—H4	120.2	C11—C12—H12	119.5
C3—C4—H4	120.2	C13—C12—H12	119.5
C4—C5—C6	121.26 (14)	C8—C13—C12	117.85 (14)
C4—C5—H5	119.4	C8—C13—C14	119.64 (14)
C6—C5—H5	119.4	C12—C13—C14	122.51 (14)
C5—C6—C1	118.50 (14)	N1—C14—C13	113.49 (13)
C5—C6—C7	121.67 (13)	N1—C14—H14A	108.9
C1—C6—C7	119.81 (14)	C13—C14—H14A	108.9
N1—C7—O2	126.42 (14)	N1—C14—H14B	108.9
N1—C7—C6	121.08 (13)	C13—C14—H14B	108.9
O2—C7—C6	112.49 (13)	H14A—C14—H14B	107.7
O1—C1—C2—C3	−179.47 (14)	C1—C6—C7—O2	−176.25 (13)
C6—C1—C2—C3	0.3 (2)	C7—O2—C8—C13	−3.2 (2)
C1—C2—C3—C4	0.4 (2)	C7—O2—C8—C9	176.88 (13)
C2—C3—C4—C5	−0.2 (3)	C13—C8—C9—C10	−0.3 (2)
C3—C4—C5—C6	−0.6 (2)	O2—C8—C9—C10	179.67 (13)
C4—C5—C6—C1	1.2 (2)	C8—C9—C10—C11	0.5 (2)
C4—C5—C6—C7	−176.86 (14)	C9—C10—C11—C12	−0.3 (2)
O1—C1—C6—C5	178.68 (13)	C10—C11—C12—C13	−0.2 (2)
C2—C1—C6—C5	−1.0 (2)	C9—C8—C13—C12	−0.2 (2)
O1—C1—C6—C7	−3.2 (2)	O2—C8—C13—C12	179.85 (13)
C2—C1—C6—C7	177.07 (13)	C9—C8—C13—C14	−179.68 (14)
C14—N1—C7—O2	2.7 (2)	O2—C8—C13—C14	0.4 (2)
C14—N1—C7—C6	−176.26 (13)	C11—C12—C13—C8	0.4 (2)
C8—O2—C7—N1	1.7 (2)	C11—C12—C13—C14	179.89 (15)
C8—O2—C7—C6	−179.26 (11)	C7—N1—C14—C13	−5.1 (2)
C5—C6—C7—N1	−179.12 (14)	C8—C13—C14—N1	3.6 (2)

| C1—C6—C7—N1 | 2.8 (2) | C12—C13—C14—N1 | −175.88 (13) |
| C5—C6—C7—O2 | 1.8 (2) | | |

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N1	0.84	1.78	2.5586 (16)	154
C14—H14*A*···O1[i]	0.99	2.45	3.3551 (19)	151

Symmetry code: (i) −*x*+3/2, *y*+1, −*z*+3/2.