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Crystal structures of 3,5-bis[(*E*)-3-hydroxybenzylidene]-1-methylpiperidin-4-one and 3,5-bis[(*E*)-2-chlorobenzylidene]-1-methylpiperidin-4-one

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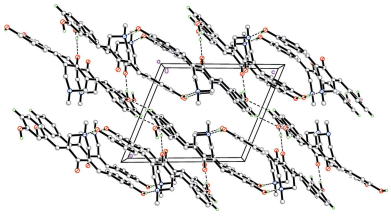
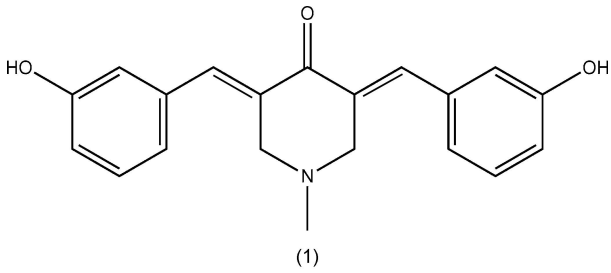
The title compounds, $C_{20}H_{19}NO_3$, (1), and $C_{20}H_{17}Cl_2NO$, (2), are the 3-hydroxybenzylidene and 2-chlorobenzylidene derivatives, respectively, of curcumin [systematic name: (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione]. The dihedral angles between the benzene rings in each compound are 21.07 (6)° for (1) and 13.4 (3)° for (2). In both compounds, the piperidinone rings adopt a sofa confirmation and the methyl group attached to the N atom is in an equatorial position. In the crystal of (1), two pairs of O—H···N and O—H···O hydrogen bonds link the molecules, forming chains along [10$\bar{1}$]. The chains are linked *via* C—H···O hydrogen bonds, forming undulating sheets parallel to the *ac* plane. In the crystal of (2), molecules are linked by weak C—H···Cl hydrogen bonds, forming chains along the [204] direction. The chains are linked along the *a*-axis direction by π–π interactions [inter-centroid distance = 3.779 (4) Å]. For compound (2), the crystal studied was a non-merohedral twin with the refined ratio of the twin components being 0.116 (6):0.886 (6).

1. Chemical context

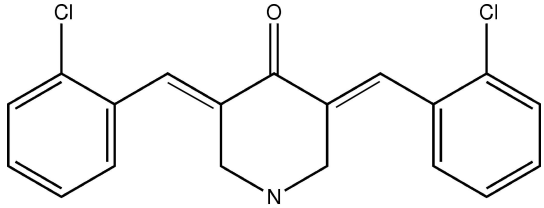
Curcumin (diferuloylmethane) is a naturally occurring biologically active compound, isolated from the root of the tumeric plant (*Curcuma longa*) (Dandia *et al.*, 2012). It has been shown to exhibit anti-oxidant (Rostom *et al.*, 2009), anti-inflammatory (Suzuki *et al.*, 2005), antiviral (Kumar *et al.*, 2007) and antibacterial (Bandgar *et al.*, 2012) activities, and thus has potential against various malignant cancers, diabetes, allergies, arthritis and other chronic illnesses (Yadav *et al.*, 2010; Reddy *et al.*, 2009; Aggarwal *et al.*, 2003; Insuasty *et al.*, 2013; Wu *et al.*, 2013). For the purpose of finding new derivatives with increased systemic bioavailability and enhanced pharmacological activity (Zhao *et al.*, 2010), chemical modifications as well as the synthesis of curcumin analogues have been attempted by many research groups in order to find a better treatment for various diseases (Siddiqui *et al.*, 2006; Gregory *et al.*, 2013). Analogous compounds to (*E*)-3,5-bis(benzylidene)-4-piperidones present noteworthy cytotoxic activity against leukemia cell lines and colon cancer, among others (Gregory *et al.*, 2013). Different substituents were designed to investigate and discuss the structure–activity relationship (Insuasty *et al.*, 2013). Herein, we report on the synthesis, characterization and crystal structures of two mono-carbonyl analogues of curcumin, namely *N*-methyl-(3*E*,5*E*)-3,5-bis(3-hydroxy-



benzylidene)-4-piperidone (1) and *N*-methyl-(3*E*,5*E*)-3,5-bis(2-chlorobenzylidene)-4-piperidone (2).



(1)



(2)

2. Structural commentary

The molecular structures of compounds (1) and (2) are shown in Figs. 1 and 2, respectively. Compound (1) crystallized in the triclinic space group $P\overline{1}$ (Z = 2), while compound (2) crystallized in the monoclinic space group $P2_1/n$ (Z = 4).

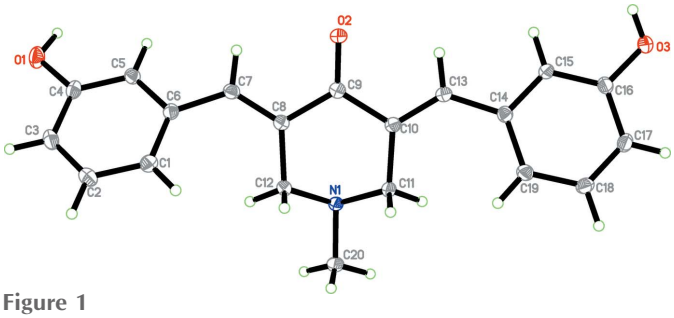


Figure 1
The molecular structure of compound (1), showing 50% probability displacement ellipsoids and the atom labelling.

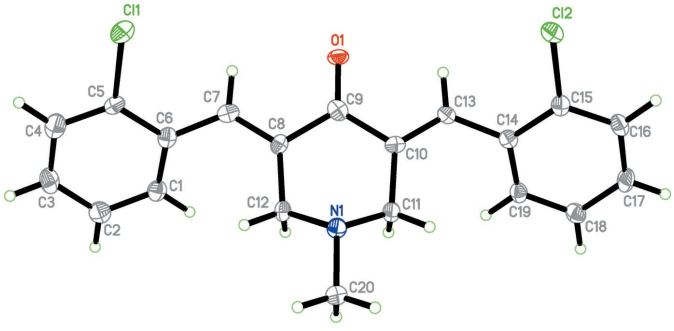


Figure 2
The molecular structure of compound (2), showing 50% probability displacement ellipsoids and the atom labelling.

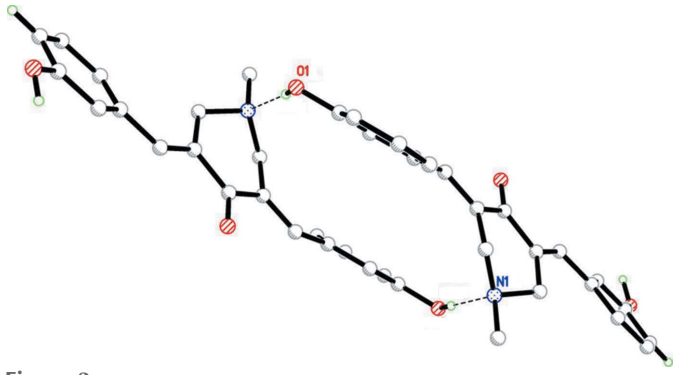


Figure 3
An inversion dimer found in compound (1), formed by O—H···N hydrogen bonds (dashed lines; see Table 1).

The benzene rings (C1–C6 and C14–C19) are inclined to one another by 21.07 (6)° in (1) and by 13.4 (3)° in (2). Both compounds exhibit *E* conformations about the C7═C8 and C13═C10 bonds. In both compounds, the piperidinone ring (N1/C8–C12) adopts a sofa conformation with atom N1 displaced from the mean plane through the five C atoms (C8–C12) by 0.7052 (10) Å in (1) and 0.705 (5) Å in (2). The puckering parameters for the piperidinone ring conformation in (1) are Q = 0.5280 (12) Å, θ = 55.17 (14)° and φ = 353.08 (17)°, while for (2) they are Q = 0.526 (6) Å, θ = 126.1 (7)° and φ = 182.8 (8)°. In both compounds the methyl group attached to atom N1 is in an equatorial position on the piperidinone ring.

3. Supramolecular features

In the crystal of compound (1), molecules are linked *via* pairs of O—H···N hydrogen bonds, forming inversion dimers enclosing an $R_2^2(18)$ ring motif (Table 1 and Fig. 3). These dimers are linked by pairs of O—H···O hydrogen bonds, enclosing an $R_2^2(18)$ ring motif, forming chains along [10$\overline{1}$]

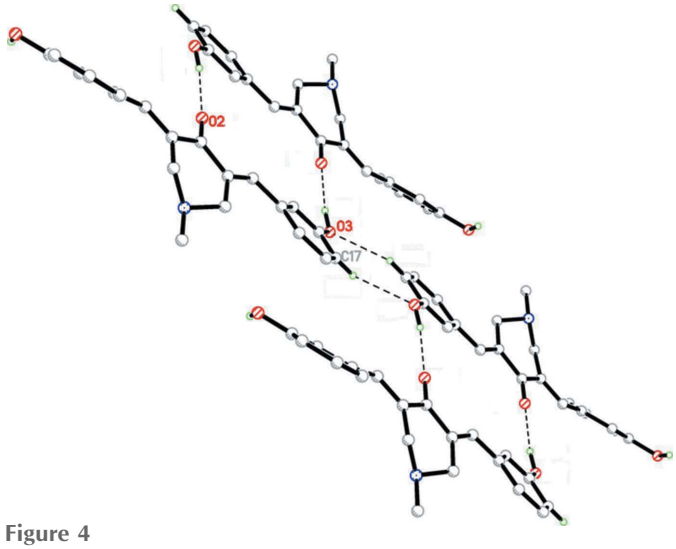


Figure 4
Inversion dimers found in compound (1), formed by O—H···O and C—H···N hydrogen bonds (dashed lines; see Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O1*···N1^{i}	0.96 (2)	1.81 (2)	2.7278 (14)	160 (2)
O3—H1*O3*···O2^{ii}	0.88 (2)	1.87 (2)	2.7359 (15)	171 (2)
C17—H17*A*···O3^{iii}	0.95	2.51	3.4032 (16)	157

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

(Table 1 and Fig. 4). The chains are linked *via* pairs of C—H···O hydrogen bonds (Table 1 and Fig. 4), forming undulating sheets lying parallel to the *ac* plane (Fig. 5).

In the crystal of compound (2), molecules are linked by a weak C4—H4*A*···Cl2^{i} hydrogen bond, forming zigzag chains along [204] (Table 2 and Fig. 6). The chains are linked along the *a*-axis direction by π–π interactions [$Cg2\cdots Cg3^{i}$ = 3.779 (4) Å, where *Cg*2 and *Cg*3 are the centroids of rings C1–C6 and C14–C19, respectively; symmetry code: (i) $-x+1, -y, -z$].

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.36, last update February 2015; Groom & Allen, 2014) of substructure (3*E*,5*E*)-3,5-dibenzylidene-1-methylpiperidin-4-one gave 49 hits. One compound, 3,5-bis(4-chlorobenzylidene)-1-methylpiperidin-4-one, is the 4-chlorobenzylidene isomer of compound (2) (UNOXOL; Nesterov *et al.*, 2011). Here, the benzene rings are inclined to one another by 7.58 (8)°, compared to 21.07 (6)° in (1) and 13.4 (3)° in (2). The piperidinone ring also adopts a sofa conformation with the N atom displaced from the mean plane of the five C atoms by 0.7714 (15) Å, compared to 0.7052 (10) Å in (1) and 0.705 (5) Å in (2).

5. Synthesis and crystallization

Both compounds were synthesized according to a partially modified procedure of a previous report (Gregory *et al.*, 2013).

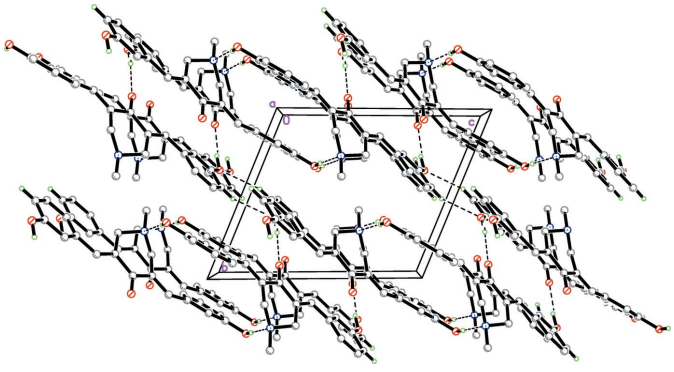


Figure 5
The crystal packing of compound (1), viewed along the *a* axis. Dashed lines indicate hydrogen bonds (see Table 1). H atoms not involved in the hydrogen bonding have been omitted for clarity.

Table 2
Hydrogen-bond geometry (Å, °) for (2).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4*A*···Cl2^{i}	0.95	2.85	3.587 (7)	135

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

Compound (1): The corresponding *N*-methyl-4-piperidone (0.99 g, 0.01 mol), 3-hydroxybenzaldehyde (2.23 g, 0.02 mol), 40% aq. NaOH (0.7 ml) and 95% EtOH (5 ml) were mixed with stirring at room temperature for 30 min. The reaction mixture was subjected to microwave irradiation for 3 min at a power of 180 W and temperature of 333 K. The reaction product was cooled and cold water was added. The precipitate formed was filtered and recrystallized from a mixture of *n*-hexane–ethyl acetate to afford dark yellowish crystals of compound (1) (yield: 3.4 g, 34.5%; m.p. 409–410 K). R_f = 0.43 (*n*-hexane:EtOAc = 1:1). UV (MeOH) λ_{max}: 364 nm (ε 4,600). IR (KBr) ν_{max} cm^{-1}: 3400, 1658, 1600 and 1504 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3): δ (p.p.m.) 8.04 (2H, *s*), 7.31 (2H, *d*, *J* = 7.5 Hz), 7.26 (2H, *t*, *J* = 7.5 Hz), 6.99 (2H, *d*, *J* = 8.0 Hz), 6.93 (2H, *t*, *J* = 7.5 Hz), 3.72 (4H, *s*) and 2.41 (3H, *s*). ^{13}C NMR (125 MHz, CDCl3): δ (p.p.m.) 185.9, 156.6, 133.2, 130.7, 130.5, 130.3, 122.6, 119.4, 115.7, 57.2, 45.2. HR–ESI–TOFMS: calculated for $C_{20}H_{19}NO_3$ [*M* + H]$^{+}$, *m*/*z* 321.1365, found *m*/*z* 322.1434.

Compound (2): The corresponding *N*-methyl-4-piperidone (0.98 g, 0.01 mol), 2-chlorobenzaldehyde (2.20 g, 0.02 mol), 40% aq. NaOH (0.7 ml) and 95% EtOH (5 ml) was stirred at room temperature for 30 min. The reaction mixture was subjected to microwave irradiation for 3 min at a power of 180 W and temperature of 333 K. The reaction product was cooled and cold water was added. The precipitate formed was filtered and recrystallized from a mixture of *n*-hexane–ethyl acetate to afford yellowish crystals of compound (2) (yield: 3.8 g, 38.4%; m.p. 408–410 K). R_f = 0.60 (CH_2Cl_2:MeOH = 9.5:0.5). UV (MeOH) λ_{max}: 309 nm (ε 4,400). IR (KBr) ν_{max} cm^{-1}: 3328, 1640 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3): δ (p.p.m.) 8.00 (2H, *s*), 7.46 (2H, *dd*, *J* = 8.0, 1.5 Hz), 7.31 (2H,

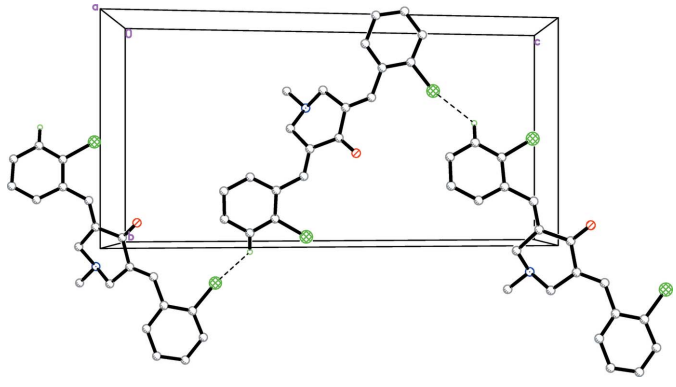


Figure 6
A view along the *a* axis of the crystal packing of compound (2), showing a zigzag chain formed by weak C—H···Cl hydrogen bonds (dashed lines; see Table 2). H atoms not involved in the hydrogen bonding have been omitted for clarity.

Table 3
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_{20}H_{19}NO_3$	$C_{20}H_{17}Cl_2NO$
M_r	321.36	358.24
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$
Temperature (K)	100	100
a, b, c (Å)	7.4852 (6), 9.8588 (9), 11.6115 (10)	7.540 (3), 10.623 (4), 21.119 (7)
α, β, γ (°)	111.7924 (17), 96.7983 (18), 92.8848 (17)	90, 98.671 (5), 90
V (Å^3)	785.90 (12)	1672.2 (10)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.39
Crystal size (mm)	0.29 × 0.24 × 0.11	0.32 × 0.08 × 0.08
Data collection		
Diffractometer	Bruker APEX DUO CCD area detector	Bruker APEX DUO CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)	Multi-scan (*SADABS*; Bruker, 2009)
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	10462, 3562, 3133	3105, 3105, 2591
R_{int}	0.021	0.084
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.606
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.117, 1.04	0.077, 0.192, 1.18
No. of reflections	3562	3105
No. of parameters	226	218
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.21	0.45, −0.43

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

dd, J = 8.0, 1.5 Hz), 7.30 (2H, *d*, J = 7.5 Hz), 7.24 (2H, *dd*, J = 7.5, 1.5 Hz), 3.61 (4H, *s*), 2.37 (3H, *s*). ^{13}C NMR (125 MHz, CDCl3): δ (p.p.m.) 186.1, 135.2, 134.3, 134.0, 133.6, 130.3, 130.0, 129.9, 126.4, 56.7, 45.5. HR–ESI–TOFMS: calculated for $C_{20}H_{17}Cl_2NO$ $[M + H]^+$, m/z 357.0687, found m/z 358.0776.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The O-bound H atoms were located in difference Fourier maps and freely refined. The remaining H atoms were positioned geometrically and refined using a riding model: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(C-methyl) and 1.2U_{eq}(C) for other H atoms. A rotating group model was applied to the methyl groups. For compound (2) the crystal studied was a non-merohedral twin with a ratio of the twin components of 0.116 (6):0.886 (6).

Acknowledgements

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supporting information

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Crystal structures of 3,5-bis[(*E*)-3-hydroxybenzylidene]-1-methylpiperidin-4-one and 3,5-bis[(*E*)-2-chlorobenzylidene]-1-methylpiperidin-4-one

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

(1) 3,5-Bis[(*E*)-3-hydroxybenzylidene]-1-methylpiperidin-4-one

Crystal data

$C_{20}H_{19}NO_3$
$M_r = 321.36$
Triclinic, $P\overline{1}$
$a = 7.4852$ (6) Å
$b = 9.8588$ (9) Å
$c = 11.6115$ (10) Å
$\alpha = 111.7924$ (17)°
$\beta = 96.7983$ (18)°
$\gamma = 92.8848$ (17)°
$V = 785.90$ (12) Å^3
$Z = 2$
$F(000) = 340$
$D_x = 1.358$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3138 reflections
$\theta = 2.8$–$32.1°$
$\mu = 0.09$ mm^{-1}
$T = 100$ K
Block, orange
0.29 × 0.24 × 0.11 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
10462 measured reflections
3562 independent reflections
3133 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.117$
$S = 1.04$
3562 reflections
226 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.2741P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.16705 (13)	−0.33469 (10)	−0.27862 (8)	0.0217 (2)
O2	0.78550 (12)	−0.06971 (10)	0.30379 (9)	0.0219 (2)
O3	0.36575 (12)	0.35383 (10)	0.81746 (9)	0.0197 (2)
N1	1.15110 (13)	0.28041 (10)	0.38630 (9)	0.0139 (2)
C1	1.36371 (16)	−0.10777 (13)	0.09923 (11)	0.0159 (2)
H1A	1.4117	−0.0550	0.1849	0.019*
C2	1.47889 (17)	−0.16263 (13)	0.01131 (12)	0.0182 (3)
H2A	1.6059	−0.1478	0.0376	0.022*
C3	1.41151 (17)	−0.23866 (13)	−0.11397 (12)	0.0184 (3)
H3A	1.4922	−0.2770	−0.1728	0.022*
C4	1.22557 (17)	−0.25933 (13)	−0.15432 (11)	0.0159 (3)
C5	1.10880 (16)	−0.20577 (12)	−0.06675 (11)	0.0145 (2)
H5A	0.9819	−0.2202	−0.0936	0.017*
C6	1.17643 (16)	−0.13047 (12)	0.06113 (11)	0.0137 (2)
C7	1.04624 (16)	−0.09053 (12)	0.14976 (11)	0.0141 (2)
H7A	0.9348	−0.1514	0.1238	0.017*
C8	1.06141 (16)	0.02010 (12)	0.26281 (11)	0.0136 (2)
C9	0.91333 (16)	0.02744 (13)	0.33844 (11)	0.0152 (2)
C10	0.92406 (16)	0.15518 (12)	0.45975 (11)	0.0139 (2)
C11	1.08023 (16)	0.27250 (12)	0.49664 (11)	0.0144 (2)
H11A	1.0401	0.3687	0.5454	0.017*
H11B	1.1779	0.2515	0.5511	0.017*
C12	1.21650 (16)	0.13979 (12)	0.31593 (11)	0.0148 (2)
H12A	1.3070	0.1144	0.3721	0.018*
H12B	1.2760	0.1484	0.2468	0.018*
C13	0.78975 (16)	0.15721 (12)	0.52792 (11)	0.0145 (2)
H13A	0.7002	0.0755	0.4914	0.017*
C14	0.75909 (16)	0.26419 (12)	0.64853 (11)	0.0136 (2)
C15	0.58209 (16)	0.25978 (12)	0.67642 (11)	0.0143 (2)
H15A	0.4913	0.1888	0.6179	0.017*
C16	0.53717 (16)	0.35752 (12)	0.78829 (11)	0.0150 (2)
C17	0.66948 (17)	0.46108 (13)	0.87504 (11)	0.0173 (3)
H17A	0.6396	0.5296	0.9509	0.021*
C18	0.84563 (17)	0.46288 (13)	0.84920 (11)	0.0165 (3)
H18A	0.9366	0.5320	0.9093	0.020*
C19	0.89262 (16)	0.36657 (13)	0.73795 (11)	0.0154 (2)
H19A	1.0142	0.3699	0.7224	0.018*

C20	1.29894 (17)	0.39929 (13)	0.42690 (12)	0.0183 (3)
H20A	1.2574	0.4907	0.4814	0.027*
H20B	1.3364	0.4123	0.3533	0.027*
H20C	1.4017	0.3742	0.4731	0.027*
H1O1	1.044 (3)	−0.321 (2)	−0.302 (2)	0.049 (6)*
H1O3	0.311 (3)	0.266 (2)	0.7732 (18)	0.038 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0232 (5)	0.0259 (5)	0.0132 (4)	0.0063 (4)	0.0045 (4)	0.0032 (4)
O2	0.0192 (5)	0.0202 (4)	0.0187 (5)	−0.0078 (3)	0.0065 (4)	−0.0011 (4)
O3	0.0171 (4)	0.0197 (4)	0.0178 (5)	−0.0004 (3)	0.0076 (3)	0.0008 (4)
N1	0.0144 (5)	0.0132 (4)	0.0126 (5)	−0.0025 (4)	0.0037 (4)	0.0030 (4)
C1	0.0172 (6)	0.0146 (5)	0.0154 (6)	0.0012 (4)	0.0019 (4)	0.0055 (4)
C2	0.0142 (6)	0.0200 (6)	0.0225 (6)	0.0028 (4)	0.0044 (5)	0.0100 (5)
C3	0.0185 (6)	0.0192 (6)	0.0198 (6)	0.0053 (5)	0.0085 (5)	0.0079 (5)
C4	0.0210 (6)	0.0139 (5)	0.0132 (6)	0.0029 (4)	0.0044 (5)	0.0047 (4)
C5	0.0142 (5)	0.0140 (5)	0.0157 (6)	0.0014 (4)	0.0035 (4)	0.0058 (4)
C6	0.0158 (6)	0.0109 (5)	0.0151 (6)	0.0014 (4)	0.0044 (4)	0.0053 (4)
C7	0.0136 (5)	0.0147 (5)	0.0141 (6)	−0.0003 (4)	0.0021 (4)	0.0058 (4)
C8	0.0129 (5)	0.0137 (5)	0.0142 (6)	0.0008 (4)	0.0025 (4)	0.0053 (4)
C9	0.0147 (6)	0.0152 (5)	0.0151 (6)	0.0001 (4)	0.0029 (4)	0.0049 (4)
C10	0.0138 (5)	0.0141 (5)	0.0126 (5)	−0.0005 (4)	0.0015 (4)	0.0042 (4)
C11	0.0148 (6)	0.0151 (5)	0.0116 (5)	−0.0017 (4)	0.0029 (4)	0.0031 (4)
C12	0.0137 (5)	0.0148 (5)	0.0147 (6)	−0.0007 (4)	0.0043 (4)	0.0037 (4)
C13	0.0142 (5)	0.0140 (5)	0.0137 (6)	−0.0012 (4)	0.0014 (4)	0.0039 (4)
C14	0.0155 (6)	0.0136 (5)	0.0124 (5)	0.0009 (4)	0.0029 (4)	0.0056 (4)
C15	0.0153 (6)	0.0142 (5)	0.0118 (5)	−0.0013 (4)	0.0019 (4)	0.0036 (4)
C16	0.0153 (6)	0.0151 (5)	0.0152 (6)	0.0017 (4)	0.0045 (4)	0.0058 (4)
C17	0.0230 (6)	0.0145 (5)	0.0130 (6)	0.0006 (5)	0.0044 (5)	0.0035 (4)
C18	0.0191 (6)	0.0149 (5)	0.0138 (6)	−0.0036 (4)	−0.0004 (4)	0.0052 (4)
C19	0.0146 (6)	0.0175 (5)	0.0146 (6)	−0.0008 (4)	0.0022 (4)	0.0070 (5)
C20	0.0183 (6)	0.0153 (5)	0.0188 (6)	−0.0044 (4)	0.0047 (5)	0.0039 (5)

Geometric parameters (Å, º)

O1—C4	1.3596 (15)	C9—C10	1.4908 (16)
O1—H1O1	0.96 (2)	C10—C13	1.3476 (16)
O2—C9	1.2351 (14)	C10—C11	1.5051 (15)
O3—C16	1.3674 (14)	C11—H11A	0.9900
O3—H1O3	0.87 (2)	C11—H11B	0.9900
N1—C12	1.4668 (15)	C12—H12A	0.9900
N1—C20	1.4684 (14)	C12—H12B	0.9900
N1—C11	1.4697 (15)	C13—C14	1.4595 (16)
C1—C2	1.3868 (17)	C13—H13A	0.9500
C1—C6	1.3996 (17)	C14—C15	1.4030 (16)
C1—H1A	0.9500	C14—C19	1.4038 (16)

C2—C3	1.3824 (18)	C15—C16	1.3912 (16)
C2—H2A	0.9500	C15—H15A	0.9500
C3—C4	1.3944 (18)	C16—C17	1.3915 (17)
C3—H3A	0.9500	C17—C18	1.3871 (17)
C4—C5	1.3910 (16)	C17—H17A	0.9500
C5—C6	1.4064 (16)	C18—C19	1.3872 (17)
C5—H5A	0.9500	C18—H18A	0.9500
C6—C7	1.4625 (16)	C19—H19A	0.9500
C7—C8	1.3472 (16)	C20—H20A	0.9800
C7—H7A	0.9500	C20—H20B	0.9800
C8—C9	1.4819 (16)	C20—H20C	0.9800
C8—C12	1.5076 (15)		

C4—O1—H1O1	112.0 (13)	C10—C11—H11A	109.3
C16—O3—H1O3	108.1 (12)	N1—C11—H11B	109.3
C12—N1—C20	110.15 (9)	C10—C11—H11B	109.3
C12—N1—C11	109.61 (9)	H11A—C11—H11B	108.0
C20—N1—C11	109.52 (9)	N1—C12—C8	110.31 (9)
C2—C1—C6	119.72 (11)	N1—C12—H12A	109.6
C2—C1—H1A	120.1	C8—C12—H12A	109.6
C6—C1—H1A	120.1	N1—C12—H12B	109.6
C3—C2—C1	120.94 (11)	C8—C12—H12B	109.6
C3—C2—H2A	119.5	H12A—C12—H12B	108.1
C1—C2—H2A	119.5	C10—C13—C14	130.67 (11)
C2—C3—C4	120.23 (11)	C10—C13—H13A	114.7
C2—C3—H3A	119.9	C14—C13—H13A	114.7
C4—C3—H3A	119.9	C15—C14—C19	118.59 (11)
O1—C4—C5	123.05 (11)	C15—C14—C13	116.26 (10)
O1—C4—C3	117.67 (11)	C19—C14—C13	125.13 (11)
C5—C4—C3	119.27 (11)	C16—C15—C14	121.15 (11)
C4—C5—C6	120.74 (11)	C16—C15—H15A	119.4
C4—C5—H5A	119.6	C14—C15—H15A	119.4
C6—C5—H5A	119.6	O3—C16—C15	121.89 (11)
C1—C6—C5	119.07 (11)	O3—C16—C17	118.25 (11)
C1—C6—C7	122.82 (11)	C15—C16—C17	119.85 (11)
C5—C6—C7	117.90 (10)	C18—C17—C16	119.08 (11)
C8—C7—C6	129.38 (11)	C18—C17—H17A	120.5
C8—C7—H7A	115.3	C16—C17—H17A	120.5
C6—C7—H7A	115.3	C17—C18—C19	121.80 (11)
C7—C8—C9	117.96 (10)	C17—C18—H18A	119.1
C7—C8—C12	124.30 (10)	C19—C18—H18A	119.1
C9—C8—C12	117.72 (10)	C18—C19—C14	119.49 (11)
O2—C9—C8	121.55 (11)	C18—C19—H19A	120.3
O2—C9—C10	120.44 (11)	C14—C19—H19A	120.3
C8—C9—C10	118.00 (10)	N1—C20—H20A	109.5
C13—C10—C9	116.70 (10)	N1—C20—H20B	109.5
C13—C10—C11	124.79 (10)	H20A—C20—H20B	109.5
C9—C10—C11	118.51 (10)	N1—C20—H20C	109.5

N1—C11—C10	111.60 (9)	H20A—C20—H20C	109.5
N1—C11—H11A	109.3	H20B—C20—H20C	109.5
C6—C1—C2—C3	0.52 (18)	C12—N1—C11—C10	−60.87 (12)
C1—C2—C3—C4	1.06 (18)	C20—N1—C11—C10	178.18 (10)
C2—C3—C4—O1	179.88 (11)	C13—C10—C11—N1	−152.54 (12)
C2—C3—C4—C5	−1.56 (18)	C9—C10—C11—N1	26.59 (15)
O1—C4—C5—C6	178.98 (11)	C20—N1—C12—C8	−174.22 (9)
C3—C4—C5—C6	0.50 (17)	C11—N1—C12—C8	65.22 (12)
C2—C1—C6—C5	−1.56 (17)	C7—C8—C12—N1	142.85 (12)
C2—C1—C6—C7	172.99 (11)	C9—C8—C12—N1	−35.19 (14)
C4—C5—C6—C1	1.06 (17)	C9—C10—C13—C14	−179.80 (12)
C4—C5—C6—C7	−173.76 (10)	C11—C10—C13—C14	−0.7 (2)
C1—C6—C7—C8	31.69 (19)	C10—C13—C14—C15	160.79 (13)
C5—C6—C7—C8	−153.70 (12)	C10—C13—C14—C19	−20.9 (2)
C6—C7—C8—C9	−174.71 (11)	C19—C14—C15—C16	2.09 (18)
C6—C7—C8—C12	7.3 (2)	C13—C14—C15—C16	−179.43 (11)
C7—C8—C9—O2	4.94 (18)	C14—C15—C16—O3	−179.37 (11)
C12—C8—C9—O2	−176.91 (11)	C14—C15—C16—C17	−0.52 (18)
C7—C8—C9—C10	−176.05 (11)	O3—C16—C17—C18	177.59 (11)
C12—C8—C9—C10	2.11 (16)	C15—C16—C17—C18	−1.30 (18)
O2—C9—C10—C13	0.53 (18)	C16—C17—C18—C19	1.55 (19)
C8—C9—C10—C13	−178.49 (11)	C17—C18—C19—C14	0.05 (18)
O2—C9—C10—C11	−178.66 (11)	C15—C14—C19—C18	−1.85 (17)
C8—C9—C10—C11	2.31 (17)	C13—C14—C19—C18	179.83 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···N1^{i}	0.96 (2)	1.81 (2)	2.7278 (14)	160 (2)
O3—H1*O*3···O2^{ii}	0.88 (2)	1.87 (2)	2.7359 (15)	171 (2)
C17—H17*A*···O3^{iii}	0.95	2.51	3.4032 (16)	157

Symmetry codes: (i) −*x*+2, −*y*, −*z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+2.

(2) 3,5-Bis[(*E*)-2-chlorobenzylidene]-1-methylpiperidin-4-one

Crystal data

$C_{20}H_{17}Cl_2NO$
M_r = 358.24
Monoclinic, $P2_1/n$
a = 7.540 (3) Å
b = 10.623 (4) Å
c = 21.119 (7) Å
β = 98.671 (5)°
V = 1672.2 (10) Å^3
Z = 4

$F(000)$ = 744
D_x = 1.423 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3908 reflections
θ = 2.7–29.2°
μ = 0.39 mm^{-1}
T = 100 K
Needle, yellow
0.32 × 0.08 × 0.08 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)

3105 measured reflections

3105 independent reflections
2591 reflections with $I > 2\sigma(I)$
$R_{int} = 0.084$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.0°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -5 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.192$
$S = 1.18$
3105 reflections
218 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 13.4429P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.8841 (2)	0.46525 (14)	0.06491 (7)	0.0261 (4)
Cl2	0.6925 (2)	−0.18217 (14)	−0.22186 (7)	0.0242 (4)
O1	0.6046 (5)	0.0962 (4)	−0.04698 (18)	0.0193 (9)
N1	0.9749 (6)	−0.1131 (4)	0.0667 (2)	0.0179 (10)
C1	0.7905 (8)	0.1999 (6)	0.1897 (3)	0.0205 (13)
H1A	0.7492	0.1153	0.1892	0.025*
C2	0.8325 (8)	0.2615 (6)	0.2487 (3)	0.0244 (13)
H2A	0.8193	0.2199	0.2876	0.029*
C3	0.8940 (8)	0.3854 (6)	0.2491 (3)	0.0263 (14)
H3A	0.9266	0.4275	0.2889	0.032*
C4	0.9085 (8)	0.4479 (6)	0.1928 (3)	0.0264 (14)
H4A	0.9477	0.5329	0.1934	0.032*
C5	0.8648 (8)	0.3841 (5)	0.1355 (3)	0.0182 (12)
C6	0.8072 (7)	0.2581 (5)	0.1317 (3)	0.0178 (12)
C7	0.7554 (7)	0.1956 (5)	0.0699 (3)	0.0184 (12)
H7A	0.6965	0.2461	0.0359	0.022*
C8	0.7825 (7)	0.0744 (5)	0.0562 (3)	0.0156 (12)

C9	0.7007 (7)	0.0275 (6)	−0.0089 (3)	0.0181 (12)
C10	0.7323 (7)	−0.1071 (5)	−0.0242 (3)	0.0158 (12)
C11	0.8378 (8)	−0.1877 (5)	0.0269 (3)	0.0186 (12)
H11A	0.7555	−0.2250	0.0542	0.022*
H11B	0.8959	−0.2573	0.0066	0.022*
C12	0.8874 (8)	−0.0179 (5)	0.1009 (3)	0.0179 (12)
H12A	0.9794	0.0279	0.1305	0.021*
H12B	0.8056	−0.0598	0.1268	0.021*
C13	0.6595 (7)	−0.1495 (5)	−0.0815 (3)	0.0165 (12)
H13A	0.6044	−0.0878	−0.1106	0.020*
C14	0.6534 (7)	−0.2798 (5)	−0.1058 (3)	0.0161 (12)
C15	0.6583 (7)	−0.3058 (5)	−0.1704 (3)	0.0185 (12)
C16	0.6392 (8)	−0.4257 (6)	−0.1957 (3)	0.0210 (13)
H16A	0.6420	−0.4397	−0.2400	0.025*
C17	0.6158 (8)	−0.5253 (6)	−0.1554 (3)	0.0229 (13)
H17A	0.6032	−0.6084	−0.1721	0.027*
C18	0.6106 (8)	−0.5046 (6)	−0.0912 (3)	0.0210 (13)
H18A	0.5949	−0.5729	−0.0635	0.025*
C19	0.6288 (7)	−0.3818 (5)	−0.0674 (3)	0.0187 (12)
H19A	0.6242	−0.3679	−0.0232	0.022*
C20	1.0862 (8)	−0.1939 (6)	0.1114 (3)	0.0225 (13)
H20A	1.1440	−0.2573	0.0877	0.034*
H20B	1.1783	−0.1432	0.1375	0.034*
H20C	1.0117	−0.2359	0.1393	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0287 (8)	0.0196 (7)	0.0305 (8)	−0.0023 (6)	0.0065 (6)	0.0026 (6)
Cl2	0.0292 (8)	0.0260 (8)	0.0176 (7)	−0.0003 (6)	0.0038 (6)	0.0015 (6)
O1	0.020 (2)	0.018 (2)	0.019 (2)	0.0055 (17)	0.0001 (17)	0.0049 (17)
N1	0.012 (2)	0.019 (3)	0.022 (2)	0.002 (2)	0.000 (2)	−0.002 (2)
C1	0.019 (3)	0.020 (3)	0.023 (3)	0.003 (2)	0.005 (2)	−0.002 (2)
C2	0.019 (3)	0.027 (3)	0.027 (3)	0.006 (3)	0.002 (3)	−0.002 (3)
C3	0.023 (3)	0.029 (4)	0.027 (3)	0.007 (3)	0.002 (3)	−0.012 (3)
C4	0.021 (3)	0.023 (3)	0.035 (4)	0.001 (3)	0.001 (3)	−0.005 (3)
C5	0.016 (3)	0.015 (3)	0.023 (3)	0.001 (2)	0.003 (2)	0.004 (2)
C6	0.012 (3)	0.018 (3)	0.023 (3)	0.003 (2)	0.004 (2)	−0.003 (2)
C7	0.014 (3)	0.019 (3)	0.023 (3)	0.001 (2)	0.005 (2)	0.004 (2)
C8	0.015 (3)	0.015 (3)	0.019 (3)	0.000 (2)	0.007 (2)	−0.002 (2)
C9	0.013 (3)	0.025 (3)	0.018 (3)	−0.004 (2)	0.007 (2)	0.000 (2)
C10	0.013 (3)	0.018 (3)	0.017 (3)	0.003 (2)	0.006 (2)	0.004 (2)
C11	0.020 (3)	0.017 (3)	0.019 (3)	0.000 (2)	0.003 (2)	−0.003 (2)
C12	0.019 (3)	0.017 (3)	0.018 (3)	0.000 (2)	0.004 (2)	−0.005 (2)
C13	0.016 (3)	0.019 (3)	0.014 (3)	0.000 (2)	0.002 (2)	0.000 (2)
C14	0.011 (3)	0.020 (3)	0.017 (3)	0.002 (2)	0.002 (2)	−0.001 (2)
C15	0.015 (3)	0.020 (3)	0.020 (3)	0.001 (2)	0.002 (2)	−0.002 (2)
C16	0.020 (3)	0.026 (3)	0.017 (3)	0.000 (3)	0.001 (2)	−0.005 (2)

C17	0.023 (3)	0.018 (3)	0.027 (3)	−0.004 (3)	0.001 (3)	−0.008 (3)
C18	0.018 (3)	0.024 (3)	0.020 (3)	−0.003 (3)	−0.001 (2)	−0.001 (2)
C19	0.016 (3)	0.021 (3)	0.019 (3)	0.001 (2)	0.001 (2)	−0.004 (2)
C20	0.025 (3)	0.020 (3)	0.022 (3)	0.002 (3)	0.001 (3)	0.001 (2)

Geometric parameters (Å, º)

Cl1—C5	1.747 (6)	C10—C13	1.331 (8)
Cl2—C15	1.749 (6)	C10—C11	1.508 (8)
O1—C9	1.236 (7)	C11—H11A	0.9900
N1—C20	1.447 (7)	C11—H11B	0.9900
N1—C12	1.457 (7)	C12—H12A	0.9900
N1—C11	1.462 (7)	C12—H12B	0.9900
C1—C6	1.396 (8)	C13—C14	1.474 (8)
C1—C2	1.402 (8)	C13—H13A	0.9500
C1—H1A	0.9500	C14—C19	1.383 (8)
C2—C3	1.395 (9)	C14—C15	1.398 (8)
C2—H2A	0.9500	C15—C16	1.381 (8)
C3—C4	1.381 (9)	C16—C17	1.386 (8)
C3—H3A	0.9500	C16—H16A	0.9500
C4—C5	1.382 (8)	C17—C18	1.381 (8)
C4—H4A	0.9500	C17—H17A	0.9500
C5—C6	1.406 (8)	C18—C19	1.397 (8)
C6—C7	1.464 (8)	C18—H18A	0.9500
C7—C8	1.343 (8)	C19—H19A	0.9500
C7—H7A	0.9500	C20—H20A	0.9800
C8—C12	1.501 (8)	C20—H20B	0.9800
C8—C9	1.505 (8)	C20—H20C	0.9800
C9—C10	1.492 (8)		

C20—N1—C12	110.4 (4)	N1—C11—H11B	109.5
C20—N1—C11	110.1 (5)	C10—C11—H11B	109.5
C12—N1—C11	109.1 (4)	H11A—C11—H11B	108.1
C6—C1—C2	122.4 (6)	N1—C12—C8	112.1 (4)
C6—C1—H1A	118.8	N1—C12—H12A	109.2
C2—C1—H1A	118.8	C8—C12—H12A	109.2
C3—C2—C1	118.5 (6)	N1—C12—H12B	109.2
C3—C2—H2A	120.8	C8—C12—H12B	109.2
C1—C2—H2A	120.8	H12A—C12—H12B	107.9
C4—C3—C2	121.2 (6)	C10—C13—C14	128.4 (5)
C4—C3—H3A	119.4	C10—C13—H13A	115.8
C2—C3—H3A	119.4	C14—C13—H13A	115.8
C3—C4—C5	118.6 (6)	C19—C14—C15	116.3 (5)
C3—C4—H4A	120.7	C19—C14—C13	122.2 (5)
C5—C4—H4A	120.7	C15—C14—C13	121.4 (5)
C4—C5—C6	123.2 (6)	C16—C15—C14	122.9 (5)
C4—C5—Cl1	117.7 (5)	C16—C15—Cl2	118.0 (4)
C6—C5—Cl1	119.0 (5)	C14—C15—Cl2	119.1 (4)

C1—C6—C5	116.1 (5)	C15—C16—C17	118.8 (5)
C1—C6—C7	122.3 (5)	C15—C16—H16A	120.6
C5—C6—C7	121.5 (5)	C17—C16—H16A	120.6
C8—C7—C6	126.7 (5)	C18—C17—C16	120.4 (6)
C8—C7—H7A	116.6	C18—C17—H17A	119.8
C6—C7—H7A	116.6	C16—C17—H17A	119.8
C7—C8—C12	125.1 (5)	C17—C18—C19	119.1 (6)
C7—C8—C9	117.3 (5)	C17—C18—H18A	120.4
C12—C8—C9	117.6 (5)	C19—C18—H18A	120.4
O1—C9—C10	121.5 (5)	C14—C19—C18	122.4 (5)
O1—C9—C8	121.2 (5)	C14—C19—H19A	118.8
C10—C9—C8	117.2 (5)	C18—C19—H19A	118.8
C13—C10—C9	117.6 (5)	N1—C20—H20A	109.5
C13—C10—C11	124.0 (5)	N1—C20—H20B	109.5
C9—C10—C11	118.3 (5)	H20A—C20—H20B	109.5
N1—C11—C10	110.7 (5)	N1—C20—H20C	109.5
N1—C11—H11A	109.5	H20A—C20—H20C	109.5
C10—C11—H11A	109.5	H20B—C20—H20C	109.5

C6—C1—C2—C3	−0.4 (9)	C20—N1—C11—C10	−174.5 (4)
C1—C2—C3—C4	2.0 (9)	C12—N1—C11—C10	64.2 (6)
C2—C3—C4—C5	−1.6 (9)	C13—C10—C11—N1	149.3 (5)
C3—C4—C5—C6	−0.5 (9)	C9—C10—C11—N1	−33.2 (7)
C3—C4—C5—Cl1	180.0 (5)	C20—N1—C12—C8	175.3 (5)
C2—C1—C6—C5	−1.5 (8)	C11—N1—C12—C8	−63.6 (6)
C2—C1—C6—C7	−177.1 (5)	C7—C8—C12—N1	−149.2 (5)
C4—C5—C6—C1	1.9 (8)	C9—C8—C12—N1	31.0 (7)
Cl1—C5—C6—C1	−178.5 (4)	C9—C10—C13—C14	−172.8 (5)
C4—C5—C6—C7	177.6 (5)	C11—C10—C13—C14	4.8 (9)
Cl1—C5—C6—C7	−2.9 (7)	C10—C13—C14—C19	37.6 (9)
C1—C6—C7—C8	−39.9 (9)	C10—C13—C14—C15	−147.5 (6)
C5—C6—C7—C8	144.7 (6)	C19—C14—C15—C16	0.3 (8)
C6—C7—C8—C12	−5.9 (9)	C13—C14—C15—C16	−175.0 (5)
C6—C7—C8—C9	173.9 (5)	C19—C14—C15—Cl2	−179.0 (4)
C7—C8—C9—O1	−3.8 (8)	C13—C14—C15—Cl2	5.8 (7)
C12—C8—C9—O1	176.1 (5)	C14—C15—C16—C17	−0.6 (9)
C7—C8—C9—C10	179.6 (5)	Cl2—C15—C16—C17	178.6 (4)
C12—C8—C9—C10	−0.6 (7)	C15—C16—C17—C18	0.4 (9)
O1—C9—C10—C13	2.9 (8)	C16—C17—C18—C19	0.2 (9)
C8—C9—C10—C13	179.6 (5)	C15—C14—C19—C18	0.3 (8)
O1—C9—C10—C11	−174.7 (5)	C13—C14—C19—C18	175.5 (5)
C8—C9—C10—C11	1.9 (7)	C17—C18—C19—C14	−0.5 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C4—H4*A*···Cl2^{i}	0.95	2.85	3.587 (7)	135

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