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7-Hydroxyhexacyclo[7.5.1.0^{1,7}.0^{6,13}.0^{8,12}.0^{10,14}]-pentadecan-15-one-11-spirocyclopentane

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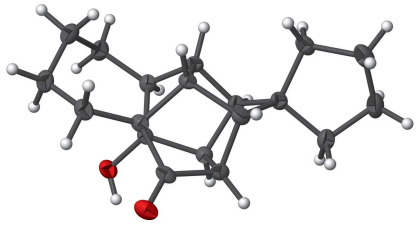
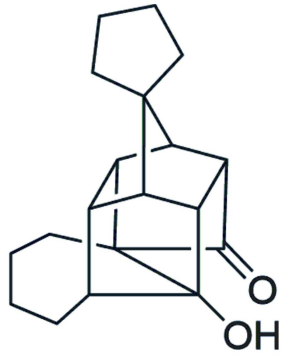
Structural data: full structural data are available from iucrdata.iucr.org

The reorganization of the carbon skeleton in a spiro cage dione to an unusual cage system, $C_{19}H_{24}O_2$, using acid-promoted rearrangement with the aid of zinc dust as a reducing agent in the reaction medium is reported. The resulting trishomocubane hydroxyketone derivative includes five-membered rings having an envelope conformation and one seven-membered ring with a twist-chair conformation.

3D view



Chemical scheme



Structure description

Cage molecules act as useful precursors for the synthesis of diverse natural and non-natural products (Marchand *et al.*, 1999). Many of these compounds are found to be key synthons in material chemistry (Eaton *et al.*, 2002; Lal *et al.*, 2015), in medicinal chemistry, and pharmaceutical drug design (Chalmers *et al.*, 2016). Some of the functionalized cage systems are important templates for the design of supramolecules. As a result of the rigid architecture and considerable strain energy of cage moieties, they are involved in unusual skeletal rearrangements, generating intricate polycycles that are often difficult to design by other synthetic protocols (Kotha *et al.*, 2017).

As part of our ongoing research efforts in this field, we present herein the synthesis and the structure of the title compound (Fig. 1). The title compound **II** was synthesized (Fig. 2) from inexpensive commercially available starting materials such as 1,4-hydroquinone, using our earlier reported strategy, *via* a Claisen rearrangement, Diels–Alder reaction, [2 + 2] photocycloaddition and ring-closing metathesis (RCM), followed by catalytic hydrogenation (Kotha & Dipak, 2006).

The molecule consists of eight fused rings of which one seven-membered, one six-membered and six five-membered rings are fused into a caged carbon skeleton. All five-membered rings are in envelope conformations, whereas the seven-membered ring is in a twist-chair conformation.

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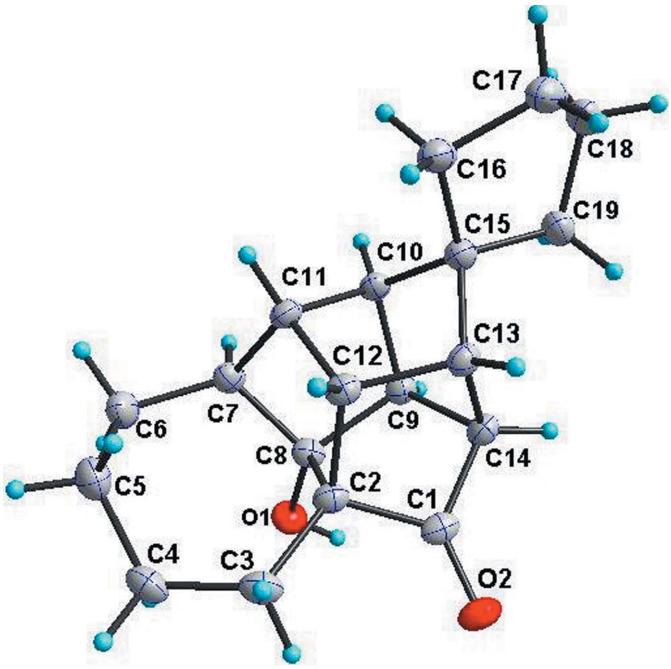

Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Synthesis and crystallization

A mixture of heptacyclic cage propellanedione **I** (100 mg, 0.35 mmol) and activated zinc dust (300 mg, 4.55 mmol) in 5 ml of glacial acetic acid was stirred at room temperature overnight. Insoluble zinc metal and salts were removed by filtration. The resulting filtrate was concentrated, diluted with cold water, and extracted with dichloromethane. The combined organic layers were washed with aqueous $NaHCO_3$, brine, and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure to give the crude rearranged cage hydroxyketone, which was purified by crystallization from mixed solvents of petroleum ether and ethyl acetate (4:1) to afford the title compound **II** (87 mg, 86%) as a colourless crystalline solid, m.p. 395–397 K.

IR (neat, cm^{-1}): 3440, 2935, 2861, 1756, 1451, 1308, 1244, 1158; ^{1}H NMR (500 MHz, $CDCl_3$, p.p.m.): 2.41–2.39 (*m*, 1H), 2.26–2.16 (*m*, 5H), 2.14–2.06 (*m*, 2H), 1.99 (*s*, 1H), 1.82–1.71 (*m*, 2H), 1.68–1.62 (*m*, 4H), 1.52–1.34 (*m*, 7H), 1.31–1.17 (*m*, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, p.p.m.): 217.7, 85.8, 58.3, 56.6, 56.4, 53.2, 50.2, 50.1, 49.6, 48.7, 47.2, 33.0, 31.2, 28.9, 26.2, 26.1, 26.0, 24.85, 24.81; HRMS (ESI) *m*/*z* calculated for $C_{19}H_{24}NaO_2$ $[M + Na]^+$ 307.1669; found: 307.1670.

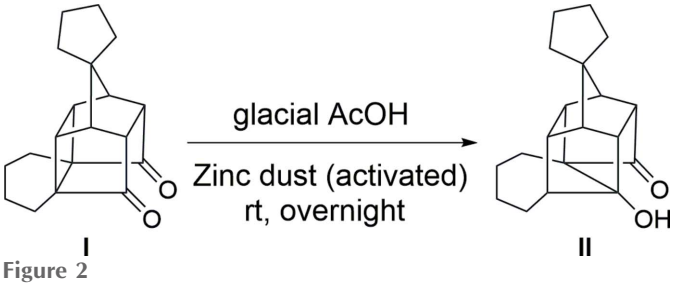

Figure 2
Reduction of cage propellane dione **I** with Zn/AcOH.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{24}O_2$
M_r	284.38
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, *b*, *c* (Å)	6.3600 (2), 11.0807 (4), 11.5351 (4)
α, β, γ (°)	114.539 (4), 91.465 (3), 93.401 (3)
V (Å^3)	737.07 (5)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.08
Crystal size (mm)	0.13 × 0.11 × 0.06
Data collection	
Diffractometer	Rigaku Saturn724+
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.815, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7967, 2593, 2255
R_{int}	0.044
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.114, 1.11
No. of reflections	2593
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.25

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The molecule crystallizes in a centrosymmetric space group, with a racemic mixture of enantiomers. The relative configuration of the nine chiral centres was assigned as *S*-C2, *S*-C7, *R*-C8, *S*-C9, *R*-C10, *R*-C11, *R*-C12, *S*-C13 and *R*-C14.

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x180090 [https://doi.org/10.1107/S2414314618000901]

7-Hydroxyhexacyclo[7.5.1.0^{1,7}.0^{6,13}.0^{8,12}.0^{10,14}]pentadecan-15-one-11-spirocyclopentane

Sambasivarao Kotha, Subba Rao Cheekatla and Rama Gunta

7-Hydroxyhexacyclo[7.5.1.0^{1,7}.0^{6,13}.0^{8,12}.0^{10,14}]pentadecan-15-one-11-spirocyclopentane

Crystal data

$C_{19}H_{24}O_2$
M_r = 284.38
Triclinic, $P\overline{1}$
a = 6.3600 (2) Å
b = 11.0807 (4) Å
c = 11.5351 (4) Å
α = 114.539 (4)°
β = 91.465 (3)°
γ = 93.401 (3)°
V = 737.07 (5) Å^3
Z = 2
$F(000)$ = 308
D_x = 1.281 Mg m^{-3}
Melting point = 395–397 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5950 reflections
θ = 1.9–31.2°
μ = 0.08 mm^{-1}
T = 293 K
Block, colourless
0.13 × 0.11 × 0.06 mm

Data collection

Rigaku Saturn724+ diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.815, T_{max} = 1.000
7967 measured reflections
2593 independent reflections
2255 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −7→7
k = −13→13
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.114
S = 1.11
2593 reflections
191 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.2482P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Special details

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H) groups, All C(H,H) groups At 1.5 times of: All O(H) groups 2.a Ternary CH refined with riding coordinates: C7(H7), C13(H13), C10(H10), C14(H14), C9(H9), C11(H11), C12(H12) 2.b Secondary CH2 refined with riding coordinates: C6(H6A,H6B), C3(H3A,H3B), C5(H5A,H5B), C4(H4A,H4B), C17(H17A,H17B), C19(H19A, H19B), C16(H16A,H16B), C18(H18A,H18B) 2.c Idealised tetrahedral OH refined as rotating group: O1(H1)
All H atoms were placed in their geometrically calculated positions and refined using a riding model with C–H distances of 0.98 Å for all H atoms bound to tertiary C(sp^3) atoms and 0.97 Å for all other H atoms bound to secondary C(sp^3) atoms. The hydroxyl O—H bond length was fixed to 0.82 Å. Isotropic displacement parameters for H atoms were calculated as $U_{iso}(H) = xU_{eq}(C/O)$, where $x = 1.2$ for all methine and methylene groups, and $x = 1.5$ for the hydroxyl group.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.36404 (17)	0.91284 (11)	0.24611 (11)	0.0252 (3)
H1	0.3257	0.9389	0.3193	0.038*
O2	0.75618 (16)	1.03470 (11)	0.50985 (10)	0.0259 (3)
C1	0.7323 (2)	0.92662 (15)	0.41932 (15)	0.0199 (3)
C2	0.7505 (2)	0.89395 (15)	0.27990 (15)	0.0198 (3)
C3	0.8338 (3)	1.01079 (16)	0.25321 (16)	0.0249 (4)
H3A	0.9865	1.0123	0.2544	0.030*
H3B	0.7976	1.0921	0.3226	0.030*
C4	0.7555 (3)	1.01269 (17)	0.12836 (16)	0.0284 (4)
H4A	0.6089	1.0331	0.1346	0.034*
H4B	0.8355	1.0834	0.1162	0.034*
C5	0.7737 (3)	0.88268 (17)	0.01230 (16)	0.0303 (4)
H5A	0.9016	0.8440	0.0231	0.036*
H5B	0.7855	0.9009	−0.0627	0.036*
C6	0.5864 (3)	0.78268 (17)	−0.00940 (16)	0.0279 (4)
H6A	0.6022	0.7070	−0.0897	0.033*
H6B	0.4604	0.8233	−0.0198	0.033*
C7	0.5474 (2)	0.72978 (15)	0.09132 (15)	0.0208 (4)
H7	0.4183	0.6701	0.0634	0.025*
C8	0.5245 (2)	0.82645 (15)	0.22937 (15)	0.0190 (3)
C9	0.5050 (2)	0.73109 (15)	0.30108 (14)	0.0193 (3)
H9	0.3623	0.7183	0.3262	0.023*
C10	0.5980 (2)	0.59946 (15)	0.20791 (14)	0.0195 (3)
H10	0.4939	0.5245	0.1620	0.023*
C11	0.7151 (2)	0.65541 (15)	0.12496 (14)	0.0196 (3)
H11	0.7830	0.5903	0.0524	0.024*
C12	0.8694 (2)	0.76285 (15)	0.23240 (14)	0.0188 (3)
H12	1.0116	0.7723	0.2050	0.023*
C13	0.8622 (2)	0.71750 (15)	0.34580 (14)	0.0197 (3)
H13	0.9938	0.7353	0.3983	0.024*
C14	0.6743 (2)	0.79265 (15)	0.41509 (14)	0.0206 (4)
H14	0.6398	0.7879	0.4955	0.025*
C15	0.7715 (2)	0.57240 (15)	0.28579 (15)	0.0214 (4)
C16	0.9272 (3)	0.47262 (16)	0.20525 (16)	0.0264 (4)

H16A	0.8594	0.4104	0.1244	0.032*
H16B	1.0491	0.5188	0.1887	0.032*
C17	0.9918 (3)	0.40057 (18)	0.28674 (17)	0.0354 (4)
H17A	1.0424	0.3147	0.2347	0.042*
H17B	1.1004	0.4532	0.3516	0.042*
C18	0.7878 (3)	0.38491 (17)	0.34615 (17)	0.0357 (5)
H18A	0.8147	0.3666	0.4202	0.043*
H18B	0.6931	0.3138	0.2851	0.043*
C19	0.6968 (3)	0.51950 (16)	0.38404 (16)	0.0272 (4)
H19A	0.7481	0.5803	0.4697	0.033*
H19B	0.5440	0.5097	0.3814	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0202 (6)	0.0262 (6)	0.0305 (7)	0.0069 (5)	0.0017 (5)	0.0125 (6)
O2	0.0223 (6)	0.0205 (6)	0.0259 (6)	0.0006 (5)	−0.0008 (5)	0.0008 (5)
C1	0.0121 (7)	0.0193 (8)	0.0229 (8)	0.0024 (6)	−0.0019 (6)	0.0035 (7)
C2	0.0185 (8)	0.0169 (8)	0.0211 (8)	0.0002 (6)	−0.0006 (6)	0.0053 (7)
C3	0.0228 (8)	0.0185 (8)	0.0314 (9)	−0.0008 (6)	0.0003 (7)	0.0089 (7)
C4	0.0289 (9)	0.0242 (9)	0.0373 (10)	−0.0007 (7)	0.0034 (7)	0.0182 (8)
C5	0.0361 (10)	0.0316 (10)	0.0286 (9)	0.0020 (8)	0.0049 (7)	0.0176 (8)
C6	0.0342 (9)	0.0272 (9)	0.0241 (9)	0.0017 (7)	−0.0016 (7)	0.0129 (8)
C7	0.0204 (8)	0.0195 (8)	0.0212 (8)	−0.0017 (6)	−0.0025 (6)	0.0078 (7)
C8	0.0152 (7)	0.0189 (8)	0.0229 (8)	0.0017 (6)	−0.0007 (6)	0.0087 (7)
C9	0.0168 (7)	0.0196 (8)	0.0203 (8)	−0.0001 (6)	−0.0005 (6)	0.0075 (7)
C10	0.0215 (8)	0.0156 (8)	0.0187 (8)	−0.0014 (6)	−0.0016 (6)	0.0050 (6)
C11	0.0226 (8)	0.0168 (8)	0.0162 (8)	0.0024 (6)	0.0002 (6)	0.0036 (6)
C12	0.0160 (7)	0.0188 (8)	0.0195 (8)	0.0016 (6)	0.0013 (6)	0.0058 (7)
C13	0.0186 (7)	0.0197 (8)	0.0177 (8)	0.0015 (6)	−0.0027 (6)	0.0049 (7)
C14	0.0216 (8)	0.0210 (8)	0.0165 (8)	0.0012 (6)	0.0000 (6)	0.0053 (7)
C15	0.0243 (8)	0.0192 (8)	0.0196 (8)	0.0028 (6)	−0.0008 (6)	0.0070 (7)
C16	0.0297 (9)	0.0209 (8)	0.0241 (9)	0.0057 (7)	−0.0024 (7)	0.0046 (7)
C17	0.0463 (11)	0.0264 (10)	0.0288 (10)	0.0133 (8)	−0.0061 (8)	0.0060 (8)
C18	0.0572 (12)	0.0227 (9)	0.0279 (9)	0.0032 (8)	−0.0057 (9)	0.0117 (8)
C19	0.0341 (9)	0.0243 (9)	0.0248 (9)	0.0015 (7)	−0.0017 (7)	0.0122 (7)

Geometric parameters (Å, º)

O2—C1	1.2163 (19)	C10—C15	1.526 (2)
O1—H1	0.8200	C4—H4A	0.9700
O1—C8	1.4025 (18)	C4—H4B	0.9700
C1—C14	1.489 (2)	C14—H14	0.9800
C1—C2	1.504 (2)	C14—C9	1.565 (2)
C6—H6A	0.9700	C2—C12	1.572 (2)
C6—H6B	0.9700	C2—C8	1.560 (2)
C6—C7	1.522 (2)	C17—H17A	0.9700
C6—C5	1.519 (2)	C17—H17B	0.9700

C3—H3A	0.9700	C17—C16	1.527 (2)
C3—H3B	0.9700	C17—C18	1.516 (3)
C3—C4	1.521 (2)	C9—H9	0.9800
C3—C2	1.520 (2)	C9—C8	1.591 (2)
C7—H7	0.9800	C19—H19A	0.9700
C7—C11	1.522 (2)	C19—H19B	0.9700
C7—C8	1.523 (2)	C19—C15	1.549 (2)
C13—H13	0.9800	C19—C18	1.525 (2)
C13—C14	1.541 (2)	C16—H16A	0.9700
C13—C15	1.530 (2)	C16—H16B	0.9700
C13—C12	1.585 (2)	C16—C15	1.546 (2)
C5—H5A	0.9700	C11—H11	0.9800
C5—H5B	0.9700	C11—C12	1.578 (2)
C5—C4	1.519 (2)	C18—H18A	0.9700
C10—H10	0.9800	C18—H18B	0.9700
C10—C9	1.570 (2)	C12—H12	0.9800
C10—C11	1.526 (2)		

C8—O1—H1	109.5	C3—C2—C8	120.48 (13)
O2—C1—C14	130.14 (14)	C8—C2—C12	97.08 (11)
O2—C1—C2	128.57 (14)	H17A—C17—H17B	109.1
C14—C1—C2	101.29 (12)	C16—C17—H17A	111.2
H6A—C6—H6B	107.1	C16—C17—H17B	111.2
C7—C6—H6A	107.7	C18—C17—H17A	111.2
C7—C6—H6B	107.7	C18—C17—H17B	111.2
C5—C6—H6A	107.7	C18—C17—C16	102.78 (14)
C5—C6—H6B	107.7	C10—C9—H9	114.2
C5—C6—C7	118.51 (14)	C10—C9—C8	104.35 (11)
H3A—C3—H3B	107.3	C14—C9—C10	103.93 (12)
C4—C3—H3A	108.1	C14—C9—H9	114.2
C4—C3—H3B	108.1	C14—C9—C8	104.67 (11)
C2—C3—H3A	108.1	C8—C9—H9	114.2
C2—C3—H3B	108.1	H19A—C19—H19B	108.7
C2—C3—C4	116.65 (14)	C15—C19—H19A	110.5
C6—C7—H7	107.2	C15—C19—H19B	110.5
C6—C7—C8	119.86 (13)	C18—C19—H19A	110.5
C11—C7—C6	119.97 (13)	C18—C19—H19B	110.5
C11—C7—H7	107.2	C18—C19—C15	106.10 (13)
C11—C7—C8	94.09 (11)	C17—C16—H16A	110.8
C8—C7—H7	107.2	C17—C16—H16B	110.8
C14—C13—H13	115.6	C17—C16—C15	104.70 (13)
C14—C13—C12	99.50 (11)	H16A—C16—H16B	108.9
C15—C13—H13	115.6	C15—C16—H16A	110.8
C15—C13—C14	102.84 (12)	C15—C16—H16B	110.8
C15—C13—C12	105.66 (12)	C7—C11—C10	102.41 (12)
C12—C13—H13	115.6	C7—C11—H11	115.6
C6—C5—H5A	109.0	C7—C11—C12	107.14 (12)
C6—C5—H5B	109.0	C10—C11—H11	115.6

H5A—C5—H5B	107.8	C10—C11—C12	98.33 (11)
C4—C5—C6	112.79 (14)	C12—C11—H11	115.6
C4—C5—H5A	109.0	C13—C15—C19	113.97 (13)
C4—C5—H5B	109.0	C13—C15—C16	114.25 (13)
C9—C10—H10	115.4	C10—C15—C13	93.32 (12)
C11—C10—H10	115.4	C10—C15—C19	116.05 (13)
C11—C10—C9	98.14 (11)	C10—C15—C16	114.56 (13)
C15—C10—H10	115.4	C16—C15—C19	104.95 (13)
C15—C10—C9	105.94 (12)	C17—C18—C19	103.31 (14)
C15—C10—C11	104.71 (12)	C17—C18—H18A	111.1
C3—C4—H4A	108.8	C17—C18—H18B	111.1
C3—C4—H4B	108.8	C19—C18—H18A	111.1
C5—C4—C3	113.87 (13)	C19—C18—H18B	111.1
C5—C4—H4A	108.8	H18A—C18—H18B	109.1
C5—C4—H4B	108.8	C13—C12—H12	114.1
H4A—C4—H4B	107.7	C2—C12—C13	105.03 (11)
C1—C14—C13	100.18 (12)	C2—C12—C11	104.64 (11)
C1—C14—H14	117.5	C2—C12—H12	114.1
C1—C14—C9	103.04 (12)	C11—C12—C13	103.68 (11)
C13—C14—H14	117.5	C11—C12—H12	114.1
C13—C14—C9	98.00 (11)	O1—C8—C7	114.29 (12)
C9—C14—H14	117.5	O1—C8—C2	115.98 (12)
C1—C2—C3	114.04 (13)	O1—C8—C9	116.75 (12)
C1—C2—C12	102.23 (12)	C7—C8—C2	105.24 (12)
C1—C2—C8	99.12 (11)	C7—C8—C9	102.90 (12)
C3—C2—C12	120.17 (13)	C2—C8—C9	99.74 (11)

O2—C1—C14—C13	−123.78 (16)	C14—C9—C8—C7	128.39 (12)
O2—C1—C14—C9	135.46 (16)	C14—C9—C8—C2	20.15 (14)
O2—C1—C2—C3	7.6 (2)	C2—C1—C14—C13	57.20 (13)
O2—C1—C2—C12	138.86 (15)	C2—C1—C14—C9	−43.56 (13)
O2—C1—C2—C8	−121.79 (16)	C2—C3—C4—C5	−49.74 (19)
C1—C14—C9—C10	122.62 (12)	C17—C16—C15—C13	106.45 (16)
C1—C14—C9—C8	13.42 (14)	C17—C16—C15—C10	−147.55 (14)
C1—C2—C12—C13	12.06 (14)	C17—C16—C15—C19	−19.11 (17)
C1—C2—C12—C11	120.91 (12)	C9—C10—C11—C7	−49.50 (13)
C1—C2—C8—O1	80.03 (15)	C9—C10—C11—C12	60.21 (12)
C1—C2—C8—C7	−152.60 (12)	C9—C10—C15—C13	−44.32 (13)
C1—C2—C8—C9	−46.25 (13)	C9—C10—C15—C19	74.45 (16)
C6—C7—C11—C10	−169.91 (14)	C9—C10—C15—C16	−162.93 (13)
C6—C7—C11—C12	87.20 (16)	C16—C17—C18—C19	−42.56 (17)
C6—C7—C8—O1	56.73 (18)	C11—C7—C8—O1	−175.07 (12)
C6—C7—C8—C2	−71.66 (16)	C11—C7—C8—C2	56.54 (13)
C6—C7—C8—C9	−175.68 (13)	C11—C7—C8—C9	−47.48 (12)
C6—C5—C4—C3	84.99 (18)	C11—C10—C9—C14	−92.20 (12)
C3—C2—C12—C13	139.52 (14)	C11—C10—C9—C8	17.24 (14)
C3—C2—C12—C11	−111.63 (15)	C11—C10—C15—C13	58.82 (13)
C3—C2—C8—O1	−44.95 (19)	C11—C10—C15—C19	177.59 (13)

C3—C2—C8—C7	82.42 (16)	C11—C10—C15—C16	−59.79 (16)
C3—C2—C8—C9	−171.23 (13)	C15—C13—C14—C1	−155.62 (12)
C7—C6—C5—C4	−63.8 (2)	C15—C13—C14—C9	−50.74 (13)
C7—C11—C12—C13	123.26 (12)	C15—C13—C12—C2	127.24 (12)
C7—C11—C12—C2	13.41 (15)	C15—C13—C12—C11	17.69 (14)
C13—C14—C9—C10	20.16 (14)	C15—C10—C9—C14	15.71 (15)
C13—C14—C9—C8	−89.05 (13)	C15—C10—C9—C8	125.15 (12)
C5—C6—C7—C11	−59.9 (2)	C15—C10—C11—C7	−158.42 (12)
C5—C6—C7—C8	55.3 (2)	C15—C10—C11—C12	−48.72 (14)
C10—C9—C8—O1	145.51 (13)	C15—C19—C18—C17	30.67 (17)
C10—C9—C8—C7	19.49 (14)	C18—C17—C16—C15	38.27 (17)
C10—C9—C8—C2	−88.75 (13)	C18—C19—C15—C13	−132.77 (14)
C10—C11—C12—C13	17.45 (13)	C18—C19—C15—C10	120.51 (15)
C10—C11—C12—C2	−92.39 (12)	C18—C19—C15—C16	−7.03 (17)
C4—C3—C2—C1	−149.20 (14)	C12—C13—C14—C1	−47.02 (13)
C4—C3—C2—C12	88.96 (17)	C12—C13—C14—C9	57.85 (13)
C4—C3—C2—C8	−31.6 (2)	C12—C13—C15—C10	−44.42 (13)
C14—C1—C2—C3	−173.38 (12)	C12—C13—C15—C19	−164.89 (12)
C14—C1—C2—C12	−42.10 (13)	C12—C13—C15—C16	74.44 (15)
C14—C1—C2—C8	57.26 (13)	C12—C2—C8—O1	−176.31 (12)
C14—C13—C15—C10	59.45 (13)	C12—C2—C8—C7	−48.94 (13)
C14—C13—C15—C19	−61.02 (16)	C12—C2—C8—C9	57.41 (12)
C14—C13—C15—C16	178.31 (12)	C8—C7—C11—C10	61.96 (13)
C14—C13—C12—C2	20.92 (14)	C8—C7—C11—C12	−40.92 (13)
C14—C13—C12—C11	−88.63 (13)	C8—C2—C12—C13	−88.92 (12)
C14—C9—C8—O1	−105.59 (14)	C8—C2—C12—C11	19.94 (13)