Acta Cryst. (1999). C**55**, IUC9900110 [**doi:10.1107/S0108270199098820**]

Dimethyl 2-(5,8-dichloro-10-oxotricyclo[7.3.2.$0^{2,7}$]tetradeca-2(7),3,5,11-tetraen-6-ylmethyl)malonate

S. Meinhardt, M. Schürmann, H. Preut and P. Eilbracht

Abstract

The title compound is a tricyclic polyfunctional system bearing an aromatic ring with a chlorine and a methylmalonic substituent and a bicyclo[3.3.2]decane subunit with another chlorine and an enone functionality.

Comment

1,3–5-η-Cycloheptene-1,3-diyl complexes of iron carbonyls can be decomposed by various methods to give different organic products, mostly with additional carbonylation (Hirschfelder & Eilbracht, 1995, 1996). In the present case, an iron compound bearing an enediyne side chain with $CuCl_2$ gives, together with the normal product, in an unexpected, and hitherto not observed cyclization product with aromatization and incorportion of two chlorine units.

Experimental

The title compound was obtained in 29% yield from dicarbonyl[1,3–5-η-2-*endo*-(8',8'-di(methoxycarbonyl)-oct-3'-en-1',5'-diyne- 1'-yl)cyclohept-4-ene-1,3-diyl]-triphenylphosphite iron as a side product together with 29% 4-*endo*-(8',8'-di(methoxycarbonyl)-oct-3'-ene-1',5'-diyn-1'-yl)- bicyclo[3.2.1]-oct-2-en-8-one upon treatment with $CuCl_2$ in dioxane. It was isolated and purified upon chromatography on silica with petroleum ether/*tert*-butyl methyl ether (1:1) and recrystallization from hexane.

Refinement

The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (Sheldrick, 1997). All H atoms were taken from a ΔF map and refined isotropically.

Computing details

Data collection: Nonius MACH3 Argus; cell refinement: Nonius MACH3 Argus; data reduction: CORINC (Dräger & Gattow, 1971); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL*Plus (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

(QA0159)

CIF access

Crystal data

$C_{20}H_{20}Cl_2O_5$	$V = 1872.6\ (4)$ Å^3
$M_r = 411.26$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$
$a = 8.043\ (1)$ Å	$\mu = 0.38$ mm^{-1}
$b = 13.288\ (2)$ Å	$T = 291\ (1)$ K
$c = 17.629\ (2)$ Å	0.50 × 0.35 × 0.30 mm
$\beta = 96.34\ (3)^o$	

Data collection

Nonius MACH3 diffractometer	3323 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (CORINC; Dräger & Gattow, 1971)	$R_{int} = 0.035$
$T_{min} = 0.905$, $T_{max} = 1.000$	3 standard reflections
8968 measured reflections	every 60 min
4285 independent reflections	intensity decay: 0.1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	325 parameters
$wR(F^2) = 0.112$	All H-atom parameters refined
$S = 1.01$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
4285 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}

References

Dräger, M. & Gattow, G. (1971). *CORINC. Acta Chem. Scand.* **25**, 761–762 revised by Wiehl, L. & Schollmeyer, D. (1994). Universität Mainz, Germany.

Hirschfelder, A. & Eilbracht, P. (1995). *Synthesis*, pp. 587.

Hirschfelder, A. & Eilbracht, P. (1996). *Synthesis*, pp. 488.

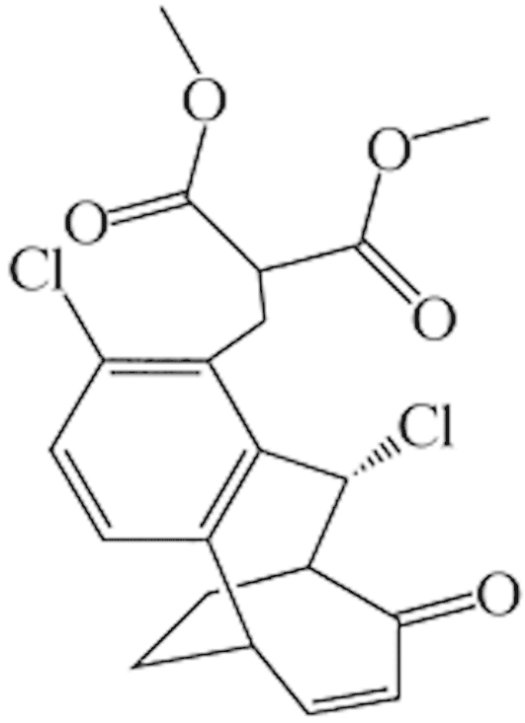
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1 Siemens Analytical Y-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97*. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

Scheme 1



supplementary materials

(QA0159)

Crystal data

$C_{20}H_{20}Cl_2O_5$	F_{000} = 856
M_r = 411.26	D_x = 1.459 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71069 Å
a = 8.043 (1) Å	Cell parameters from 25 reflections
b = 13.288 (2) Å	θ = 13.3–16.2º
c = 17.629 (2) Å	μ = 0.38 mm^{-1}
β = 96.34 (3)º	T = 291 (1) K
V = 1872.6 (4) Å^3	Block, colourless
Z = 4	0.50 × 0.35 × 0.30 mm

Data collection

Nonius MACH3 diffractometer	R_{int} = 0.035
Radiation source: fine-focus sealed tube	θ_{max} = 27.5º
Monochromator: graphite	θ_{min} = 3.1º
T = 291(2) K	h = 0→10
ω–2θ scans	k = −17→17
Absorption correction: ψ scan (CORINC; Dräger & Gattow, 1971)	l = −22→22
T_{min} = 0.905, T_{max} = 1.000	3 standard reflections
8968 measured reflections	every 60 min
4285 independent reflections	intensity decay: 0.1%
3323 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)]$ = 0.040	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.4165P]$ where $P = (F_o^2 + 2F_c^2)/3$?
$wR(F^2)$ = 0.112	$(\Delta/\sigma)_{max}$ = <0.001
S = 1.01	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
4285 reflections	$\Delta\rho_{min}$ = −0.34 e Å^{-3}
325 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0143 (16)
Secondary atom site location: difference Fourier map	

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.11929 (6)	0.03109 (3)	0.09693 (3)	0.04978 (15)
Cl2	−0.16248 (8)	0.29302 (5)	−0.15086 (3)	0.06745 (19)
O1	0.25331 (16)	0.50285 (9)	−0.02365 (7)	0.0435 (3)
O2	0.2749 (2)	0.37200 (11)	−0.10147 (9)	0.0646 (4)
O3	0.30135 (18)	0.33035 (13)	0.11415 (9)	0.0623 (4)
O4	0.08976 (17)	0.43620 (11)	0.12275 (7)	0.0511 (3)
O5	−0.0919 (2)	0.28758 (11)	0.24133 (10)	0.0667 (4)
C1	−0.0633 (2)	0.12039 (13)	0.19961 (9)	0.0386 (4)
H1	0.036 (3)	0.1270 (14)	0.2331 (11)	0.042 (5)*
C2	−0.1651 (2)	0.21118 (13)	0.22052 (9)	0.0425 (4)
C3	−0.3476 (3)	0.20536 (15)	0.21717 (11)	0.0494 (4)
H3	−0.395 (3)	0.2549 (19)	0.2485 (14)	0.067 (7)*
C4	−0.4432 (2)	0.14356 (15)	0.17283 (11)	0.0472 (4)
H4	−0.562 (3)	0.1496 (19)	0.1726 (14)	0.071 (7)*
C5	−0.3856 (2)	0.06915 (13)	0.11658 (10)	0.0396 (4)
H5	−0.485 (3)	0.0370 (14)	0.0940 (11)	0.038 (5)*
C6	−0.2740 (3)	−0.01562 (13)	0.15266 (12)	0.0464 (4)
H6A	−0.343 (3)	−0.0664 (18)	0.1736 (13)	0.061 (6)*
H6B	−0.225 (3)	−0.0472 (15)	0.1116 (12)	0.041 (5)*
C7	−0.1427 (3)	0.01928 (14)	0.21517 (11)	0.0476 (4)
H7A	−0.055 (3)	−0.0337 (18)	0.2203 (13)	0.061 (6)*
H7B	−0.188 (3)	0.0256 (16)	0.2632 (14)	0.056 (6)*
C8	−0.01237 (19)	0.13653 (11)	0.11905 (9)	0.0316 (3)
H8	0.063 (2)	0.1913 (13)	0.1234 (10)	0.028 (4)*
C9	−0.14563 (18)	0.15624 (11)	0.05302 (8)	0.0290 (3)
C10	−0.31266 (19)	0.12573 (11)	0.05269 (9)	0.0318 (3)
C11	−0.4270 (2)	0.15030 (14)	−0.00959 (10)	0.0402 (4)
H11	−0.542 (3)	0.1285 (14)	−0.0076 (11)	0.043 (5)*
C12	−0.3819 (2)	0.20183 (14)	−0.07121 (10)	0.0430 (4)
H12	−0.464 (3)	0.2182 (15)	−0.1125 (13)	0.052 (6)*
C13	−0.2171 (2)	0.22965 (13)	−0.07091 (9)	0.0388 (4)
C14	−0.09543 (19)	0.20944 (11)	−0.01009 (9)	0.0312 (3)
C15	0.0817 (2)	0.24470 (12)	−0.01570 (10)	0.0363 (3)

H15B	0.102 (2)	0.2346 (14)	−0.0677 (12)	0.040 (5)*
H15A	0.160 (2)	0.2061 (14)	0.0176 (11)	0.039 (5)*
C16	0.1064 (2)	0.35728 (12)	0.00369 (9)	0.0334 (3)
H16	0.003 (2)	0.3910 (14)	−0.0053 (11)	0.040 (5)*
C17	0.2220 (2)	0.40875 (13)	−0.04741 (10)	0.0380 (4)
C18	0.3487 (3)	0.56516 (18)	−0.07000 (14)	0.0551 (5)
H18A	0.381 (4)	0.621 (2)	−0.0397 (17)	0.092 (9)*
H18B	0.435 (3)	0.5299 (19)	−0.0840 (15)	0.065 (7)*
H18C	0.276 (3)	0.5796 (18)	−0.1203 (15)	0.065 (7)*
C19	0.1783 (2)	0.37256 (12)	0.08607 (10)	0.0382 (4)
C20	0.1534 (4)	0.4559 (2)	0.20169 (13)	0.0674 (7)
H20A	0.075 (4)	0.500 (2)	0.220 (2)	0.102 (11)*
H20B	0.254 (4)	0.487 (2)	0.2012 (17)	0.083 (9)*
H20C	0.161 (3)	0.395 (2)	0.2274 (15)	0.072 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0429 (3)	0.0460 (3)	0.0592 (3)	0.01623 (18)	0.0000 (2)	−0.00451 (19)
Cl2	0.0721 (4)	0.0882 (4)	0.0413 (3)	−0.0142 (3)	0.0028 (2)	0.0227 (2)
O1	0.0419 (7)	0.0427 (6)	0.0474 (7)	−0.0091 (5)	0.0115 (5)	−0.0003 (5)
O2	0.0828 (11)	0.0553 (8)	0.0634 (9)	−0.0154 (8)	0.0421 (8)	−0.0103 (7)
O3	0.0503 (8)	0.0740 (10)	0.0589 (9)	0.0086 (7)	−0.0109 (7)	0.0043 (7)
O4	0.0536 (8)	0.0578 (8)	0.0419 (7)	−0.0015 (6)	0.0053 (6)	−0.0134 (6)
O5	0.0693 (10)	0.0540 (9)	0.0778 (11)	−0.0114 (7)	0.0134 (8)	−0.0278 (8)
C1	0.0414 (9)	0.0405 (9)	0.0318 (8)	−0.0014 (7)	−0.0059 (7)	0.0010 (6)
C2	0.0538 (10)	0.0430 (9)	0.0312 (8)	−0.0034 (8)	0.0068 (7)	−0.0056 (6)
C3	0.0550 (11)	0.0506 (11)	0.0456 (10)	0.0027 (9)	0.0189 (8)	−0.0046 (8)
C4	0.0399 (9)	0.0554 (11)	0.0486 (10)	−0.0002 (8)	0.0145 (8)	0.0060 (8)
C5	0.0360 (8)	0.0410 (9)	0.0416 (8)	−0.0109 (7)	0.0034 (7)	0.0029 (7)
C6	0.0538 (11)	0.0338 (9)	0.0514 (10)	−0.0082 (8)	0.0049 (9)	0.0058 (8)
C7	0.0566 (11)	0.0415 (10)	0.0435 (10)	0.0001 (8)	0.0005 (8)	0.0105 (7)
C8	0.0288 (7)	0.0297 (7)	0.0355 (8)	0.0017 (6)	−0.0007 (6)	−0.0034 (6)
C9	0.0285 (7)	0.0271 (7)	0.0308 (7)	0.0011 (5)	0.0012 (5)	−0.0042 (5)
C10	0.0308 (7)	0.0312 (7)	0.0331 (7)	−0.0020 (6)	0.0021 (6)	−0.0027 (6)
C11	0.0303 (8)	0.0459 (9)	0.0429 (9)	−0.0039 (7)	−0.0032 (7)	−0.0024 (7)
C12	0.0396 (9)	0.0496 (10)	0.0368 (8)	−0.0002 (7)	−0.0091 (7)	0.0006 (7)
C13	0.0457 (9)	0.0389 (8)	0.0317 (8)	−0.0028 (7)	0.0034 (7)	0.0020 (6)
C14	0.0317 (7)	0.0296 (7)	0.0326 (7)	−0.0001 (6)	0.0047 (6)	−0.0052 (6)
C15	0.0338 (8)	0.0359 (8)	0.0411 (9)	−0.0008 (6)	0.0121 (7)	−0.0027 (7)
C16	0.0271 (7)	0.0361 (8)	0.0376 (8)	−0.0001 (6)	0.0067 (6)	−0.0009 (6)
C17	0.0327 (8)	0.0410 (8)	0.0412 (8)	−0.0019 (7)	0.0079 (7)	0.0019 (7)
C18	0.0566 (13)	0.0505 (12)	0.0608 (13)	−0.0151 (10)	0.0184 (11)	0.0045 (10)
C19	0.0338 (8)	0.0379 (8)	0.0428 (9)	−0.0079 (6)	0.0041 (7)	0.0019 (7)
C20	0.091 (2)	0.0672 (16)	0.0427 (11)	−0.0202 (14)	0.0015 (12)	−0.0133 (11)

Geometric parameters (Å, °)

Cl1—C8	1.8242 (15)	C7—H7B	0.96 (2)

Cl2—C13	1.7392 (17)	C8—C9	1.515 (2)
O1—C17	1.334 (2)	C8—H8	0.943 (18)
O1—C18	1.442 (2)	C9—C10	1.403 (2)
O2—C17	1.191 (2)	C9—C14	1.414 (2)
O3—C19	1.196 (2)	C10—C11	1.391 (2)
O4—C19	1.320 (2)	C11—C12	1.367 (3)
O4—C20	1.453 (3)	C11—H11	0.97 (2)
O5—C2	1.210 (2)	C12—C13	1.376 (3)
C1—C7	1.525 (2)	C12—H12	0.95 (2)
C1—C2	1.526 (3)	C13—C14	1.395 (2)
C1—C8	1.536 (2)	C14—C15	1.513 (2)
C1—H1	0.95 (2)	C15—C16	1.543 (2)
C2—C3	1.464 (3)	C15—H15B	0.96 (2)
C3—C4	1.321 (3)	C15—H15A	0.96 (2)
C3—H3	0.97 (3)	C16—C19	1.516 (2)
C4—C5	1.509 (3)	C16—C17	1.526 (2)
C4—H4	0.96 (3)	C16—H16	0.944 (19)
C5—C10	1.525 (2)	C18—H18A	0.94 (3)
C5—C6	1.534 (3)	C18—H18B	0.90 (3)
C5—H5	0.95 (2)	C18—H18C	1.03 (3)
C6—C7	1.513 (3)	C20—H20A	0.94 (4)
C6—H6A	0.97 (2)	C20—H20B	0.91 (3)
C6—H6B	0.96 (2)	C20—H20C	0.93 (3)
C7—H7A	1.00 (2)		
C17—O1—C18	117.01 (15)	C11—C10—C5	115.08 (14)
C19—O4—C20	115.63 (19)	C9—C10—C5	125.88 (14)
C7—C1—C2	114.00 (16)	C12—C11—C10	122.31 (15)
C7—C1—C8	116.68 (15)	C12—C11—H11	121.0 (11)
C2—C1—C8	108.54 (13)	C10—C11—H11	116.7 (11)
C7—C1—H1	108.2 (12)	C11—C12—C13	118.16 (16)
C2—C1—H1	102.5 (12)	C11—C12—H12	120.0 (13)
C8—C1—H1	105.6 (12)	C13—C12—H12	121.8 (13)
O5—C2—C3	120.59 (18)	C12—C13—C14	123.01 (15)
O5—C2—C1	118.71 (18)	C12—C13—Cl2	117.15 (13)
C3—C2—C1	120.69 (15)	C14—C13—Cl2	119.84 (13)
C4—C3—C2	124.91 (17)	C13—C14—C9	117.64 (14)
C4—C3—H3	121.4 (15)	C13—C14—C15	118.38 (15)
C2—C3—H3	113.6 (15)	C9—C14—C15	123.98 (14)
C3—C4—C5	126.54 (17)	C14—C15—C16	112.65 (13)
C3—C4—H4	117.8 (15)	C14—C15—H15B	106.3 (12)
C5—C4—H4	115.5 (15)	C16—C15—H15B	108.5 (11)
C4—C5—C10	109.48 (14)	C14—C15—H15A	110.7 (12)
C4—C5—C6	114.64 (15)	C16—C15—H15A	108.8 (11)
C10—C5—C6	114.39 (15)	H15B—C15—H15A	109.9 (17)
C4—C5—H5	105.4 (12)	C19—C16—C17	108.23 (13)
C10—C5—H5	106.5 (12)	C19—C16—C15	111.62 (14)
C6—C5—H5	105.6 (11)	C17—C16—C15	112.07 (13)
C7—C6—C5	113.99 (15)	C19—C16—H16	109.4 (11)
C7—C6—H6A	108.4 (14)	C17—C16—H16	105.8 (11)

C5—C6—H6A	109.7 (14)	C15—C16—H16	109.5 (11)
C7—C6—H6B	112.0 (12)	O2—C17—O1	124.34 (16)
C5—C6—H6B	106.1 (12)	O2—C17—C16	125.71 (16)
H6A—C6—H6B	106.3 (18)	O1—C17—C16	109.93 (14)
C6—C7—C1	114.29 (15)	O1—C18—H18A	105.4 (18)
C6—C7—H7A	106.4 (14)	O1—C18—H18B	109.5 (16)
C1—C7—H7A	109.3 (14)	H18A—C18—H18B	113 (2)
C6—C7—H7B	111.3 (14)	O1—C18—H18C	107.9 (14)
C1—C7—H7B	106.8 (13)	H18A—C18—H18C	116 (2)
H7A—C7—H7B	108.6 (19)	H18B—C18—H18C	104 (2)
C9—C8—C1	119.73 (13)	O3—C19—O4	124.34 (17)
C9—C8—Cl1	110.28 (10)	O3—C19—C16	122.95 (17)
C1—C8—Cl1	108.11 (11)	O4—C19—C16	112.70 (14)
C9—C8—H8	108.7 (10)	O4—C20—H20A	105 (2)
C1—C8—H8	105.4 (10)	O4—C20—H20B	107.0 (19)
Cl1—C8—H8	103.3 (10)	H20A—C20—H20B	110 (3)
C10—C9—C14	119.85 (13)	O4—C20—H20C	107.9 (16)
C10—C9—C8	123.30 (14)	H20A—C20—H20C	113 (3)
C14—C9—C8	116.84 (13)	H20B—C20—H20C	113 (3)
C11—C10—C9	119.01 (14)		
C7—C1—C2—O5	149.23 (18)	C9—C10—C11—C12	1.1 (3)
C8—C1—C2—O5	−78.9 (2)	C5—C10—C11—C12	179.36 (16)
C7—C1—C2—C3	−29.4 (2)	C10—C11—C12—C13	0.2 (3)
C8—C1—C2—C3	102.49 (18)	C11—C12—C13—C14	−1.3 (3)
O5—C2—C3—C4	155.4 (2)	C11—C12—C13—Cl2	178.81 (14)
C1—C2—C3—C4	−26.0 (3)	C12—C13—C14—C9	1.2 (2)
C2—C3—C4—C5	−1.2 (3)	Cl2—C13—C14—C9	−178.96 (12)
C3—C4—C5—C10	−65.5 (2)	C12—C13—C14—C15	−179.31 (16)
C3—C4—C5—C6	64.6 (2)	Cl2—C13—C14—C15	0.5 (2)
C4—C5—C6—C7	−42.9 (2)	C10—C9—C14—C13	0.1 (2)
C10—C5—C6—C7	84.8 (2)	C8—C9—C14—C13	−179.02 (13)
C5—C6—C7—C1	−38.6 (3)	C10—C9—C14—C15	−179.34 (14)
C2—C1—C7—C6	83.2 (2)	C8—C9—C14—C15	1.5 (2)
C8—C1—C7—C6	−44.7 (2)	C13—C14—C15—C16	80.28 (18)
C7—C1—C8—C9	74.6 (2)	C9—C14—C15—C16	−100.25 (17)
C2—C1—C8—C9	−55.90 (18)	C14—C15—C16—C19	96.62 (17)
C7—C1—C8—Cl1	−52.81 (17)	C14—C15—C16—C17	−141.79 (14)
C2—C1—C8—Cl1	176.75 (11)	C18—O1—C17—O2	4.2 (3)
C1—C8—C9—C10	−24.2 (2)	C18—O1—C17—C16	−174.54 (16)
Cl1—C8—C9—C10	102.16 (15)	C19—C16—C17—O2	131.1 (2)
C1—C8—C9—C14	154.93 (14)	C15—C16—C17—O2	7.6 (3)
Cl1—C8—C9—C14	−78.72 (15)	C19—C16—C17—O1	−50.18 (18)
C14—C9—C10—C11	−1.2 (2)	C15—C16—C17—O1	−173.70 (14)
C8—C9—C10—C11	177.87 (14)	C20—O4—C19—O3	1.7 (3)
C14—C9—C10—C5	−179.28 (15)	C20—O4—C19—C16	−178.87 (17)
C8—C9—C10—C5	−0.2 (2)	C17—C16—C19—O3	−72.0 (2)
C4—C5—C10—C11	−89.94 (18)	C15—C16—C19—O3	51.8 (2)
C6—C5—C10—C11	139.83 (16)	C17—C16—C19—O4	108.50 (16)
C4—C5—C10—C9	88.19 (19)	C15—C16—C19—O4	−127.71 (15)

C6—C5—C10—C9	−42.0 (2)