Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

anti-1′,6′,7′,8′,9′,14′,15′,16′-Octachlorodispiro[1,3-dioxolane-2,17′-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadecane-18′,2″-1,3-dioxolane]-7′,15′-diene

Megan E. Tenbusch, Matthew D. Brooker, Jacob C. Timmerman, Daniel S. Jones* and Markus Etzkorn*

Department of Chemistry, The University of North Carolina at Charlotte, 9201 University City Blvd, Charlotte, NC 28223, USA
Correspondence e-mail: djones@uncc.edu, metzkorn@uncc.edu

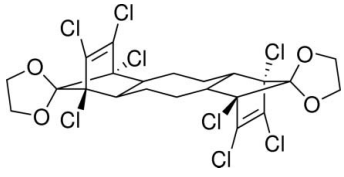
Received 15 June 2010; accepted 23 June 2010

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.118; data-to-parameter ratio = 14.7.

The title compound, $C_{22}H_{20}Cl_8O_4$, was prepared as part of the synthesis of precursors for the preparation of fluorinated molecular tweezers. The molecule sits on an inversion center, thus requiring that the cyclooctane ring adopt a chair conformation.

Related literature

For related structures, see: Garcia *et al.* (1991*b*,*c*). For related chemistry on analogous polycyclic scaffolds, see: Garcia *et al.* (1991*a*); Chou *et al.* (2005)



Experimental

Crystal data

$C_{22}H_{20}Cl_8O_4$
M_r = 631.98
Monoclinic, $P2_1/c$
a = 9.5332 (7) Å
b = 7.9121 (6) Å
c = 17.014 (2) Å
β = 101.099 (8)°
V = 1259.3 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 8.44 mm^{-1}
T = 295 K
0.25 × 0.20 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.190, T_{max} = 0.561
4703 measured reflections
2275 independent reflections
1702 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
3 standard reflections every 62 reflections
intensity decay: 13%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.118
S = 1.05
2275 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *DIRDIF08* (Beurskens *et al.*, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported in part by funds provided by The University of North Carolina at Charlotte.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2171).

References

Beurskens, P. T., Beurskens, G., de Gelder, R., Garciía-Granda, S., Gould, R. O. & Smits, J. M. M. (2008). *The DIRDIF2008 Program System*. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Chou, T.-H., Liao, K.-C. & Lin, J.-J. (2005). *Org. Lett.* **7**, 4843–4846.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Garcia, J. G., Fronczek, F. R. & McLaughlin, M. L. (1991*a*). *Acta Cryst.* C**47**, 206–209.
Garcia, J. G., Fronczek, F. R. & McLaughlin, M. L. (1991*b*). *Acta Cryst.* C**47**, 451–453.
Garcia, J. G., Fronczek, F. R. & McLaughlin, M. L. (1991*c*). *Tetrahedron Lett.* **32**, 3289–3292.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1882 [**doi:10.1107/S1600536810024669**]

anti-1',6',7',8',9',14',15',16'-Octachlorodispiro[1,3-dioxolane-2,17'-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadecane-18',2''-1,3-dioxolane]-7',15'-diene

M. E. Tenbusch, M. D. Brooker, J. C. Timmerman, D. S. Jones and M. Etzkorn

Comment

The twofold Diels-Alder reaction of cyclooctadiene **1** with two equivalents of cyclopentadiene or cyclopentadienone derivatives (**2a-c**) furnishes the corresponding polycyclic bisadducts *endo,endo,syn*-**3** and *endo,endo,anti*- **4** in a 1:4 ratio (Garcia *et* al., 1991*a,b,c*). For the synthesis of compounds with new luminescent properties (Chou *et al.*, 2005) or the construction of molecular tweezers *syn* derivative **3** is an ideal starting material with the required orientation of both double bonds on one side of the molecule. Nevertheless, the separation of *syn* isomer **3c** from *anti* ketal **4c** prior to subsequent functionalization was often unsatisfactory in our hands. Thus, we converted cyclooctadiene **1** with the spiroketal **2 d** to the spiropolycyclic bisadducts **3 d** and **4 d** in 85–90% yield, typically with an isomer distribution that did not differ significantly from the non-spirocyclic ketal case (**1**+**2c**). Furthermore, compound **3 d** was easily separated from *anti*-isomer **4 d** by repeated recrystallization from hot diethyl ether, *i.e.*, the ether solution becomes more enriched in *syn*-isomer **3 d**, and initially the clean *anti*-isomer **4 d** precipitates upon cooling. We were able to grow single crystals of **4 d** from chloroform and determined the crystal structure of compound **4 d**, thus confirming the correct spectroscopic assignment of both isomers.

Two closely related structures have been found. The first (Garcia *et al., 1*991*b*) has an open ketal structure on each of the bridgehead carbon atoms, while the second (Garcia *et al., 1*991*c*) has no substituents on the bridgehead carbon atoms. Each of these two structures sits on an inversion center and thus assumes a conformation nearly identical to that of the title compound.

Experimental

A mixture of cyclooctadiene **1** (3 g, 29 mmol) and spiroketal **2 d** (15 g, 57 mmol) was refluxed in toluene (5 ml) for three hours. The beige paste was filtered, washed with methylene chloride (70 ml), dried and washed again with methanol (*ca* 15 ml) to remove small amounts of the mono-Diels-Alder adduct. The remaining colorless solid (14.5 g, 83%) contained a 1:4 mixture of **3 d** and **4 d**, respectively. After one recrystallization from hot diethyl ether the pure *anti*-isomer **4 d** was obtained as a colorless precipitate.

Mp.> 295 °C (decomposition); *IR (KBr)*: ν~ = 2952, 2905 (CH_2),1596 (C═C), 1467 (CH_2 deformation), 1355, 1284, 1267, 1245, 1222, 1181, 1132, 1105,1091, 1037 (C—Cl), 1009, 946, 891, 851, 809, 770, 730 cm^{-1}; *^{1}H NMR ($CDCl_3$; 500 MHz):* δ = 4.20–4.10 (m, 8H; H-4, -5, -4'', -5''), 2.78–2.62 (m, 4H; H-2', -5', 10', -13'), 2.20–2.00 (m, 4H; H-3', -4', -11', -12'), 0.95–0.75 (m, 4H; H-3', -4', -11', -12'); *^{13}C NMR ($CDCL_3$,75.6 MHz):* δ=128.5 (C-7', -8', -15', -16'), 120.5 (C-17', -18'), 77.6 (C-1', -6', 9', -14'), 67.7* (C-4, -4''), 66.5* (C-5, -5''), 51.8(C-2', -5', -10', 13'), 21.9 (C-3', -4', -11', -12'); *EA:* calc. C (41.81) H (3.19); found C: 41.83, H: 3.16 (calc.).

Refinement

H atoms were constrained using a riding model. The methylene C—H bond lengths were fixed at 0.97 Å and the methine C—H bond lengths at 0.98 Å, with U_{iso}(H) = 1.2 $U_{eq.}$ (C).

Figures

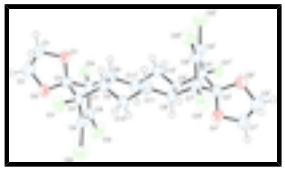


Fig. 1. A view of the title compound with 50% probability displacement ellipsoids. [Symmetry code: (i) -*x* + 2, -*y* + 2, -*z* + 2]

Fig. 2. Synthesis scheme.

anti-1',6',7',8',9',14',15',16'-Octachlorodispiro[1,3-dioxolane- 2,17'-pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadecane-18',2''-1,3- dioxolane]-7',15'-diene

Crystal data

$C_{22}H_{20}Cl_8O_4$	F(000) = 640
M_r = 631.98	D_x = 1.677 Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54184 Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections
a = 9.5332 (7) Å	θ = 5.3–18.2°
b = 7.9121 (6) Å	μ = 8.44 mm^{-1}
c = 17.014 (2) Å	T = 295 K
β = 101.099 (8)°	Prism, colorless
V = 1259.3 (2) Å^3	0.25 × 0.20 × 0.08 mm
Z = 2	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.047
graphite	θ_{max} = 67.4°, θ_{min} = 4.7°
non–profiled ω/2θ scans	h = −11→11
Absorption correction: multi-scan (Blessing, 1995)	k = −9→9
T_{min} = 0.190, T_{max} = 0.561	l = −20→0
4703 measured reflections	3 standard reflections every 62 reflections
2275 independent reflections	intensity decay: 13%
1702 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.5139P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2275 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
155 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL*
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0010 (3)

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}
Cl1	0.56200 (8)	0.74022 (12)	1.00965 (5)	0.0547 (3)
Cl4	0.77203 (10)	0.88651 (12)	0.73738 (5)	0.0557 (3)
Cl2	0.79698 (10)	0.44785 (12)	0.98707 (7)	0.0657 (3)
Cl3	0.93205 (10)	0.54119 (14)	0.82005 (6)	0.0648 (3)
O1	0.5602 (2)	0.9949 (3)	0.85728 (14)	0.0479 (5)
O2	0.5274 (2)	0.7211 (3)	0.81904 (14)	0.0494 (6)
C5	0.7945 (3)	0.9248 (4)	0.97774 (18)	0.0380 (6)
H5	0.7385	1.0223	0.9895	0.046*
C10	0.9019 (3)	0.8836 (4)	1.05363 (19)	0.0410 (7)
H10A	0.9704	0.8028	1.0405	0.049*
H10B	0.8517	0.8296	1.0914	0.049*
C11	0.9836 (3)	1.0369 (4)	1.09459 (19)	0.0434 (7)
H11A	0.9466	1.1379	1.0655	0.052*
H11B	0.9643	1.0463	1.1483	0.052*
C7	0.7734 (3)	0.8387 (4)	0.83817 (19)	0.0424 (7)
C1	0.4108 (3)	0.9714 (5)	0.8255 (2)	0.0544 (9)
H1A	0.3719	1.0666	0.7925	0.065*

H1B	0.3574	0.9574	0.8682	0.065*
C8	0.8224 (3)	0.6619 (4)	0.8649 (2)	0.0439 (7)
C6	0.8545 (3)	0.9680 (4)	0.89984 (17)	0.0381 (6)
H6	0.8212	1.0815	0.8822	0.046*
C3	0.6241 (3)	0.8363 (4)	0.86189 (19)	0.0404 (7)
C4	0.6875 (3)	0.7784 (4)	0.94892 (18)	0.0392 (7)
C9	0.7714 (3)	0.6257 (4)	0.9301 (2)	0.0432 (7)
C2	0.4067 (4)	0.8167 (6)	0.7776 (3)	0.0729 (12)
H2A	0.318	0.7555	0.7762	0.088*
H2B	0.4167	0.8422	0.7232	0.088*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0427 (4)	0.0648 (5)	0.0619 (5)	−0.0091 (4)	0.0232 (4)	−0.0018 (4)
Cl4	0.0560 (5)	0.0698 (6)	0.0420 (4)	−0.0103 (4)	0.0113 (3)	−0.0032 (4)
Cl2	0.0621 (6)	0.0497 (5)	0.0861 (7)	0.0058 (4)	0.0161 (5)	0.0163 (4)
Cl3	0.0525 (5)	0.0752 (6)	0.0686 (6)	0.0162 (4)	0.0161 (4)	−0.0218 (5)
O1	0.0365 (11)	0.0445 (12)	0.0602 (14)	0.0041 (9)	0.0033 (10)	−0.0058 (10)
O2	0.0357 (11)	0.0508 (13)	0.0591 (14)	−0.0048 (9)	0.0021 (10)	−0.0114 (11)
C5	0.0330 (14)	0.0402 (15)	0.0423 (16)	−0.0014 (12)	0.0113 (12)	−0.0037 (12)
C10	0.0362 (15)	0.0455 (16)	0.0430 (16)	−0.0041 (13)	0.0119 (13)	0.0019 (13)
C11	0.0381 (16)	0.0537 (18)	0.0406 (17)	−0.0047 (13)	0.0127 (13)	−0.0034 (14)
C7	0.0374 (15)	0.0500 (18)	0.0412 (16)	−0.0025 (14)	0.0108 (13)	−0.0043 (13)
C1	0.0339 (16)	0.062 (2)	0.065 (2)	0.0057 (15)	0.0040 (15)	0.0036 (17)
C8	0.0331 (14)	0.0465 (17)	0.0527 (18)	0.0015 (13)	0.0097 (13)	−0.0124 (14)
C6	0.0356 (15)	0.0406 (15)	0.0388 (16)	−0.0018 (12)	0.0086 (12)	−0.0017 (12)
C3	0.0331 (15)	0.0401 (15)	0.0474 (17)	−0.0008 (12)	0.0061 (13)	−0.0062 (13)
C4	0.0329 (14)	0.0427 (16)	0.0442 (16)	−0.0007 (12)	0.0126 (12)	−0.0020 (13)
C9	0.0361 (15)	0.0390 (15)	0.0538 (19)	0.0000 (13)	0.0071 (14)	−0.0007 (14)
C2	0.046 (2)	0.077 (3)	0.085 (3)	0.008 (2)	−0.014 (2)	−0.015 (2)

Geometric parameters (Å, °)

Cl1—C4	1.751 (3)	C11—H11A	0.97
Cl4—C7	1.754 (3)	C11—H11B	0.97
Cl2—C9	1.700 (3)	C7—C8	1.516 (4)
Cl3—C8	1.701 (3)	C7—C3	1.553 (4)
O1—C3	1.391 (4)	C7—C6	1.560 (4)
O1—C1	1.435 (4)	C1—C2	1.467 (6)
O2—C3	1.397 (4)	C1—H1A	0.97
O2—C2	1.443 (4)	C1—H1B	0.97
C5—C10	1.521 (4)	C8—C9	1.326 (5)
C5—C4	1.559 (4)	C6—C11^{i}	1.528 (4)
C5—C6	1.579 (4)	C6—H6	0.98
C5—H5	0.98	C3—C4	1.557 (4)
C10—C11	1.535 (4)	C4—C9	1.517 (4)
C10—H10A	0.97	C2—H2A	0.97

C10—H10B	0.97	C2—H2B	0.97
C11—C6^{i}	1.528 (4)		
C3—O1—C1	107.2 (2)	H1A—C1—H1B	109
C3—O2—C2	107.3 (3)	C9—C8—C7	108.0 (3)
C10—C5—C4	113.6 (3)	C9—C8—Cl3	127.6 (3)
C10—C5—C6	117.7 (2)	C7—C8—Cl3	124.3 (2)
C4—C5—C6	102.6 (2)	C11^{i}—C6—C7	112.9 (2)
C10—C5—H5	107.5	C11^{i}—C6—C5	117.9 (2)
C4—C5—H5	107.5	C7—C6—C5	102.1 (2)
C6—C5—H5	107.5	C11^{i}—C6—H6	107.8
C5—C10—C11	114.6 (3)	C7—C6—H6	107.8
C5—C10—H10A	108.6	C5—C6—H6	107.8
C11—C10—H10A	108.6	O1—C3—O2	108.7 (2)
C5—C10—H10B	108.6	O1—C3—C7	112.8 (3)
C11—C10—H10B	108.6	O2—C3—C7	114.7 (3)
H10A—C10—H10B	107.6	O1—C3—C4	113.9 (2)
C6^{i}—C11—C10	115.3 (3)	O2—C3—C4	113.6 (3)
C6^{i}—C11—H11A	108.5	C7—C3—C4	92.5 (2)
C10—C11—H11A	108.5	C9—C4—C3	99.0 (2)
C6^{i}—C11—H11B	108.5	C9—C4—C5	108.6 (2)
C10—C11—H11B	108.5	C3—C4—C5	101.0 (2)
H11A—C11—H11B	107.5	C9—C4—Cl1	115.8 (2)
C8—C7—C3	99.0 (2)	C3—C4—Cl1	115.3 (2)
C8—C7—C6	108.6 (3)	C5—C4—Cl1	115.0 (2)
C3—C7—C6	101.2 (2)	C8—C9—C4	107.3 (3)
C8—C7—Cl4	115.9 (2)	C8—C9—Cl2	128.4 (3)
C3—C7—Cl4	115.0 (2)	C4—C9—Cl2	124.2 (2)
C6—C7—Cl4	115.2 (2)	O2—C2—C1	103.4 (3)
O1—C1—C2	103.6 (3)	O2—C2—H2A	111.1
O1—C1—H1A	111	C1—C2—H2A	111.1
C2—C1—H1A	111	O2—C2—H2B	111.1
O1—C1—H1B	111	C1—C2—H2B	111.1
C2—C1—H1B	111	H2A—C2—H2B	109

Symmetry codes: (i) −*x*+2, −*y*+2, −*z*+2.

Fig. 1

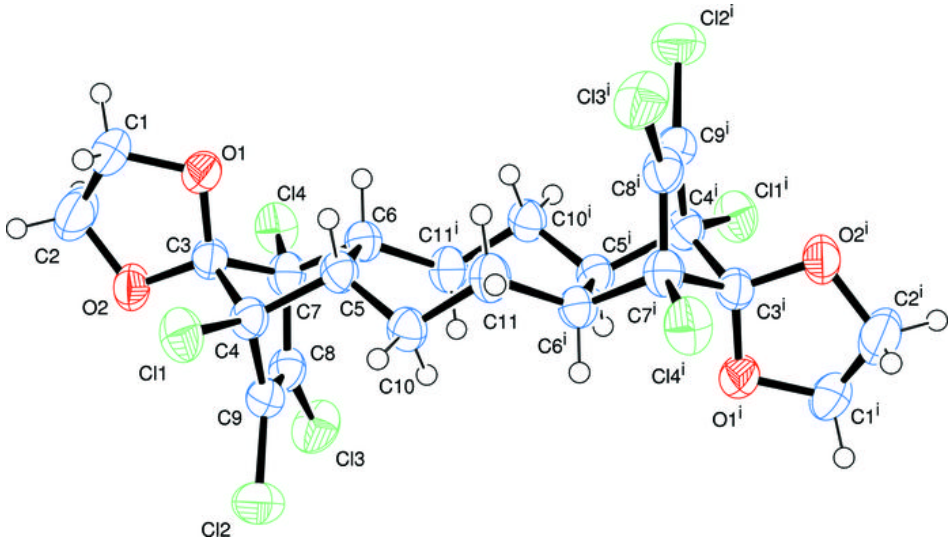
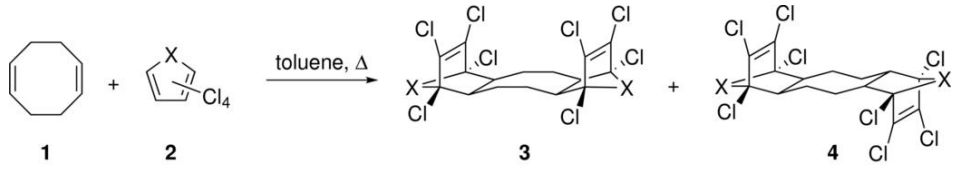

Cl2i
Cl3i
C9i
C8i
C4i
Cl1i
O2i
C2i
C1i
O1i
Cl4i
C3i
C7i
C6i
C5i
C10i
C11i
C1
O1
C2
O2
C3
Cl4
C6
C11
C10
C5
C7
C8
C4
Cl1
C9
Cl3
Cl2

Fig. 2



[X = CH_2 (**a**); CCl_2 (**b**); $C(OCH_3)_2$ (**c**); $C(OCH_2)_2$ (**d**)]