Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

syn-1,2,3,4,5,6,7,8,11,11,12,12-Dodecachloro-9,10-dimethoxy-1,4,5,8-tetrahydro-1,4:5,8-dimethanoanthracene

Amanda J. Watson, Megan E. O'Brien, Matthew D. Brooker, Daniel S. Jones* and Markus Etzkorn*

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

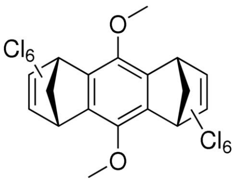
Received 14 July 2007; accepted 16 July 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.057; wR factor = 0.167; data-to-parameter ratio = 15.1.

The title compound, $C_{18}H_6Cl_{12}O_2$, is a valuable precursor for the synthesis of molecular tweezers. These tweezers require a tether part and two pincer units with *syn* orientation that can create a cavity large enough to include suitable guest compounds by noncovalent interaction. The title compound is an ideal tether unit with *syn*-oriented double bonds, a π–π distance of 6.28 (1) Å, and the relative ease of functionalization of the two dichloroethene subunits.

Related literature

The title structure can be directly compared with one structure in the Cambridge Structural Database [Version 5.28 (Allen, 2002); *ConQuest*, Version 1.9 (Bruno *et al.*, 2002)], refcode RIHKIC (Sun & Watson, 1996). See also: Ashton *et al.* (1992); Benkhoff *et al.* (1997); Hart *et al.* (1983); Klärner *et al.* (2004); Little *et al.* (1972, 1974); Mehta *et al.* (1989).



Experimental

Crystal data

$C_{18}H_6Cl_{12}O_2$
M_r = 679.63
Triclinic, $P\overline{1}$
a = 9.0234 (9) Å
b = 10.4481 (13) Å
c = 14.1446 (16) Å
α = 95.513 (10)°
β = 102.642 (9)°
γ = 106.388 (9)°
V = 1230.5 (3) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 12.53 mm^{-1}
T = 293 (2) K
0.25 × 0.22 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: analytical (Alcock, 1970)
T_{min} = 0.083, T_{max} = 0.262
9251 measured reflections
4420 independent reflections
3337 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
3 standard reflections every 142 reflections intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.167
S = 1.06
4420 reflections
292 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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: FL2148).

References

Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Ashton, P. R., Brown, G. R., Isaacs, N. S., Giuffrida, D., Kohnke, F. H., Mathias, J. P., Slawin, A. M. Z., Smith, D. R., Stoddart, J. F. & Williams, D. J. (1992). *J. Am. Chem. Soc.* **114**, 6330–6353.
Benkhoff, J., Boese, R. & Klärner, F.-G. (1997). *Liebigs Ann. Recl.* pp. 501–506.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
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.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Hart, H., Raju, N., Meador, M. A. & Ward, D. L. (1983). *J. Org. Chem.* **48**, 4357–4360.
Klärner, F.-G., Polkowska, J., Panitzky, J., Seelbach, U. P., Burkert, U., Kamieth, M., Baumann, M., Wigger, A. E., Boese, R. & Bläser, D. (2004). *Eur. J. Org. Chem.* pp. 1405–1423.
Little, J. R., Nudenberg, W. & Rim, Y. S. (1972). German Patent No. DE 2 151 072.
Little, J. R., Nudenberg, W. & Rim, Y. S. (1974). United States Patent No. US 4 009 200.
Mehta, G., Padma, S., Karra, S. R., Gopidas, K. R., Cyr, D. R., Das, P. K. & George, M. V. (1989). *J. Org. Chem.* **54**, 1342–1346.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sun, D. & Watson, W. H. (1996). *J. Chem. Crystallogr.* **26**, 721–737.

doi:10.1107/S1600536807034757

supplementary materials

Acta Cryst. (2007). E**63**, o3565 [**doi:10.1107/S1600536807034757**]

syn-1,2,3,4,5,6,7,8,11,11,12,12-Dodecachloro-9,10-dimethoxy-1,4,5,8-tetrahydro-1,4:5,8-dimethanoanthracene

A. J. Watson, M. E. O'Brien, M. D. Brooker, D. S. Jones and M. Etzkorn

Comment

The *syn*-tetrahydro-dimethanoanthracene unit, **1**, a rigid polycycle, can be found as a substructure in various molecular architectures, *e.g.*, belt-like macrocycles and precursors of important cage hydrocarbons to name but a few (Benkhoff *et al.*, 1997; Mehta *et al.*, 1989). Several heterocyclic (*e.g.*, **2**) (Hart *et al.*, 1983; Ashton, *et al.*, 1992) or substituted derivatives (Klärner *et al.*, 2004) of the parent compound, **1**, have been reported, and a hydroquinone precursor (**7 b**) (Little, *et al.*, 1972, 1974) of the novel title compound **3 b(*syn*)** was discussed in a few patents on flame retardants.

Nevertheless, the patent literature does not disclose any details on the configuration of the precursor compound, *i.e. syn versus anti* orientation of the double bonds, a crucial detail for any further synthetic applications. Excluding any complex molecular tweezer architectures, very few X-ray structures of derivatives with *syn* oriented double bonds have been reported.

The retro-synthetic analysis dissects the tetrahydro-dimethanoanthracene scaffold into building blocks that demand Diels–Alder reactions as key steps. Benzoquinone (**4**) is converted into the norbornenobenzoquinone **5** by a short reaction sequence. Conversion of the latter dienophile with suitable dienes leads to the Diels-Alder adducts **6**. In the case of cyclopentadiene the desired *endo,endo,syn* intermediate **6a** is contaminated with the *endo,endo,anti* adduct (ratio: 62:38), and the former can be separated by repetitive recrystallization. If hexachlorocyclopentadiene is reacted with precursor **5 b**, the pure *endo,endo,syn* isomer **6 b** precipitates out of the reaction mixture and can be used without further purification. The title compound **3 b (*syn*)** is obtained either *via* the hydroquinone derivative **7 b** or in a one-step procedure.

The title structure can be directly compared to one structure in the Cambridge Structural Database [Version 5.28; (Allen, 2002); *ConQuest*, Version 1.9 (Bruno *et al.*, 2002)], 1,4,6,9-Tetrahydro-1,2,3,4,6,7,8,9-octachloro-1,4-dichloromethano-6,9-dimethoxymethanoanthracene-5,10-diol (Sun & Watson, 1996). This structure differs **1** in that the bridgehead carbon on one of the norboradiene subunits has methoxy groups instead of chlorine atoms, and the aromatic ring has two hydroxyl groups where**1** has two methoxy groups. The two methoxy methyl groups are on opposite sides of the aromatic ring. Important distances **1** inculde the π-π distance of 6.279 (7) Å (calculated as the average of the C3—C6 and the C2—C7 distances); 1.323 (8) Å, the average of the C2—C3 and C6—C7 double bond lengths; 1.565 (6) Å, the average of the C1—C11, C11—C4, C8—C12, and C12—C5 bridgehead lengths; 1.527 (5) Å, the average of the C1—C13, C4—C14, C5—C15, and C8—C16 lengths; and 1.529 (7) Å, the average of the C1—C2, C3—C4, C5—C6, and C7—C8 lengths.

The corresponding lengths for the Sun & Watson structure are, respectively, 6.539 Å, 1.301 Å, 1.602 Å, 1.550 Å, and 1.519 Å.

Experimental

Compound **6 b** was prepared after the reported procedure in US patent 4,009,200 and converted into the title compound **3 b (*syn*).** DBU (52 mg, 0.34 mmol) was added dropwise to a cooled (−23 °C) suspension of dione **5c** (100 mg, 0.15 mmol) in degassed acetonitrile (1 ml). The red mixture was allowed to warm up to room temperature and stirred for 1 hr. After cooling to −23 °C methyl iodide (109 mg, 0.77 mmol) was added slowly and the mixture stirred an additional 2 hrs at room temperature. This cycle was repeated with the same amounts of DBU and methyl iodide prior to stirring overnight at ambient temperature. The reaction was then quenched with 2% HCl (10 ml), cooled in an ice bath, and stirred vigorously for 30 min. The beige precipitate was filtered off, washed with 2% HCl (2 *x* 8 ml) and water (2 *x* 8 ml) to yield the tan solid product (96 mg, 91%). mp.: > 300 °C, IR: ~ν = 2984 (w, C—H), 1607 (m, C=C), 1485 (s, C=C), 1420 (m, C=C), 1253 (s, Ar—O—CH_3), 1146 (*m*), 1112 (*m*), 1093 (*m*), 1008 (*s*), 937 (*m*), 906 (*s*), 845 (*s*), 796 (*s*), 774 (*s*), 736 (*s*), 704 (*m*), 676 (*s*), 658 (*s*) cm^{-1}; ^1H NMR (CD_2Cl_2, 500 MHz): δ = 3.78 (*s*) p.p.m.; ^{13}C NMR (CD_2Cl_2, 125.7 MHz): δ = 150.5, 139.4, 136.8, 112.8, 82.8, 66.4 p.p.m..

Refinement

H atoms were constrained using a riding model. The methyl C—H bond lengths were fixed at 0.96 Å, with $U_{iso}(H) = 1.5 U_{eq.}$ (C). An idealized tetrahedral geometry was used, and the torsion angles about the O—C bonds were refined. Careful analytical absorption corrections were made.

Figures

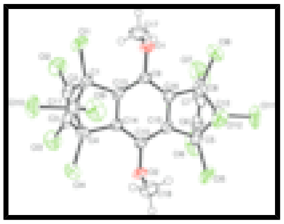


Fig. 1. View of title compound (50% probability displacement ellipsoids).

Fig. 2. Schematic views of the structures of (1), (2/anti), (2/*syn*), (3 b/anti) and (3 b/*syn*).

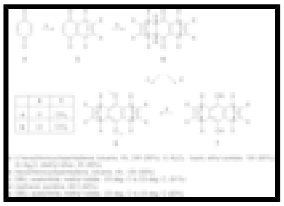


Fig. 3. Reaction scheme for the formation of the title compound.

syn-1,2,3,4,5,6,7,8,11,11,12,12-Dodecachloro-9,10-dimethoxy-1,4,5,8-\ tetrahydro-1,4:5,8-dimethanoanthracene

Crystal data

$C_{18}H_6Cl_{12}O_2$	$Z = 2$
$M_r = 679.63$	$F_{000} = 668$
Triclinic, $P\bar{1}$	$D_x = 1.834$ Mg m^{-3}
Hall symbol: -P 1	Cu $K\alpha$ radiation $\lambda = 1.54184$ Å
$a = 9.0234$ (9) Å	Cell parameters from 25 reflections

b = 10.4481 (13) Å	θ = 5.3–17.9°
c = 14.1446 (16) Å	μ = 12.53 mm^{-1}
α = 95.513 (10)°	T = 293 (2) K
β = 102.642 (9)°	Prism, colorless
γ = 106.388 (9)°	0.25 × 0.22 × 0.18 mm
V = 1230.5 (3) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.057
Radiation source: normal-focus sealed tube	θ_{max} = 67.4°
Monochromator: graphite	θ_{min} = 3.3°
T = 293(2) K	$h = -10 \rightarrow 10$
non–profiled ω/2θ scans	$k = -12 \rightarrow 12$
Absorption correction: analytical (Alcock, 1970)	$l = -16 \rightarrow 16$
T_{min} = 0.083, T_{max} = 0.262	3 standard reflections
9251 measured reflections	every 142 reflections
4420 independent reflections	intensity decay: 3%
3337 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0879P)^2 + 0.9391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.057	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR(F^2)$ = 0.167	$\Delta\rho_{\text{max}}$ = 0.57 e Å^{-3}
S = 1.06	$\Delta\rho_{\text{min}}$ = −0.67 e Å^{-3}
4420 reflections	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
292 parameters	Extinction coefficient: 0.0031 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl3	−0.01029 (19)	0.31078 (19)	−0.07565 (9)	0.0786 (5)
Cl7	0.1101 (3)	0.95985 (17)	0.29703 (14)	0.1033 (7)
Cl2	−0.3435 (2)	0.3885 (2)	−0.05138 (11)	0.1043 (7)

C3	−0.0963 (5)	0.2952 (5)	0.0187 (3)	0.0521 (11)
C2	−0.2274 (6)	0.3227 (6)	0.0278 (3)	0.0614 (14)
Cl12	0.21539 (12)	0.58029 (13)	0.52544 (7)	0.0536 (3)
Cl4	0.10264 (15)	0.15678 (13)	0.10525 (9)	0.0592 (3)
Cl5	0.51750 (12)	0.67200 (16)	0.40722 (9)	0.0689 (4)
Cl8	−0.03198 (17)	0.77442 (14)	0.45323 (9)	0.0663 (4)
Cl11	0.37149 (17)	0.86235 (15)	0.54832 (9)	0.0738 (4)
Cl1	−0.44172 (14)	0.2719 (2)	0.14267 (12)	0.0925 (6)
Cl9	−0.15908 (18)	0.13406 (14)	0.25791 (11)	0.0730 (4)
Cl6	0.4443 (2)	0.88797 (15)	0.26215 (10)	0.0864 (5)
Cl10	−0.29921 (18)	0.02870 (17)	0.05381 (13)	0.0928 (6)
O1	−0.2393 (3)	0.5469 (4)	0.2777 (2)	0.0515 (8)
O2	0.3151 (3)	0.4264 (3)	0.2426 (2)	0.0456 (7)
C15	0.1861 (4)	0.5720 (4)	0.3114 (3)	0.0363 (8)
C9	−0.1039 (4)	0.5201 (4)	0.2664 (3)	0.0391 (9)
C12	0.2542 (5)	0.7175 (5)	0.4624 (3)	0.0465 (10)
C16	0.0469 (5)	0.6002 (4)	0.3208 (3)	0.0371 (8)
C10	0.1794 (4)	0.4574 (4)	0.2498 (3)	0.0346 (8)
C4	−0.0257 (5)	0.2530 (5)	0.1145 (3)	0.0440 (9)
C13	−0.1097 (4)	0.4080 (4)	0.2029 (3)	0.0395 (9)
C14	0.0295 (4)	0.3786 (4)	0.1943 (3)	0.0359 (8)
C6	0.3174 (6)	0.8136 (5)	0.3272 (3)	0.0562 (12)
C5	0.3265 (5)	0.6894 (4)	0.3738 (3)	0.0426 (9)
C1	−0.2483 (5)	0.3003 (5)	0.1291 (3)	0.0546 (12)
C8	0.1027 (5)	0.7332 (5)	0.3933 (3)	0.0459 (10)
C18	0.3629 (6)	0.3502 (7)	0.3163 (4)	0.0690 (15)
H18A	0.3632	0.3932	0.3794	0.103*
H18B	0.4682	0.3464	0.3171	0.103*
H18C	0.2891	0.26	0.3014	0.103*
C7	0.1883 (7)	0.8419 (5)	0.3395 (4)	0.0598 (13)
C11	−0.1837 (6)	0.1758 (5)	0.1387 (3)	0.0554 (12)
C17	−0.2952 (7)	0.6256 (8)	0.2108 (4)	0.081 (2)
H17A	−0.2221	0.716	0.226	0.122*
H17B	−0.3987	0.6279	0.216	0.122*
H17C	−0.3026	0.5863	0.1451	0.122*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl3	0.0899 (10)	0.1066 (12)	0.0416 (6)	0.0322 (9)	0.0220 (6)	0.0076 (7)
Cl7	0.1754 (19)	0.0533 (9)	0.0991 (12)	0.0522 (11)	0.0431 (12)	0.0300 (8)
Cl2	0.0935 (11)	0.1611 (19)	0.0523 (8)	0.0722 (12)	−0.0246 (7)	−0.0085 (9)
C3	0.050 (2)	0.061 (3)	0.035 (2)	0.011 (2)	0.0039 (18)	−0.006 (2)
C2	0.052 (3)	0.083 (4)	0.033 (2)	0.019 (3)	−0.0121 (19)	−0.011 (2)
Cl12	0.0448 (5)	0.0621 (7)	0.0421 (5)	0.0011 (5)	0.0046 (4)	0.0166 (5)
Cl4	0.0646 (7)	0.0510 (7)	0.0624 (7)	0.0218 (6)	0.0173 (5)	−0.0034 (5)
Cl5	0.0318 (5)	0.0948 (11)	0.0565 (7)	−0.0039 (6)	0.0018 (4)	−0.0044 (6)
Cl8	0.0770 (8)	0.0639 (8)	0.0610 (7)	0.0278 (7)	0.0233 (6)	−0.0058 (6)

Cl11	0.0735 (8)	0.0640 (9)	0.0485 (6)	−0.0236 (7)	0.0141 (6)	−0.0175 (6)
Cl1	0.0298 (5)	0.1238 (15)	0.0936 (10)	0.0014 (7)	0.0074 (6)	−0.0364 (10)
Cl9	0.0870 (9)	0.0560 (8)	0.0751 (8)	0.0054 (7)	0.0398 (7)	0.0146 (6)
Cl6	0.1128 (12)	0.0578 (9)	0.0646 (8)	−0.0239 (8)	0.0437 (8)	0.0023 (6)
Cl10	0.0692 (9)	0.0681 (10)	0.1015 (11)	−0.0210 (7)	0.0199 (8)	−0.0391 (9)
O1	0.0396 (15)	0.073 (2)	0.0451 (16)	0.0267 (16)	0.0071 (12)	0.0039 (15)
O2	0.0321 (13)	0.057 (2)	0.0462 (16)	0.0149 (13)	0.0075 (12)	0.0058 (14)
C15	0.0313 (17)	0.037 (2)	0.0326 (18)	0.0019 (16)	0.0038 (14)	0.0042 (15)
C9	0.0335 (18)	0.050 (2)	0.0325 (18)	0.0164 (18)	0.0038 (15)	0.0042 (17)
C12	0.047 (2)	0.039 (2)	0.039 (2)	−0.0070 (19)	0.0105 (18)	−0.0016 (18)
C16	0.041 (2)	0.036 (2)	0.0298 (18)	0.0100 (17)	0.0033 (15)	0.0051 (15)
C10	0.0293 (17)	0.039 (2)	0.0321 (18)	0.0070 (16)	0.0048 (14)	0.0063 (15)
C4	0.038 (2)	0.045 (2)	0.041 (2)	0.0054 (18)	0.0079 (16)	−0.0042 (18)
C13	0.0317 (18)	0.046 (2)	0.0328 (18)	0.0074 (17)	0.0016 (15)	−0.0002 (16)
C14	0.0323 (18)	0.040 (2)	0.0309 (17)	0.0085 (16)	0.0034 (14)	0.0045 (15)
C6	0.074 (3)	0.037 (3)	0.042 (2)	−0.007 (2)	0.019 (2)	−0.0002 (19)
C5	0.0351 (19)	0.041 (2)	0.036 (2)	−0.0059 (17)	0.0041 (16)	0.0012 (17)
C1	0.0277 (19)	0.068 (3)	0.051 (2)	0.005 (2)	−0.0013 (17)	−0.014 (2)
C8	0.055 (2)	0.038 (2)	0.041 (2)	0.009 (2)	0.0137 (18)	0.0013 (17)
C18	0.057 (3)	0.085 (4)	0.067 (3)	0.036 (3)	0.001 (2)	0.013 (3)
C7	0.092 (4)	0.032 (3)	0.048 (3)	0.007 (2)	0.019 (2)	0.0054 (19)
C11	0.047 (2)	0.046 (3)	0.055 (3)	−0.005 (2)	0.012 (2)	−0.011 (2)
C17	0.077 (4)	0.134 (6)	0.060 (3)	0.071 (4)	0.019 (3)	0.027 (3)

Geometric parameters (Å, °)

Cl3—C3	1.684 (5)	C15—C5	1.521 (5)
Cl7—C7	1.681 (5)	C9—C16	1.385 (5)
Cl2—C2	1.692 (5)	C9—C13	1.387 (6)
C3—C2	1.323 (7)	C12—C8	1.557 (6)
C3—C4	1.527 (6)	C12—C5	1.574 (6)
C2—C1	1.518 (7)	C16—C8	1.531 (6)
Cl12—C12	1.753 (5)	C10—C14	1.380 (5)
Cl4—C4	1.751 (4)	C4—C14	1.531 (5)
Cl5—C5	1.750 (4)	C4—C11	1.555 (6)
Cl8—C8	1.748 (5)	C13—C14	1.402 (5)
Cl11—C12	1.751 (4)	C13—C1	1.526 (5)
Cl1—C1	1.742 (4)	C6—C7	1.323 (8)
Cl9—C11	1.764 (5)	C6—C5	1.525 (6)
Cl6—C6	1.691 (5)	C1—C11	1.575 (7)
Cl10—C11	1.756 (5)	C8—C7	1.547 (7)
O1—C9	1.366 (5)	C18—H18A	0.96
O1—C17	1.414 (6)	C18—H18B	0.96
O2—C10	1.373 (4)	C18—H18C	0.96
O2—C18	1.436 (6)	C17—H17A	0.96
C15—C10	1.391 (6)	C17—H17B	0.96
C15—C16	1.398 (5)	C17—H17C	0.96
C2—C3—C4	107.4 (4)	C5—C6—Cl6	123.7 (4)
C2—C3—Cl3	128.4 (4)	C15—C5—C6	105.9 (3)

C4—C3—Cl3	124.1 (3)	C15—C5—C12	98.8 (3)
C3—C2—C1	107.9 (4)	C6—C5—C12	98.5 (4)
C3—C2—Cl2	127.7 (4)	C15—C5—Cl5	120.3 (3)
C1—C2—Cl2	124.1 (4)	C6—C5—Cl5	115.2 (3)
C9—O1—C17	114.3 (4)	C12—C5—Cl5	114.9 (3)
C10—O2—C18	112.4 (3)	C2—C1—C13	106.5 (4)
C10—C15—C16	121.3 (3)	C2—C1—C11	98.7 (4)
C10—C15—C5	131.7 (4)	C13—C1—C11	98.9 (3)
C16—C15—C5	106.9 (3)	C2—C1—Cl1	115.6 (3)
O1—C9—C16	121.9 (4)	C13—C1—Cl1	119.4 (3)
O1—C9—C13	122.0 (4)	C11—C1—Cl1	114.6 (4)
C16—C9—C13	116.1 (3)	C16—C8—C7	105.2 (3)
C8—C12—C5	92.4 (3)	C16—C8—C12	100.2 (3)
C8—C12—Cl11	114.7 (3)	C7—C8—C12	97.9 (4)
C5—C12—Cl11	114.3 (3)	C16—C8—Cl8	119.0 (3)
C8—C12—Cl12	114.2 (3)	C7—C8—Cl8	116.5 (3)
C5—C12—Cl12	112.6 (3)	C12—C8—Cl8	115.0 (3)
Cl11—C12—Cl12	108.1 (2)	O2—C18—H18A	109.5
C9—C16—C15	122.4 (4)	O2—C18—H18B	109.5
C9—C16—C8	131.6 (4)	H18A—C18—H18B	109.5
C15—C16—C8	105.8 (3)	O2—C18—H18C	109.5
O2—C10—C14	121.9 (4)	H18A—C18—H18C	109.5
O2—C10—C15	121.7 (3)	H18B—C18—H18C	109.5
C14—C10—C15	116.4 (3)	C6—C7—C8	107.3 (4)
C3—C4—C14	106.5 (4)	C6—C7—Cl7	129.6 (4)
C3—C4—C11	99.1 (4)	C8—C7—Cl7	122.8 (4)
C14—C4—C11	99.2 (3)	C4—C11—C1	91.7 (4)
C3—C4—Cl4	115.0 (3)	C4—C11—Cl10	114.2 (3)
C14—C4—Cl4	119.6 (3)	C1—C11—Cl10	114.6 (3)
C11—C4—Cl4	114.5 (3)	C4—C11—Cl9	114.6 (3)
C9—C13—C14	121.6 (3)	C1—C11—Cl9	112.7 (3)
C9—C13—C1	132.0 (4)	Cl10—C11—Cl9	108.4 (3)
C14—C13—C1	106.3 (4)	O1—C17—H17A	109.5
C10—C14—C13	122.1 (4)	O1—C17—H17B	109.5
C10—C14—C4	132.0 (4)	H17A—C17—H17B	109.5
C13—C14—C4	105.8 (3)	O1—C17—H17C	109.5
C7—C6—C5	108.2 (4)	H17A—C17—H17C	109.5
C7—C6—Cl6	127.8 (4)	H17B—C17—H17C	109.5

Fig. 1

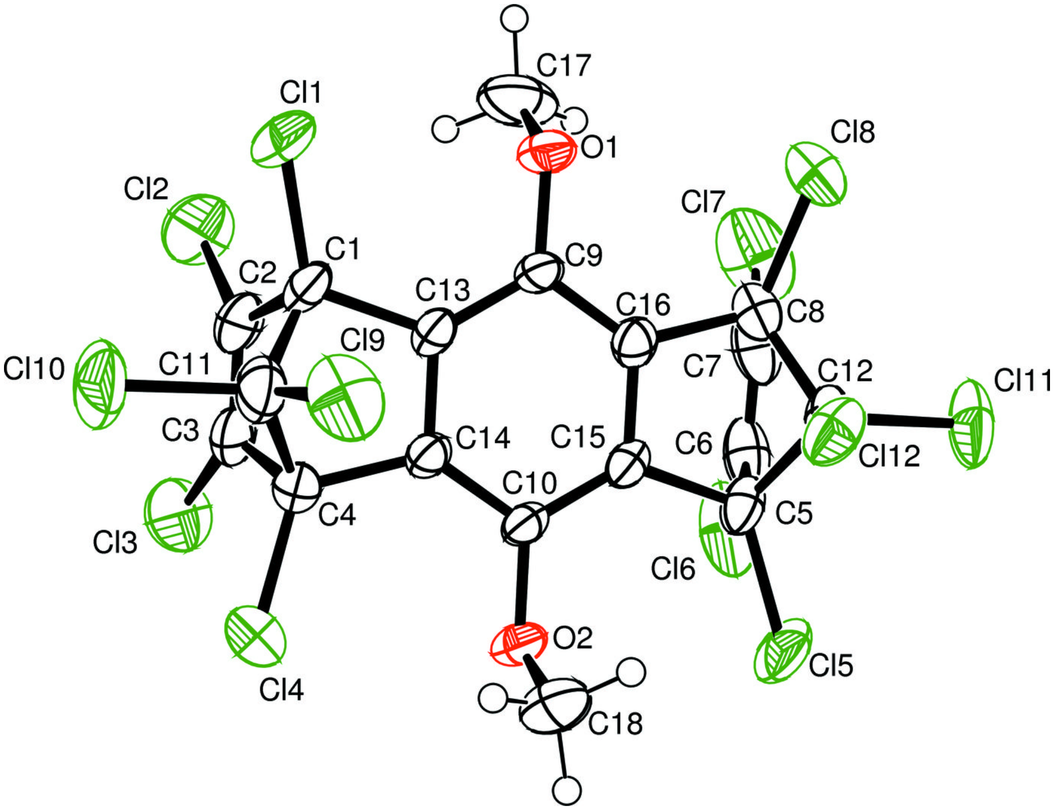
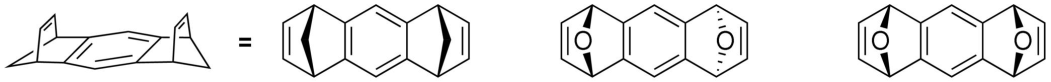
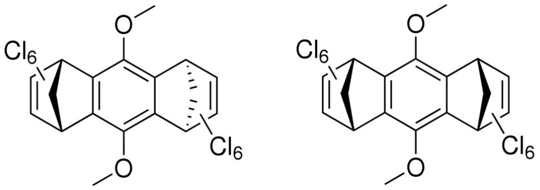

C17
Cl1
O1
Cl8
Cl2
Cl7
C1
C9
C2
C13
C16
C8
Cl9
C7
C12
Cl10
C11
Cl11
C3
C14
C15
C6
Cl12
C10
C5
Cl3
C4
Cl6
O2
Cl5
Cl4
C18

Fig. 2

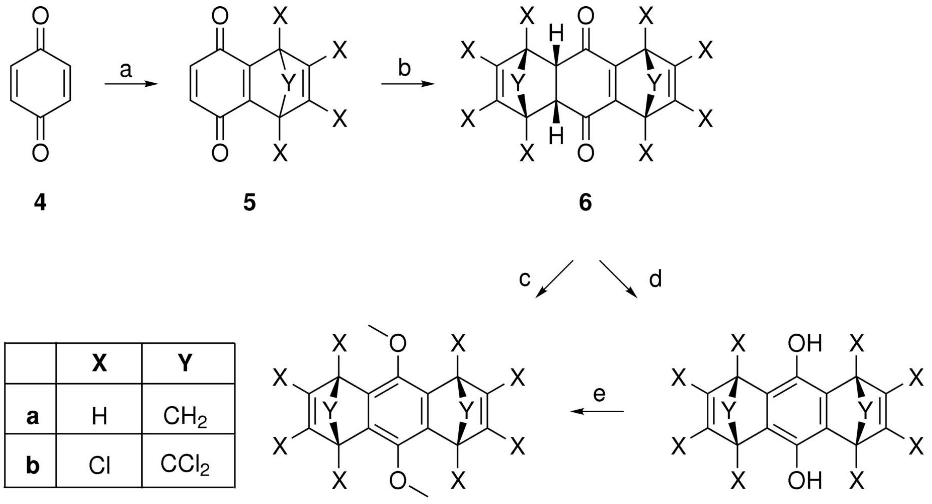


***syn*-tetrahydro-dimethanoanthracene (1)** **2 (*anti*)** **2 (*syn*)**



3b (*anti*) **3b (*syn*)**

Fig. 3



4 5 6

3 7

	X	Y
a	H	CH_2
b	Cl	CCl_2

a: i) hexachlorocyclopentadiene, toluene, rflx, 24h (95%); ii) Al_2O_3 - basic, ethyl acetate, 16h (80%); iii) Ag_2O, diethyl ether, 2h (85%)
b: hexachlorocyclopentadiene, toluene, rflx, 12h (55%)
c: DBU, acetonitrile, methyl iodide, -23 deg. C to 23 deg. C, (91%)
d: methanol, pyridine, 28 h (62%)
e: DBU, acetonitrile, methyl iodide, -23 deg. C to 23 deg. C (83%)