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Lactonization Products of 2-[(2,6-Dimethoxyphenyl)ethynyl]-3-methoxybenzoic Acid

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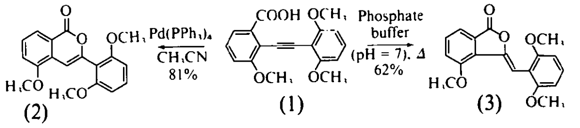
Abstract

Structural analyses of 2-[(2,6-dimethoxyphenyl)ethynyl]-3-methoxybenzoic acid, (1), and the two products of lactonization, 3-(2,6-dimethoxyphenyl)-5-methoxy-1*H*-2-benzopyran-1-one, (2), and (*Z*)-3-[(2,6-dimethoxyphenyl)methylene]-4-methoxy-1(3*H*)-isobenzofuranone, (3), three isomers of $C_{18}H_{16}O_5$, suggest an explanation for the favored pathway for lactonization. The two rings in (1) form a dihedral angle of 84.30 (4)°. The carboxy group is nearly coplanar with the benzoate ring with an O=C—C—C torsion angle of −3.7 (2)°. The triple-bond length is 1.191 (2) Å and the bond angles at the ethynyl C atoms are 176.4 (1) and 171.0 (1)°, both significantly distorted from 180°. The benzopyran ring and the dimethoxyphenyl ring in (2) form a dihedral angle of 58.90 (5)°. The pyrano C=C double-bond length is 1.324 (2) Å. Distortions appear in the two exocyclic angles [112.1 (1) and 127.3 (2)°] about the aryl substituted pyrano C atom. The isobenzofuran ring and the dimethoxyphenyl ring in (3) form a dihedral angle of 120.83 (5)°. The exocyclic C=C double-bond length is 1.323 (2) Å. Distortions appear in the benzenoid angles at the C atoms adjacent to the ring fusion [117.5 (1) and 116.7 (1)°] and in two of the three angles [121.2 (1), 131.00 (9) and 107.7 (1)°] about the furano C atom of the exocyclic C=C double bond.

Comment

Depending on the reaction conditions, compound (1) lactonizes to yield either the benzopyranone (2) or isobenzofuranone (3) (Evans *et al.*, 1994). Baldwin's rules (Baldwin, 1976) for cyclization allow lactonization of (1) to occur by either the 6-*endo*-dig or 5-*exo*-dig process yielding (2) or (3), respectively. Baldwin (1976) states that an attacking nucleophile (Nu) will approach an alkyne with an Nu···C≡C angle of 60°. Subsequent computational studies (Dykstra, Arduengo & Fukunage, 1978; Eisenstein, Procter & Dunitz, 1978; Elliot & Richards, 1982; Houk, Rondan, Schleyer, Kaufmann & Clark, 1985; Strozier, Caramella & Houk, 1979; Ivanchikova, Usubalieva, Schastnev, Moroz & Shvartsberg, 1992) suggest an obtuse angle of approach. Structural analyses of (1), (2) and (3) provide insight into which is the favored path.



2-[(2,6-Dimethoxyphenyl)ethynyl]-3-methoxybenzoic acid, (1), synthesized in an 83% yield by saponification of the methyl ester (Evans, Prince, Huang, Boss & Gandour, 1990) in methanol/water buffered at pH = 11 by K_2CO_3/KOH, (Evans, Oliver, Rosas-García & Gandour, 1994) in the presence of palladium, lactonizes to 3-(2,6-dimethoxyphenyl)-5-methoxy-1*H*-2-benzopyran-1-one, (2), in an 81% yield (Evans *et al.*, 1994), but in refluxing phosphate buffer at pH 7, it lactonizes to (*Z*)-3-[(2,6-dimethoxyphenyl)methylene]-4-methoxy-1(3*H*)-isobenzofuranone, (3), in a 62% yield (Evans *et al.*, 1994).

The carboxy group in (1) is nearly coplanar with the benzenoid ring with a C9—C14—C15—O4 torsion angle of −3.7 (2)°, which contrasts with 47.64 (6)° for the corresponding torsion angle in the methyl ester of (1) (Evans, Horn, Fronczek & Gandour, 1990). This coplanarity in (1) orients the *anti* lone pair of the carbonyl O atom O4 directly at the C≡C bond, placing O4 (van der Waals radius 1.40 Å) and the ethynyl C atom C8 (van der Waals radius 1.78 Å) within the sum (3.18 Å) of their van der Waals radii. This close O4···C8 distance [2.785 (2) Å], which is the path to (3), causes the C7—C8—C9 angle to bend to 171.0 (1)°. The O4···C7 distance, which is the path to (2), is 3.347 (2) Å. The angles of approach are 107.8 (1)° for O4···C8≡C7 and 52.4 (1)° for O4···C7≡C8. The former angle agrees

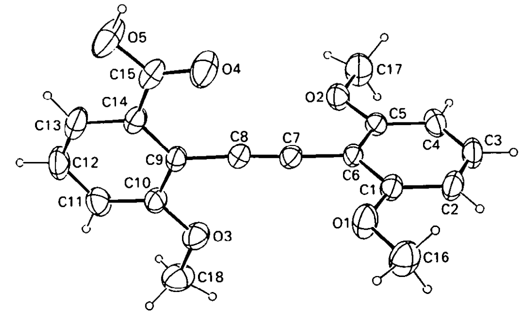


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1), with displacement ellipsoids drawn at the 40% probability level for non-H atoms. H atoms are drawn as small spheres of arbitrary radii.

with computational studies, but the latter angle agrees with the value proposed by Baldwin (1976).

The O4—C7 bond length in (2) is 1.393 (2) Å, which represents a 1.954 (3) Å decrease compared with (1); the O4—C7—C8 bond angle is 120.7 (1)°, which represents the expected increase from the Baldwin approach angle to 120°, the ideal trigonal angle. The other two angles about C7, however, show considerable distortions from 120°. Repulsion between the dimethoxyphenyl ring and the vinyl H atom H8 increases the C6—C7—C8 bond angle to 127.3 (2)° and decreases the O4—C7—C6 bond angle to 112.1 (1)°. The corresponding bond angles in the structures of 3-(2-methoxyphenyl)-1*H*-benzopyran-1-one (Prince, Miller, Fronczek & Gandour, 1989) and 3-(2,6-dihydroxyphenyl)-1*H*-2-benzopyran-1-one (Huang, Evans, Fronczek & Gandour, 1992) also show this distortion. From this analysis it can be seen that the 6-*endo*-dig lactonization involves considerable changes in the positions of O4, C7 and C8 and distortions in the bond angles about the atom under attack.

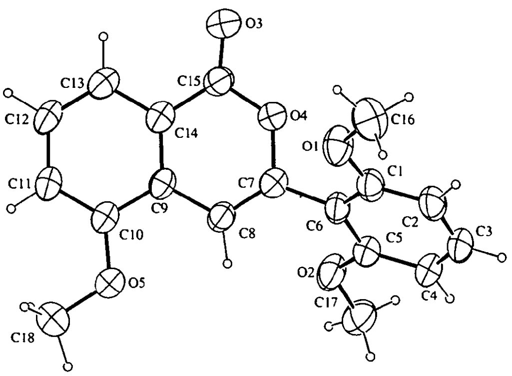


Fig. 2. *ORTEP* (Johnson, 1965) drawing of (2), with displacement ellipsoids drawn at the 40% probability level for non-H atoms. H atoms are drawn as small spheres of arbitrary radii.

The O4—C8 bond length in (3) is 1.402 (1) Å, which represents a 1.383 (2) Å decrease compared with (1); the O4—C8—C7 bond angle is 121.2 (1)°, which represents a small increase [13.4 (2)°] from the approach angle to the trigonal angle, as expected. The five-membered ring, however, distorts the benzene ring of isobenzofuranone. The bond angles C9—C10—C11 and C12—C13—C14 are 117.5 (1) and 116.7 (1)°, respectively. This distortion is also observed in the structure of (*Z*)-3-(phenylmethylene)-1(3*H*)-isobenzofuranone (Wang, Cheng, Lin, Koh & Yang, 1985). From this analysis it can be seen that the 5-*exo*-dig lactonization involves moderate changes in the positions of O4, C7 and C8 and similar magnitudes of distortions in bond angles.

Compound (2) is more stable than (3) (Evans *et al.*, 1994). The 5-*exo*-dig lactonization of (1) is the kinetic pathway while the 6-*endo*-dig lactonization is the thermodynamic pathway. In as much as the crystal structure of (1) represents the structure in solution of the carboxylate ion of (1), the starting material is predisposed to lactonize to (3) because smaller changes in atomic positions occur when comparing (1) and (3) than (1) and (2), *viz.*, the principle of least nuclear motion (for a review see Sinnott, 1988). For lactonization, computations (Ivanchikova *et al.*, 1992) favor 5-*exo*-dig as the minimum-energy pathway. Here, the intramolecular reaction follows a 'response' pathway (Bürgi & Dunitz, 1983), which is also a minimum-energy pathway.

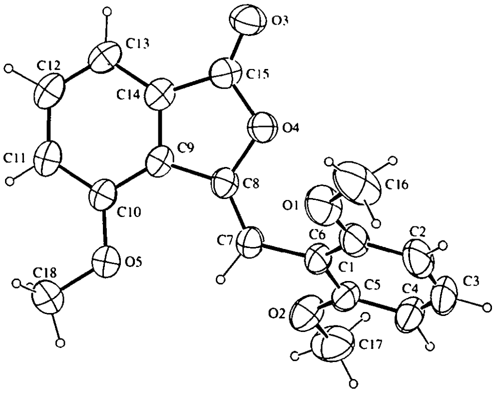


Fig. 3. *ORTEP* (Johnson, 1965) drawing of (3), with displacement ellipsoids drawn at the 40% probability level for non-H atoms. H atoms are drawn as small spheres of arbitrary radii.

Experimental

Compound (1)

Crystal data

$C_{18}H_{16}O_5$
$M_r = 312.3$
Monoclinic
$P2_1/c$
$a = 7.9263$ (7) Å
$b = 8.0539$ (9) Å
$c = 24.315$ (2) Å
$\beta = 97.859$ (7)°
$V = 1537.6$ (5) Å^3
$Z = 4$
$D_x = 1.349$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–17°
$\mu = 0.09$ mm^{-1}
$T = 298$ K
Rhombic prism
0.50 × 0.48 × 0.42 mm
Colorless
Crystal source: crystallized from ethyl acetate

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
5036 measured reflections
4455 independent reflections
3095 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -34 \rightarrow 33$
3 standard reflections
frequency: 167 min
intensity decay: <2%

Refinement

Refinement on F
$R = 0.043$

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.06$ e Å^{-3}

$wR = 0.053$
$S = 2.785$
3095 reflections
273 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.02$
Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 6.2\ (11) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$C_{18}H_{16}O_5$
$M_r = 312.3$
Triclinic
$P\overline{1}$
$a = 7.7197\ (6)$ Å
$b = 9.6126\ (8)$ Å
$c = 11.9115\ (10)$ Å
$\alpha = 110.548\ (6)^\circ$
$\beta = 101.151\ (7)^\circ$
$\gamma = 103.454\ (7)^\circ$
$V = 767.4\ (4)$ Å^3
$Z = 2$
$D_x = 1.352$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25–30^\circ$
$\mu = 0.78$ mm^{-1}
$T = 296$ K
Fragment
0.30 × 0.28 × 0.22 mm
Colorless
Crystal source: crystallized from acetonitrile

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.914$, $T_{\max} = 0.998$
3155 measured reflections
3155 independent reflections
2703 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 75^\circ$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 167 min
intensity decay: <2%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.070$
$S = 4.012$
2703 reflections
273 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 1.20\ (8) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (3)

Crystal data

$C_{18}H_{16}O_5$
$M_r = 312.2$
Triclinic
$P\overline{1}$
$a = 6.8297\ (4)$ Å
$b = 10.4824\ (10)$ Å
$c = 12.2123\ (7)$ Å
$\alpha = 69.510\ (7)^\circ$
$\beta = 76.924\ (5)^\circ$
$\gamma = 76.058\ (7)^\circ$
$V = 785.12\ (7)$ Å^3
$Z = 2$
$D_x = 1.321$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25–30^\circ$
$\mu = 0.76$ mm^{-1}
$T = 297$ K
Fragment
0.42 × 0.40 × 0.20 mm
Colorless
Crystal source: crystallized from methylene chloride

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.883$, $T_{\max} = 0.999$
3109 measured reflections
3109 independent reflections
2816 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 75^\circ$
$h = 0 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 167 min
intensity decay: <3%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.066$
$S = 4.181$
2816 reflections
273 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: $(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 1.24\ (7) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Compound (1)				
O1	0.4693 (1)	0.2656 (2)	0.74183 (4)	4.44 (2)
O2	−0.0810 (1)	0.1414 (1)	0.65684 (3)	3.65 (2)
O3	0.1339 (1)	0.6514 (1)	0.60418 (4)	4.24 (2)
O4	0.4139 (1)	0.1160 (2)	0.54671 (4)	5.44 (3)
O5	0.4186 (2)	0.1644 (2)	0.45752 (4)	6.23 (3)
C1	0.3189 (2)	0.1913 (2)	0.74752 (5)	3.17 (3)
C2	0.2837 (2)	0.1151 (2)	0.79601 (5)	3.81 (3)
C3	0.1252 (2)	0.0479 (2)	0.79757 (5)	4.07 (3)
C4	−0.0007 (2)	0.0537 (2)	0.75240 (6)	3.76 (3)
C5	0.0342 (2)	0.1289 (2)	0.70384 (5)	2.94 (3)
C6	0.1947 (2)	0.1978 (2)	0.70038 (4)	2.71 (2)
C7	0.2279 (2)	0.2778 (2)	0.65010 (4)	2.85 (2)
C8	0.2468 (2)	0.3417 (2)	0.60721 (4)	2.88 (2)
C9	0.2471 (1)	0.4351 (2)	0.55676 (4)	2.81 (2)
C10	0.1800 (2)	0.5962 (2)	0.55539 (5)	3.32 (3)
C11	0.1599 (2)	0.6883 (2)	0.50673 (6)	4.24 (3)
C12	0.2087 (2)	0.6225 (2)	0.45924 (5)	4.71 (4)
C13	0.2808 (2)	0.4684 (2)	0.45978 (5)	4.21 (3)
C14	0.3011 (2)	0.3721 (2)	0.50786 (5)	3.19 (3)
C15	0.3809 (2)	0.2070 (2)	0.50573 (5)	3.67 (3)
C16	0.5988 (2)	0.2649 (3)	0.78918 (6)	5.09 (4)
C17	−0.2504 (2)	0.0829 (3)	0.65945 (6)	5.28 (4)
C18	0.0673 (2)	0.8155 (3)	0.60619 (7)	5.25 (4)
Compound (2)				
O1	0.3538 (2)	0.7764 (1)	0.3672 (1)	5.56 (3)
O2	0.8688 (2)	0.6586 (1)	0.54049 (9)	5.19 (3)
O3	0.7599 (2)	0.9564 (1)	0.1990 (1)	6.39 (3)
O4	0.6989 (2)	0.8305 (1)	0.31651 (9)	4.40 (2)
O5	0.7031 (2)	0.2945 (1)	0.09225 (9)	5.00 (3)
C1	0.4573 (2)	0.7721 (2)	0.4716 (1)	4.27 (3)
C2	0.4153 (2)	0.8111 (2)	0.5846 (1)	5.03 (4)
C3	0.5260 (2)	0.7971 (2)	0.6827 (1)	5.44 (4)
C4	0.6771 (3)	0.7459 (2)	0.6725 (1)	5.21 (4)
C5	0.7212 (2)	0.7085 (2)	0.5598 (1)	4.24 (3)
C6	0.6125 (2)	0.7233 (2)	0.4584 (1)	3.96 (3)
C7	0.6636 (2)	0.6964 (2)	0.3404 (1)	3.91 (3)

C8	0.6759 (2)	0.5643 (2)	0.2618 (1)	3.89 (3)
C9	0.7168 (2)	0.5567 (2)	0.1466 (1)	3.58 (3)
C10	0.7247 (2)	0.4175 (2)	0.0581 (1)	3.82 (3)
C11	0.7516 (2)	0.4123 (2)	−0.0542 (1)	4.30 (3)
C12	0.7755 (2)	0.5440 (2)	−0.0800 (1)	4.62 (3)
C13	0.7728 (2)	0.6824 (2)	0.0055 (1)	4.49 (3)
C14	0.7428 (2)	0.6877 (2)	0.1190 (1)	3.87 (3)
C15	0.7364 (2)	0.8340 (2)	0.2099 (1)	4.34 (3)
C16	0.1980 (2)	0.8306 (2)	0.3757 (2)	6.18 (5)
C17	0.9791 (3)	0.6389 (2)	0.6405 (2)	5.63 (4)
C18	0.7136 (3)	0.1516 (2)	0.0066 (2)	5.61 (5)
Compound (3)				
O1	0.6333 (2)	0.3494 (1)	0.15240 (9)	6.42 (3)
O2	0.0941 (2)	0.1098 (1)	0.34304 (9)	5.88 (3)
O3	0.2102 (2)	0.7376 (1)	0.23357 (9)	5.80 (3)
O4	0.2898 (1)	0.50844 (8)	0.26571 (7)	4.24 (2)
O5	0.3269 (2)	0.21957 (9)	0.61740 (7)	4.72 (2)
C1	0.5047 (2)	0.2742 (2)	0.1426 (1)	5.29 (3)
C2	0.5140 (3)	0.2369 (2)	0.0423 (1)	7.38 (5)
C3	0.3803 (4)	0.1561 (2)	0.0446 (1)	8.42 (5)
C4	0.2365 (3)	0.1113 (2)	0.1411 (1)	6.96 (4)
C5	0.2269 (2)	0.1494 (1)	0.2410 (1)	5.06 (3)
C6	0.3593 (2)	0.2315 (1)	0.2428 (1)	4.38 (3)
C7	0.3449 (2)	0.2642 (1)	0.3530 (1)	3.94 (2)
C8	0.3126 (2)	0.3891 (1)	0.36387 (9)	3.60 (2)
C9	0.2798 (2)	0.4331 (1)	0.46809 (9)	3.51 (2)
C10	0.2831 (2)	0.3593 (1)	0.5876 (1)	3.73 (2)
C11	0.2413 (2)	0.4350 (1)	0.6663 (1)	4.28 (3)
C12	0.1970 (2)	0.5791 (1)	0.6266 (1)	4.56 (3)
C13	0.1936 (2)	0.6526 (1)	0.5093 (1)	4.46 (3)
C14	0.2355 (2)	0.5762 (1)	0.4313 (1)	3.82 (2)
C15	0.2407 (2)	0.6232 (1)	0.3032 (1)	4.31 (3)
C16	0.7833 (3)	0.4001 (2)	0.0542 (2)	8.65 (6)
C17	−0.0634 (3)	0.0418 (2)	0.3437 (2)	7.56 (5)
C18	0.3429 (3)	0.1429 (2)	0.7384 (1)	5.45 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

Compound (1)			
O1—C1	1.357 (2)	C4—C5	1.388 (2)
O1—C16	1.434 (2)	C5—C6	1.401 (2)
O2—C5	1.365 (1)	C6—C7	1.438 (2)
O2—C17	1.433 (2)	C7—C8	1.191 (2)
O3—C10	1.362 (2)	C8—C9	1.439 (2)
O3—C18	1.427 (2)	C9—C10	1.401 (2)
O4—C15	1.236 (2)	C9—C14	1.412 (2)
O5—C15	1.295 (2)	C10—C11	1.387 (2)
C1—C2	1.391 (2)	C11—C12	1.373 (2)
C1—C6	1.406 (2)	C12—C13	1.366 (3)
C2—C3	1.374 (2)	C13—C14	1.394 (2)
C3—C4	1.380 (2)	C14—C15	1.476 (2)
C1—O1—C16	117.3 (1)	C7—C8—C9	171.0 (1)
C5—O2—C17	117.5 (1)	C8—C9—C10	117.3 (1)
C10—O3—C18	118.4 (1)	C8—C9—C14	124.5 (1)
O1—C1—C2	124.2 (1)	C10—C9—C14	118.1 (1)
O1—C1—C6	115.3 (1)	O3—C10—C9	115.3 (1)
C2—C1—C6	120.5 (1)	O3—C10—C11	123.7 (1)
C1—C2—C3	119.2 (1)	C9—C10—C11	120.9 (1)
C2—C3—C4	122.0 (1)	C10—C11—C12	119.9 (2)
C3—C4—C5	119.0 (1)	C11—C12—C13	120.6 (1)
O2—C5—C4	123.8 (1)	C12—C13—C14	120.9 (1)
O2—C5—C6	115.4 (1)	C9—C14—C13	119.5 (1)
C4—C5—C6	120.8 (1)	C9—C14—C15	122.3 (1)
C1—C6—C5	118.5 (1)	C13—C14—C15	118.2 (1)
C1—C6—C7	121.3 (1)	O4—C15—O5	121.6 (2)
C5—C6—C7	120.1 (1)	O4—C15—C14	123.4 (1)
C6—C7—C8	176.4 (1)	O5—C15—C14	115.0 (1)
Compound (2)			
O1—C1	1.362 (2)	C4—C5	1.393 (2)
O1—C16	1.425 (3)	C5—C6	1.403 (2)
O2—C5	1.364 (2)	C6—C7	1.485 (2)
O2—C17	1.422 (2)	C7—C8	1.324 (2)
O3—C15	1.204 (2)	C8—C9	1.447 (2)
O4—C7	1.393 (2)	C9—C10	1.407 (2)
O4—C15	1.366 (2)	C9—C14	1.391 (2)
O5—C10	1.365 (2)	C10—C11	1.378 (2)
O5—C18	1.426 (2)	C11—C12	1.385 (3)
C1—C2	1.389 (2)	C12—C13	1.370 (2)
C1—C6	1.401 (2)	C13—C14	1.401 (2)
C2—C3	1.374 (3)	C14—C15	1.462 (2)
C3—C4	1.377 (3)		
C1—O1—C16	118.2 (1)	C6—C7—C8	127.3 (2)
C5—O2—C17	117.4 (1)	C7—C8—C9	119.7 (2)
C7—O4—C15	123.7 (1)	C8—C9—C10	121.8 (1)
C10—O5—C18	117.5 (1)	C8—C9—C14	120.0 (1)
O1—C1—C2	123.8 (2)	C10—C9—C14	118.2 (1)
O1—C1—C6	115.4 (1)	O5—C10—C9	115.4 (1)
C2—C1—C6	120.8 (2)	O5—C10—C11	124.7 (1)
C1—C2—C3	118.8 (2)	C9—C10—C11	119.9 (2)
C2—C3—C4	122.2 (2)	C10—C11—C12	120.7 (1)
C3—C4—C5	119.2 (2)	C11—C12—C13	120.8 (2)
O2—C5—C4	123.9 (2)	C12—C13—C14	118.7 (2)
O2—C5—C6	116.1 (1)	C9—C14—C13	121.6 (1)
C4—C5—C6	120.1 (2)	C9—C14—C15	119.2 (1)
C1—C6—C5	118.9 (1)	C13—C14—C15	119.2 (2)
C1—C6—C7	119.5 (1)	O3—C15—O4	117.3 (1)
C5—C6—C7	121.6 (1)	O3—C15—C14	126.1 (2)
O4—C7—C6	112.1 (1)	O4—C15—C14	116.6 (1)
O4—C7—C8	120.7 (1)		
Compound (3)			
O1—C1	1.361 (2)	C4—C5	1.395 (2)
O1—C16	1.425 (2)	C5—C6	1.399 (2)
O2—C5	1.362 (2)	C6—C7	1.478 (2)
O2—C17	1.424 (3)	C7—C8	1.323 (2)
O3—C15	1.204 (1)	C8—C9	1.455 (2)
O4—C8	1.402 (1)	C9—C10	1.395 (1)
O4—C15	1.375 (2)	C9—C14	1.383 (2)
O5—C10	1.354 (1)	C10—C11	1.391 (2)
O5—C18	1.429 (2)	C11—C12	1.393 (2)
C1—C2	1.395 (3)	C12—C13	1.372 (2)
C1—C6	1.402 (2)	C13—C14	1.389 (2)
C2—C3	1.377 (4)	C14—C15	1.461 (2)
C3—C4	1.372 (2)		
C1—O1—C16	119.7 (2)	O4—C8—C9	107.7 (1)
C5—O2—C17	118.6 (1)	C7—C8—C9	131.00 (9)
C8—O4—C15	109.2 (1)	C8—C9—C10	132.2 (1)
C10—O5—C18	117.7 (1)	C8—C9—C14	107.49 (9)
O1—C1—C2	124.2 (1)	C10—C9—C14	120.3 (1)
O1—C1—C6	115.7 (1)	O5—C10—C9	117.2 (1)
C2—C1—C6	120.2 (2)	O5—C10—C11	125.4 (1)
C1—C2—C3	118.8 (2)	C9—C10—C11	117.5 (1)
C2—C3—C4	123.0 (2)	C10—C11—C12	120.9 (1)
C3—C4—C5	118.2 (2)	C11—C12—C13	122.0 (1)
O2—C5—C4	124.0 (2)	C12—C13—C14	116.7 (1)
O2—C5—C6	115.0 (1)	C9—C14—C13	122.6 (1)
C4—C5—C6	121.0 (1)	C9—C14—C15	107.6 (1)
C1—C6—C5	119.0 (1)	C13—C14—C15	129.7 (1)
C1—C6—C7	122.9 (1)	O3—C15—O4	120.6 (1)
C5—C6—C7	118.1 (1)	O3—C15—C14	131.4 (1)
C6—C7—C8	126.5 (1)	O4—C15—C14	108.03 (9)
O4—C8—C7	121.2 (1)		

The structure of (2) was solved using *SHELXS*86 (Sheldrick, 1990). The structures of (1) and (3) were solved using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The Enraf–Nonius *MolEN* programs (Fair, 1990) were used for all other calculations.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: BK1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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endo-1,10,11,12,13,13-Hexachloro-tricyclo[8.2.1.0^{2,9}]trideca-11-ene

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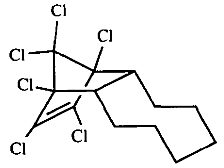
Abstract

In *endo*-1,10,11,12,13,13-hexachlorotricyclo[8.2.1.0^{2,9}]-trideca-11-ene, $C_{13}H_{14}Cl_6$, the cyclooctane ring adopts a twist-chair conformation. There is disorder involving the two outermost C atoms of the eight-membered ring in which a conformer having the opposite twist handedness has 15% population. The near-zero torsion angle of the twist-chair at the ring-fusion bond has a magnitude of 2.3 (4)°. The torsion angles about the bonds comprising the sides of the twist-chair for the major conformer are 81.1 (4) and −51.9 (4)°. The norbornene C=C bond length is 1.331 (4) Å.

Comment

The crystal structures of a number of Diels–Alder substituted cycloocta(e)ne and cyclohexa(e)ne adducts have been determined in our laboratories in the past three years (Garcia & McLaughlin, 1991; Garcia, Fronczek & McLaughlin, 1991*a*,*b*,*c*, 1992*a*,*b*; Garcia, McLaughlin & Fronczek, 1991*a*,*b*; Li, Fronczek & McLaughlin, 1992; Garcia, Morales, Fronczek & McLaughlin, 1994; Garcia & Fronczek, 1994, 1995) on account of a study of conformation-dependent π–σ–π electronic interactions (Garcia, Fronczek & McLaughlin, 1991*a*; Garcia & McLaughlin, 1991; Garcia & Fronczek, 1994). The crystal structure determination of the title compound, (I), is part of an ongoing program of structure analysis of some new derivatives bearing the cyclooctane moiety.



(I)

Structural data for *endo-endo-anti*-1,6,7,8,9,14,15,16-octachloro-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (Garcia, McLaughlin & Fronczek, 1991*a*), *endo-endo-anti*-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (Garcia, McLaughlin & Fronczek, 1991*a*), *endo-endo-anti*-1,6,7,8,9,14,15,16-octachloro-17,17-dimethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (Garcia, Fronczek & McLaughlin, 1992*b*), *endo*-1,10,11,12-tetrachloro-13,13-dimethoxytricyclo-[8.2.1.0^{2,9}]trideca-5,11-diene (Li, Fronczek & McLaughlin, 1992), *endo-endo-syn*-16,16-dimethoxy-1,5,6,7,-8,12,13,14,15,15-decachloropentacyclo[10.2.1.1^{5,8}.-0^{2,11}.0^{4,9}]hexadeca-6,13-diene (Garcia & Fronczek, 1994), *endo-endo-syn*-1,5,6,7,8,12,13,14-octachloro-15,-15,16,16-tetramethoxypentacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}]-hexadeca-6,13-diene (Garcia & Fronczek, 1994) and *endo-endo-syn*-4,13-dioxa-1,7,8,9,10,16,17,18-octachloro-19,19,20,20-tetramethoxypentacyclo[14.2.1.1^{7,10}.-0^{2,15}.0^{6,11}]eicosa-8,17-diene (Garcia & Fronczek, 1995) are in agreement with those of the title compound.

The cyclooctane ring has a twist-chair conformation (Hendrickson, 1967*b*) with bond angles θ_1 (C2—C1—C8) = 119.5 (2), θ_2 (C1—C8—C7) = 115.6 (3), θ_3 (C8—C7—C6) = 116.1 (3), θ_4 (C7—C6—C5) = 113.4 (4), θ_5 (C6—C5—C4) = 114.6 (4), θ_6 (C5—C4—C3) = 114.6 (3), θ_7 (C4—C3—C2) = 113.8 (2) and θ_8 (C3—C2—C1) = 118.7 (2)° that are distorted from the theoretical values (Hendrickson, 1967*a*) of the twist-

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