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cis-6,11,17,18-Tetrahydro-5,12-dioxatribenzo[*a,e,i*]cyclododecene-17,18-diol, C₂₂H₂₀O₄

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Abstract. $M_r = 348.4$, triclinic, $P\bar{1}$, $a = 8.633$ (1), $b = 9.035$ (1), $c = 11.957$ (1) Å, $\alpha = 74.11$ (1), $\beta = 73.61$ (1), $\gamma = 83.00$ (1)°, $V = 859.5$ (2) Å³, $Z = 2$, $D_x = 1.346$ g cm⁻³, $\lambda = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 0.86$ cm⁻¹, $F(000) = 368.0$, $T = 296$ K, $R = 0.031$ for 2016 observations (of 3010 unique data). The diol O atoms form a *gauche* interaction with O–C–O torsion angle, 42.5 (3)°, smaller than that in related compounds. Both intramolecular and intermolecular hydrogen bonding are present.

Introduction. During the course of our studies preparing stilbene cycles as backbones for intramolecular reactions (Tirado-Rives, Oliver, Fronczek & Gandour, 1984), the title compound has been isolated and its crystal structure has been determined.

Experimental. Title compound isolated from mixture produced in the reaction of 2,2'-[*o*-phenylenebis(methyleneoxy)]dibenzaldehyde with TiCl₄/BuLi. Colorless plates from evaporation of CHCl₃, m.p. 455–458 K. D_m not determined. Crystal size 0.20 × 0.42 × 0.60 mm. Space-group determination by successful refinement of centrosymmetric model. Cell dimensions from setting angles of 25 reflections having 13° > θ > 12°. Data collection on Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω -2 θ scans designed for $I = 50\sigma(I)$. Scan rates varied 0.57–20.0° min⁻¹. Reflections having 1° < θ < 25°, 0 ≤ h ≤ 10, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13 (excluding redundant data) measured, corrected for background, Lorentz, and polarization effects. Maximum value of $(\sin\theta)/\lambda = 0.59$ Å⁻¹. Three standard reflections, ±1.6% random variation. Absorption negli-

gible. Structure solved using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based upon F , using data for which $I > 3\sigma(I)$ (994 unobserved reflections), weights $w = \sigma^{-2}(F_o)$, with the Enraf–Nonius *SDP* (Frenz & Okaya, 1980). Non-H atoms anisotropic; H atoms located by ΔF synthesis and refined isotropically. Final $R = 0.031$, $R_w = 0.043$, $S = 1.413$ for 316 variables. Maximum shift 0.02 σ in final cycle, largest residual density 0.16 e Å⁻³, extinction coefficient 3.0 (3) × 10⁻⁶.

Discussion. The atomic parameters are given in Table 1.† Selected torsion angles are given in Fig. 1.

There are some noteworthy values for the angles and torsion angles associated with the diol C atoms. The angles, C(9)–C(8)–C(7) and C(6)–C(7)–C(8), are 115.4 (1) and 115.6 (1)°, respectively, which are significant distortions from their expected tetrahedral values. The torsion angles about C(7)–C(8) are surprising in that the *gauche* interactions are nearly 20° less than the typical values. This conformation brings the two hydroxyl O atoms within 2.689 (1) Å of each other. While no torsional motion about C(7)–C(8) can produce a linear intramolecular hydrogen bond, the observed twist brings the H atom on O(3) to a position equidistant from the plane defined by C(7), O(3), and O(4), and the plane bisecting the C(8)–O(4)–H(40) angle: 0.35 (2) Å from each. The O(3)–H(30)···O(4)

† Tables of distances and angles, H-atom coordinates, H-atom distances and angles, anisotropic thermal parameters, deviations from least-squares planes, and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39872 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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angle is $117(3)^\circ$ and the $\text{H}\cdots\text{O}$ distance is $2.14(2)\text{ \AA}$. This interaction probably accounts for the observed torsion angle.

For comparison, the $\text{O}-\text{C}-\text{C}-\text{O}$ torsion angle formed by the diol O atoms in *cis*-5,6-dihydro-7,12-dimethylbenz[*a*]anthracene-5,6-diol (Zacharias, Glusker, Harvey & Fu, 1977) is $-55.7(3)^\circ$ for one form and $58.0(3)^\circ$ for the other. The analogous bond

angles about the diol C atoms are $110.4(3)$ and $111.6(3)^\circ$ for one form and $110.0(3)$ and $111.3(3)^\circ$ for the other. In racemic 2,3-diphenyl-2,3-butanediol (Fronczek, Oliver & Gandour, 1982), an acyclic molecule, the torsion angle formed by the diol O atoms is $61.4(7)^\circ$. The C—C bond length between the diol C atoms in this acyclic molecule is quite long, $1.592(8)\text{ \AA}$, compared to the title compound, $1.547(2)\text{ \AA}$.

The phenylene ether bond angles are typical of aryl-alkyl ethers. The bond angles of the ether linkages, $\text{C}(14)-\text{O}(1)-\text{C}(15)$ and $\text{C}(1)-\text{O}(2)-\text{C}(22)$, are $119.4(1)$ and $115.4(1)^\circ$, respectively. These are in good agreement with the ether linkages found in a similar *o*-phenylene cycle, (*Z*)-6,11-dihydro-17,18-dimethyl-5,12-dioxatribenzo[*a,e,i*]cyclododecene [$117.6(5)$ and $117.0(5)^\circ$] (Tirado-Rives, Oliver, Fronczek & Gandour, 1984) and in 2,2'-[*o*-phenylene-bis(methyleneoxy)]diacetophenone [$118.1(3)$ and $117.2(3)^\circ$], its acyclic precursor (Colucci, Jungk, Nail, Ghane, Karagiorgos, Watkins, Fronczek & Gandour, 1985). This indicates that compensation for the ring strain of the title compound is accomplished solely by widening the bond angles of the diol. No other bond distances or angles are perturbed from their expected geometries.

Maximum deviation from the least-squares planes of the aromatic rings is $0.014(2)\text{ \AA}$. Deviations of atoms from the best planes of rings to which they are attached are O(2) $0.079(1)$, C(7) $-0.013(2)$, O(1) $0.095(1)$, C(8) $-0.037(1)$, C(15) $0.007(2)$ and C(22) $0.107(2)\text{ \AA}$. O(3) lies $-0.141(1)\text{ \AA}$ from the plane of C(1) through C(6).

The only notable intermolecular interaction is a weak hydrogen bond between the hydroxyl oxygen O(4) and the ether oxygen O(2) of the molecule related by inversion through $1, \frac{1}{2}, \frac{1}{2}$. The $\text{O}\cdots\text{O}$ distance is $3.019(1)\text{ \AA}$, $\text{H}\cdots\text{O}$ distance $2.17(2)\text{ \AA}$ and the $\text{O}-\text{H}\cdots\text{O}$ angle is $164(3)^\circ$.

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Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
O(1)	0.8649 (1)	0.8455 (1)	0.57187 (9)	3.71 (2)
O(2)	0.6672 (1)	0.5750 (1)	0.61786 (8)	3.25 (2)
O(3)	1.0221 (1)	0.3043 (1)	0.78027 (10)	4.78 (3)
O(4)	1.1729 (1)	0.5374 (1)	0.60520 (9)	4.23 (3)
C(1)	0.6286 (2)	0.4872 (2)	0.7364 (1)	2.96 (3)
C(2)	0.4719 (2)	0.4846 (2)	0.8095 (1)	3.86 (4)
C(3)	0.4374 (2)	0.3906 (2)	0.9252 (2)	4.64 (4)
C(4)	0.5562 (2)	0.2998 (2)	0.9678 (1)	4.71 (4)
C(5)	0.7128 (2)	0.3041 (2)	0.8960 (1)	3.99 (4)
C(6)	0.7537 (2)	0.3991 (1)	0.7794 (1)	2.97 (3)
C(7)	0.9277 (2)	0.3982 (2)	0.7046 (1)	3.32 (3)
C(8)	0.9997 (2)	0.5583 (2)	0.6446 (1)	2.96 (3)
C(9)	0.9623 (2)	0.6693 (2)	0.7235 (1)	2.99 (3)
C(10)	0.9991 (2)	0.6363 (2)	0.8337 (1)	3.63 (4)
C(11)	0.9611 (2)	0.7404 (2)	0.9049 (1)	4.29 (4)
C(12)	0.8843 (2)	0.8796 (2)	0.8664 (1)	4.49 (4)
C(13)	0.8475 (2)	0.9180 (2)	0.7567 (1)	4.10 (4)
C(14)	0.8881 (2)	0.8139 (2)	0.6848 (1)	3.21 (3)
C(15)	0.7464 (2)	0.9615 (2)	0.5397 (1)	3.58 (3)
C(16)	0.6959 (2)	0.9245 (2)	0.4408 (1)	3.13 (3)
C(17)	0.7369 (2)	1.0203 (2)	0.3256 (1)	3.86 (4)
C(18)	0.6919 (2)	0.9888 (2)	0.2327 (1)	4.73 (4)
C(19)	0.6038 (2)	0.8621 (2)	0.2541 (1)	4.82 (4)
C(20)	0.5625 (2)	0.7670 (2)	0.3679 (1)	4.02 (4)
C(21)	0.6070 (2)	0.7946 (2)	0.4630 (1)	3.20 (3)
C(22)	0.5471 (2)	0.6937 (2)	0.5865 (1)	3.55 (3)

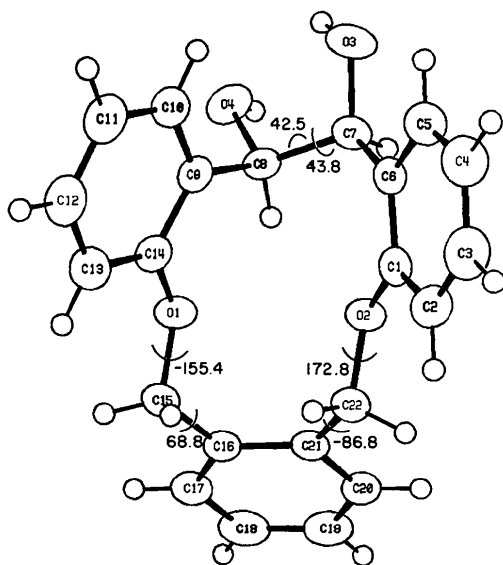


Fig. 1. Drawing of the title compound with selected torsion angles ($^\circ$) (e.s.d. = 0.3°).