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7,16-Dioxatetracyclo[16.2^{4,5}.2^{21,22}.2^{23,24}.0^{9,14}]-tetracosa-1,3,5,9,11,13,17,19,21,23-decaene

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.005 Å
R factor = 0.077
wR factor = 0.196
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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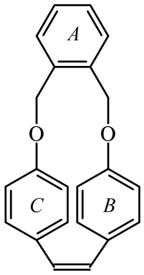
In the title molecule, $C_{22}H_{18}O_2$, the dihedral angles formed by the planes of the benzene rings are 70.0 (1), 82.9 (1) and 31.1 (1)°, respectively. In the crystal structure, inversion-related molecules are linked by C—H···O hydrogen bonds to form dimeric pairs and these, translated along the *a* direction, are linked by weak C—H···O hydrogen bonds to form molecular chains. The crystal structure is further stabilized by weak C—H···π interactions.

Comment

Stilbene-based cyclophanes possess novel optical properties due to their ability to exhibit *cis–trans* isomerization (Tanner & Wennerstrom, 1981). Such a class of cyclophanes, called stilbenophanes, can be obtained by the McMurry coupling technique (Furstner & Bogdanovic, 1996). Treatment of the dialdehyde derived by the *o*-alkylation of *p*-hydroxybenzaldehyde with *o*-xylenyl dibromide with $TiCl_4$ and Zn in THF afforded the title compound, (I) (Murali, 2002). The structure determination of (I) was undertaken as part of our study of cyclophanes.



(I)

In the title molecule (Fig. 1), the benzene rings of the *cis*-stilbene moiety, *B* (C9–C14) and *C* (C17–C22), are slightly puckered, with *para* C atoms lying on the same side of the plane of the remaining four atoms [0.065 (4) and 0.079 (4) Å in ring *B*, and 0.054 (4) and 0.053 (3) Å in ring *C*]. Similar puckering has been observed in the benzene rings of cyclophanes by Hanson & Rohrl (1972), and by Ravishankar *et al.* (2003).

The weighted least-squares plane through ring *A* (C2–C7) makes dihedral angles of 70.0 (1) and 82.9 (1)°, respectively, with the planes through rings *B* and *C*. The dihedral angle between the two benzene rings (*B* and *C*) of the *cis*-stilbene moiety is 31.1 (1)°, compared to 51.35 (7)° observed in a closely related cyclophane, *viz.* 7,14-dioxatetracyclo[14.2^{4,5}.21^{9,20}.2^{21,22}.2^{23,24}]tetracosa-1,3,5,9,11,15,17,19,21,23-decaene,

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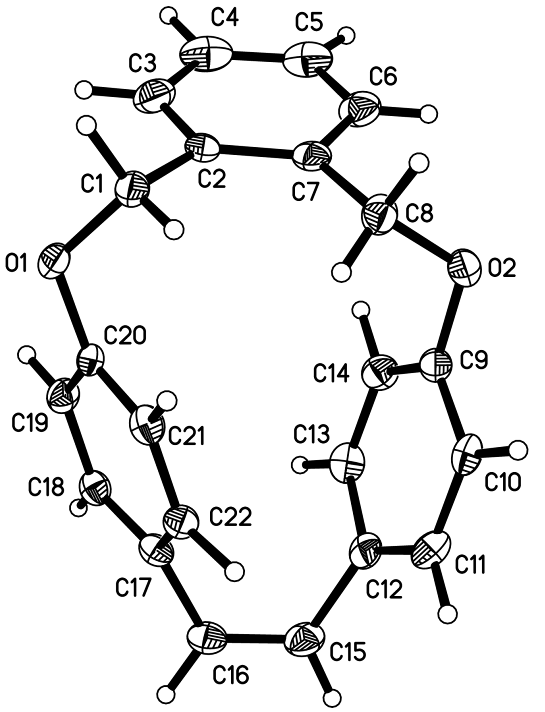

Figure 1
The structure of the title compound, with the atom-numbering scheme, and displacement ellipsoids drawn at the 30% probability level.

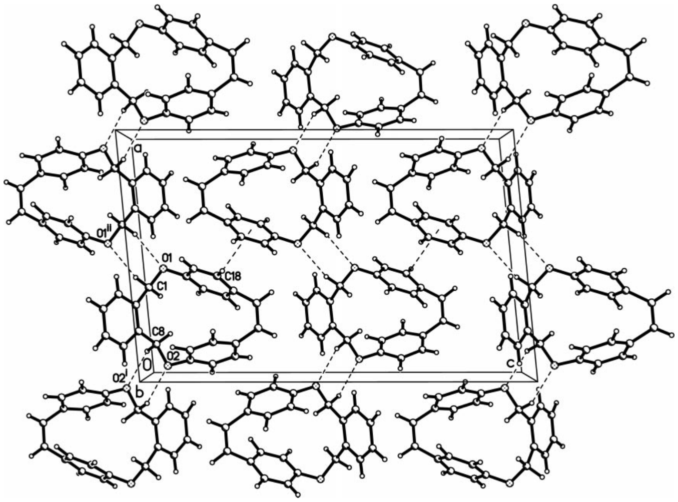

Figure 2
A view, down the *b* axis, of the hydrogen-bond network. Hydrogen bonds are indicated by dashed lines.

(II) (Ravishankar *et al.*, 2003). The centroids of rings *B* and *C* are separated by 3.739 (2) Å, indicating the absence of π–π interactions. The torsion angle C12—C15—C16—C17 has a value of −2.1 (5)°, indicating that the bonds C12—C15 and C16—C17 are more closely *cis*; compare with −7.0 (4)° in (II), −14.8 (8)° (molecule *A*) and 6.5 (9)° (molecule *B*) in 2,3-diphenylmaleic anhydride (Yoon *et al.*, 1995) and −7.5° in 1,2-diphenylcyclopentene (Bernstein, 1975). The three phenyl rings enclose a cavity with an area of *ca* 21.4 Å^2.

The mean C—C length in ring *A* [1.399 (6) Å] is longer than that in ring *B* [1.391 (2) Å] and that in ring *C* [1.390 (2) Å]; all these mean values are high compared to those reported for (II) (Ravishankar *et al.*, 2003). The O—C—C angles at the sp^3-hybridized C atoms, C1 [O1—C1—C2 = 111.9 (3)°] and C8 [O2—C8—C7 = 112.7 (3)°], show some distortion from the ideal tetrahedral value. The widening of the exocyclic bond angle O1—C20—C21 to 122.2 (3)° and consequent narrowing of O1—C20—C19 to 117.9 (3)° is due to the close approach [2.09 (5) Å] of atoms H1*A* and H21, attached to atoms C1 and C21, respectively. The close approach [2.16 (6) Å] of atoms H1*A* and H8*B* (attached to C8) causes the widening of angles C1—C2—C7 [124.8 (3)°] and C2—C7—C8 [123.4 (3)°] and narrowing of angles C1—C2—C3 [116.7 (3)°] and C6—C7—C8 [117.8 (3)°].

In the crystal structure, inversion-related molecules are linked by C8—H8*A*···O2$^{\rm i}$ [symmetry code: (i) $-x, 1-y, -z$] hydrogen bonds to form dimeric pairs. These pairs, translated along the *a* direction, are linked by weak C1—H1*B*···O1$^{\rm ii}$ [symmetry code: (ii) $1-x, 1-y, -z$] hydrogen bonds to form molecular chains. Adjacent molecular chains, related by the symmetry operation ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$), are linked by weak C—H···π interactions, to form a network (Table 2 and Fig. 2). The structure is further stabilized by van der Waals interactions.

Experimental

Reaction of *o*-xylenyl dibromide with *p*-hydroxybenzaldehyde in anhydrous DMF and in the presence of K_2CO_3 at 343 K for 48 h gave *o*-bis(*p*-formylphenoxymethyl)benzene. Treatment of the latter with 5 equivalents of $TiCl_4$ and 10 equivalents of Zn in dry THF for 24 h, under high dilution conditions, afforded the title compound in 55% yield. It was purified by column chromatography (SiO_2; hexane–chloroform = 8:2) and single crystals suitable for X-ray study were grown by vapour diffusion of hexane into a solution of the title compound in chloroform.

Crystal data

$C_{22}H_{18}O_2$
$M_r = 314.36$
Monoclinic, $P2_1/c$
$a = 13.3086$ (7) Å
$b = 5.8168$ (3) Å
$c = 20.8145$ (11) Å
$\beta = 95.463$ (1)°
$V = 1604.00$ (15) Å^3
$Z = 4$

$D_x = 1.302$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3501 reflections
$\theta = 3.5$–28.4°
$\mu = 0.08$ mm^{-1}
$T = 183$ (2) K
Slab, colourless
0.36 × 0.22 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
8283 measured reflections
3288 independent reflections

1910 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.119$
$\theta_{\rm max} = 26.5°$
$h = -15 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -23 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.196$
$S = 1.05$
3288 reflections
272 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.061 (7)

Table 1
Selected geometric parameters (°).

O1—C1—C2	111.9 (3)	C2—C7—C8	123.4 (3)
C3—C2—C1	116.7 (3)	O2—C8—C7	112.7 (3)
C7—C2—C1	124.8 (3)	C19—C20—O1	117.9 (3)
C6—C7—C8	117.8 (3)	C21—C20—O1	122.2 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

CgC denotes the centroid of phenyl ring *C*.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O2^{i}	1.02 (4)	2.41 (4)	3.256 (4)	140 (3)
C1—H1*B*···O1^{ii}	1.03 (4)	2.50 (4)	3.497 (4)	161 (3)
C18—H18···*CgC*^{iii}	1.00 (3)	2.65 (4)	3.385 (4)	130 (3)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

H atoms were located from a difference map and their positional parameters were refined, but the isotropic displacement parameters were set equal to $1.2U_{\rm eq}$(C). For H atoms, the C—H range is 0.94 (4)–1.07 (4) Å. The reflections ($\overline{3}02$), (302), (110) and (319) were removed during refinement, as the observed and calculated structure factors showed large disagreement. As a result of the large fraction of weak data at higher angles, the 2θ maximum was limited to 53°. Owing to the poor diffraction quality of the crystal, the $R_{\rm int}$ (0.119) and R (0.077) values are high.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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