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8,12-Dioxa-1,7,10(1,2)-tribenzenacyclododecaphane-2,5-dien-4-one

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In the title compound, $C_{25}H_{20}O_3$, two of the benzene rings are almost perpendicular to each other, with a dihedral angle of 88.1 (1)°. The molecular packing is stabilized by intermolecular C—H···O and π–π interactions, in addition to van der Waals forces.

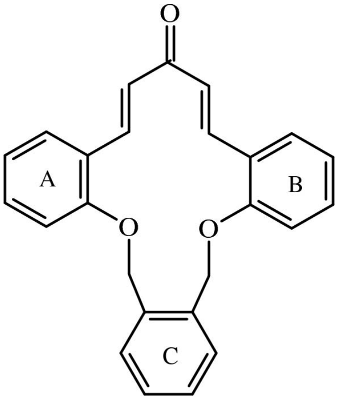
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.051
wR factor = 0.152
Data-to-parameter ratio = 16.4

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

Comment

Cyclophanes are cyclic systems consisting of at least one aromatic system bridged by one or more aliphatic chains (De Ridder *et al.*, 2001). These derivatives constitute a novel building block for the potent human immunodeficiency virus (HIV) protease inhibitor (Ettmayer *et al.*, 1996). They also act as potential reversal agents of muscle relaxants by chemical chelation (Cameron *et al.*, 2002). The importance of cyclophane derivatives prompted us to undertake the structure analysis of the title compound, (I).



(I)

The structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The C—C and C—O bond lengths of the linkages between the benzene rings are comparable with those in related cyclophane structures (Weber & Jones, 1983; Bhaskaran *et al.*, 2003). The C═C bond distances are normal in comparison with the literature value of 1.321 (13) Å (Allen *et al.*, 1987).

The exocyclic angles around atoms C8 and C17 show considerable asymmetry, with the O2—C9—C8 angle [124.5 (1)°] being wider than O2—C9—C4 [115.4 (1)°], and the O3—C18—C19 angle [124.4 (1)°] being wider than O3—C18—C23 [114.7 (1)°]. This asymmetry may be due to the short contacts H8···H10*B* (2.05 Å) and H17*A*···H19 (2.21 Å).

The torsion angles C9—O2—C10—C11 [−80.0 (2)°] and C16—C17—O3—C18 [170.8 (1)°] indicate that the orienta-

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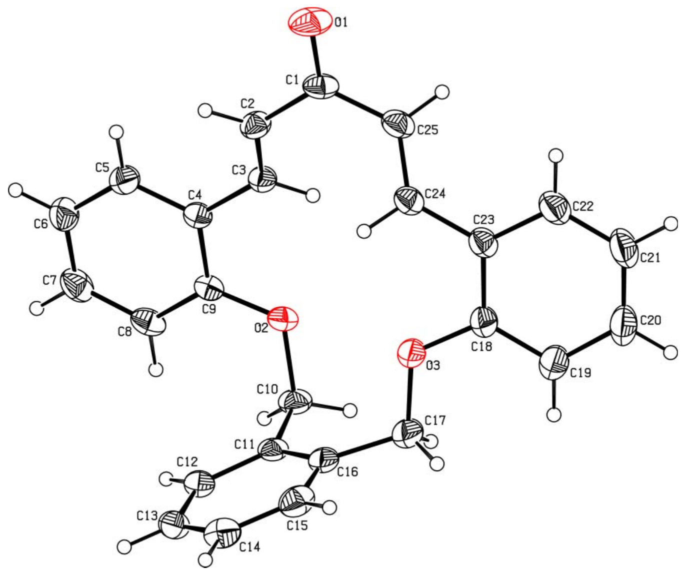

Figure 1
The molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

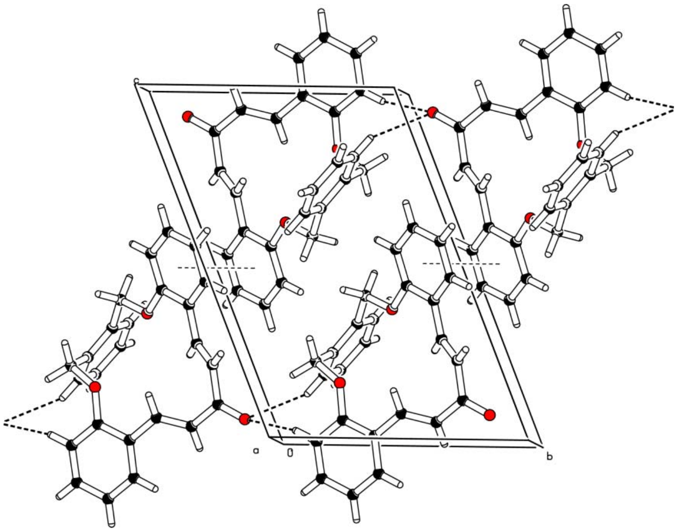

Figure 2
The molecular packing of (I), viewed down the *a* axis. Dashed lines indicate intermolecular interactions.

tions of the C—O bonds linking the two benzene rings are −synclinal and +antiperiplanar. The C═C bonds are in a *trans* configuration. This is confirmed by the torsion angles C1—C2—C3—C4 [−177.08 (13)°] and C23—C24—C25—C1 [177.00 (14)°].

Benzene rings *A* (atoms C4–C9) and *C* (C18–C23) are almost perpendicular to each other, with a dihedral angle of 88.1 (1)°. The dihedral angle between benzene rings *B* and *C* (C11–C16) is 79.7 (1)° and that between rings *A* and *B* is 18.4 (1)°.

The molecular packing is stabilized by intermolecular C—H···O interactions between C8···O1 and C12···O1 (Table 2 and Fig. 2). In addition to this, the packing is also stabilized by intermolecular π–π interactions between rings *B* at (x, y, z) and ($x - 1$, $y - 1$, z), with a centroid–centroid separation of 3.656 (1) Å (Fig. 2).

Experimental

A mixture of 2,2′-dihydroxydibenzylideneacetone (1 mmol) and potassium carbonate (4 mmol) in dry dimethyl formamide (20 ml) was stirred for 20 min and then *ortho*-xylene dibromide (1 mmol) was added. Stirring was continued until the disappearance of the starting materials. After completion of the reaction, the reaction mixture was poured into water, extracted with dichloromethane, dried with anhydrous magnesium sulfate and concentrated. The mixture was then column-chromatographed with an ethyl acetate–hexane mixture (9:1) to obtain the title compound. Compound (I) was recrystallized using methanol to yield diffraction-quality crystals.

Crystal data

$C_{25}H_{20}O_3$
M_r = 368.41
Triclinic, $P\bar{1}$
a = 7.7602 (11) Å
b = 9.8884 (14) Å
c = 13.965 (2) Å
α = 108.074 (2)°
β = 94.933 (2)°
γ = 109.974 (2)°
V = 935.1 (2) Å^3

Z = 2
D_x = 1.308 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4247 reflections
θ = 2.3–27.8°
μ = 0.09 mm^{-1}
T = 273 (2) K
Block, colourless
0.26 × 0.23 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
7971 measured reflections
4160 independent reflections

3395 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 28.0°
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.152
S = 1.05
4160 reflections
253 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 0.1401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.225 (2)	C17—O3	1.410 (2)
C2—C3	1.326 (2)	C18—O3	1.371 (2)
C9—O2	1.371 (2)	C24—C25	1.325 (2)
C10—O2	1.446 (2)		
O2—C9—C8	124.5 (1)	O3—C18—C19	124.4 (1)
O2—C9—C4	115.4 (1)	O3—C18—C23	114.7 (1)
C11—C10—O2—C9	−80.0 (2)	C16—C17—O3—C18	170.8 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O1$^{\rm i}$	0.93	2.36	3.254 (2)	161
C12—H12···O1$^{\rm i}$	0.93	2.54	3.401 (2)	154

Symmetry code: (i) $x - 1$, $y - 1$, z.

H atoms were positioned geometrically and treated as riding on their parent C atoms, with C—H distances of 0.93 and 0.97 Å and with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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