

2,7,12,17-Tetraoxa-3,4:5,6:13,14:-
15,16-tetrabenzodispiro[8.1.8.0]-
nonadecane

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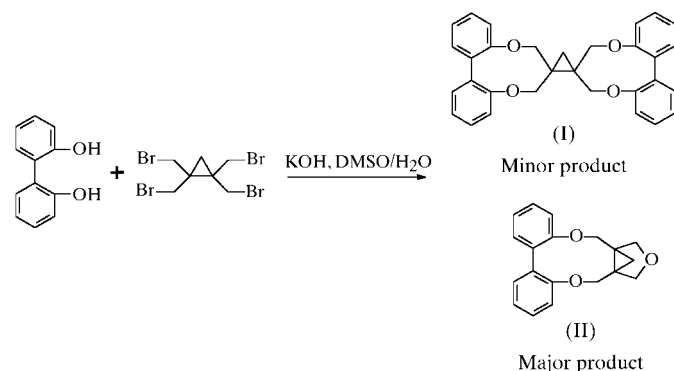
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The reaction of biphenyl-2,2'-diol with 1,1,2-tetrakis(bromomethyl)cyclopropane leads to two products, namely a propellane-type compound and a dispiro-type compound. The molecular structure of 4,5;6,7-dibenzo-3,8,12-trioxa[8.3.1]propellane has been determined previously by spectroscopic methods. The crystal structure of the dispiro product, 2,7,12,17-tetraoxa-3,4:5,6:13,14:15,16-tetrabenzodispiro[8.1.8.0]-nonadecane, $C_{31}H_{26}O_4$, revealed that the conformations of the nine-membered heterocyclic rings are due to interactions between the π -electron system of the biphenyl moiety and the lone electron pairs of the ether O atoms, the repulsion of the lone electron pairs of atoms O1...O2 and O3...O4, and steric interactions between H atoms in *ortho* positions. The conformations have C_1 symmetry and can be described approximately as twist-boat.

Comment

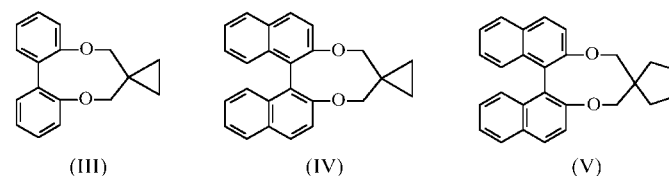
The reaction of biphenyl-2,2'-diol with 1,1,2-tetrakis(bromomethyl)cyclopropane (Scheme I), leads to two products, namely the major product 4,5;6,7-dibenzo-3,8,12-trioxa[8.3.1]propellane, (II), the molecular structure of which has been



determined by spectroscopic analyses (1H NMR, ^{13}C NMR and MS) by Jamrozik & Szlachcic (2000), and 2,7,12,17-tetraoxa-3,4:5,6:13,14:15,16-tetrabenzodispiro[8.1.8.0]nonadecane, (I).

In this type of reaction, two products are usually possible, *viz.* either dispiro-type or propellane-type compounds. The problem of dispiro-propellane isomerism was discussed by Ginsburg (1987). Because the isomers behave similarly in spectroscopic analyses, such as NMR, IR and MS, there are some difficulties in unravelling the correct structures of the products. However, the exact structure of the product can be established unambiguously through X-ray diffraction analysis whenever single crystals are available. In the reaction described above, after (II) had been separated as a solid compound (m.p. 543–544 K), another compound, (I), was found in the mother liquor that remained after the crystallization of (II). Compound (I) had a slightly different melting point (545–546 K), and as (I) was obtained in a single-crystal form we were able to determine its crystal and molecular structure.

The structures of heterocyclic spirane, dispirane and propellane derivatives have been the subject of much interest in our laboratory for some time. Examples include spiro(2*H*-3,4-dihydro-1,5-dioxadibenzo[*f,h*]cyclononene-3,1'-cyclopropane) [(III); Karle & Grochowski, 1979], spiro(3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1'-cyclopropane) [(IV); Stadnicka, 1979], spiro(3,4-dihydro-2*H*-1,5-dioxadinaphtho[2,1-*f*:1,2-*h*]cyclononene-3,1'-cyclopentane) [(V); Stadnicka & Lebioda, 1979], 2,7,12,17-tetraoxatetranaphtho[1,2-*fhfh'*]dispiro[8.0.8.1]nonadecane (Jamrozik, 1985), 2,3,2',3'-bis[8'',11''-dioxo[4.3.3]propella-(3'',4'')]biphenyl (Grochowski *et al.*, 1995) and 4,8,12,16-tetrahydro-1*H*,3*H*,9*H*,11*H*-3*a*,16*a*:8*a*,11*a*-bis(methanoxy-methano)dibenzo[*fg,mn*]octaleno[3,4-*c*:9,10-*c'*]difuran (Jamrozik *et al.*, 1996). The structure of (III) is particularly important, because (III) can be considered as one 'half' of the dispirane molecule (I).



The overall shape of (I) is shown in Fig. 1 in two different projections to emphasize the complicated spatial atomic arrangement. Selected geometric parameters of the molecule are given in Table 1. Both biphenyl moieties have torsion angles close to 60° [$C11-C12-C22-C21 = 61.5(2)$ and $C31-C32-C42-C41 = 58.1(2)^\circ$]. Similar torsion angles were observed in (III), (IV) and (V) (-58.3 , 64.2 and 63.2° , respectively). The two medium-sized nine-membered heterocyclic rings of 4*H*-2,3-dihydro-1,5-dioxonine have an almost identical shape and conformation (Table 1) and are similar to those found in (III) and (IV) (Glass, 1988). The two nine-membered rings of (I) are related by a rotation of about 120° around an axis perpendicular to the cyclopropane ring and passing through its centre. This arrangement suggests that if the cyclopropane ring contained a third identical moiety, attached to the free corner of the cyclopropane ring at C7, this moiety would have the same shape as the existing rings and would be related to them by a pseudo-threefold axis. The

intramolecular O1···O2 and O3···O4 contacts (2.908 and 2.869 Å) are somewhat larger than the sum of the van der Waals radii and are close to the distances observed in (III), (IV) and (V) (2.925, 2.999 and 2.921 Å, respectively). The repulsion of the oxygen lone pairs and their coupling with the π -electron system of the biphenyl moiety, and also the steric interactions between its H atoms in *ortho* positions, have a strong influence on the specific conformation of the nine-membered rings in these types of compounds. The conformation has no analogues among the possible forms of 1,3-cyclononadienes considered by Zuccarello *et al.* (1971). However, Yavari *et al.* (1999), in their study of (*Z,Z*)-cyclonona-1,3-diene by AM1 SCF MO (self-consistent field molecular orbital) calculations, reported the existence of a similar form [twist-boat; TB(C_1)], but with a relatively high strain energy. Using the description introduced for 1,3-cyclononadienes by Zuccarello *et al.* (1971), the conformation can be approximately defined by Scheme II, in which the observed torsion angles, defining the conformation of the nine-membered rings and given in Table 1, are represented by their signs (plus, minus or zero). It can be seen that the pseudo- C_2 symmetry of the nine-membered ring is disturbed by an apex at the cyclopropane C atom. As a result, the effective symmetry of the ring is only C_1 . Note that the conformation observed in the crystalline state, both in (I) and in (III), (IV)

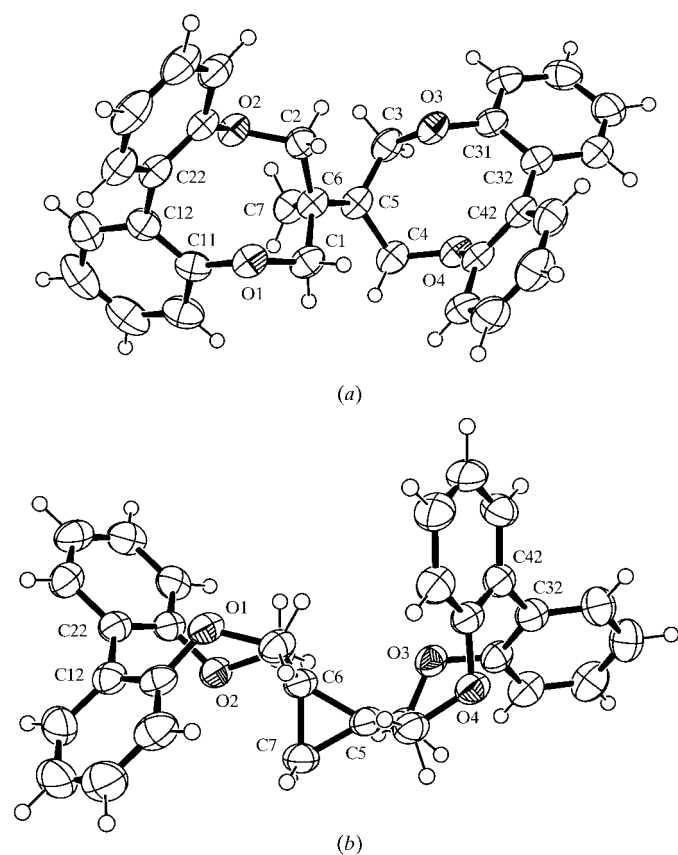
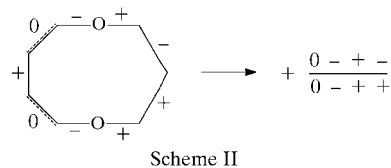


Figure 1
Views of (I) projected (a) on a plane perpendicular to the cyclopropane ring and (b) normal to the cyclopropane ring, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

and (V), differs from that found with dynamic ^1H and ^{13}C NMR (Rys & Duddeck, 1995) for the derivatives of 7,8-dihydro-6*H*-dibenzo[*f,h*][1,5]dioxinine in CDCl_3 solution, where the conformation appeared to be of the twist-chair type with an overall molecular symmetry of C_2 in most cases. It is possible that the conformation of the 4*H*-2,3-dihydro-1,5-dioxinine ring in the close vicinity of the cyclopropane ring is affected by the rigidity of the latter. The cyclopropane ring has a shape close to an ideal equilateral triangle. The average value of the endocyclic angles of the ring is 60 (1)°, and the average C—C distance is 1.516 (12) Å.



The packing in the structure projected on to (010) is presented in Fig. 2(a), which reveals a pseudo-hexagonal close packing of the molecules and their specific overall shape. The intermolecular interactions are mainly of the van der Waals type, except for the only weak C—H··· π (arene) hydrogen

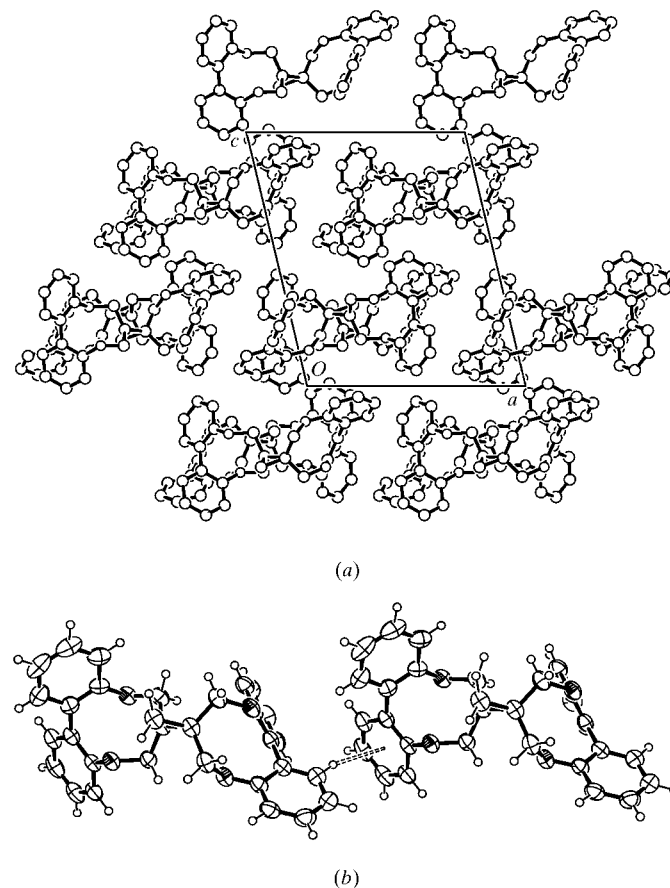


Figure 2
(a) The packing in the crystal structure projected on (010), with H atoms removed for clarity. (b) The interaction between C33—H33 and the aromatic ring C21—C26.

bond, which could be considered to be between C33—H33 and the centroid (C_g) of the aromatic ring C21—C26 for the neighbouring molecule [symmetry code: (i) $x + 1, y, z$]. The hydrogen bond is shown in Fig. 2(b) [$D-H = 0.98$ (2), $H \cdots C_g^i = 2.69$ (2), $D \cdots C_g^i = 3.65$ (1) Å and $D-H \cdots C_g^i = 165$ (1)°].

Experimental

Compound (I) was found in the mother liquor long after the precipitation of the main product of the reaction between biphenyl-2,2'-diol and 1,1,2,2-tetrakis(bromomethyl)cyclopropane (Jamrozik & Szlachcic, 2000) and was subsequently crystallized from 2-propanol. HRMS analysis; calculated for $C_{31}H_{26}O_4$: 462.1831; found: 462.1824.

Crystal data

$C_{31}H_{26}O_4$	$D_x = 1.298 \text{ Mg m}^{-3}$
$M_r = 462.52$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4265 reflections
$a = 12.4954$ (4) Å	$\theta = 1.0\text{--}25.0^\circ$
$b = 13.0617$ (5) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 14.9097$ (7) Å	$T = 293$ (2) K
$\beta = 103.4840$ (13)°	Plate, colourless
$V = 2366.35$ (16) Å ³	$0.25 \times 0.16 \times 0.06 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.017$
φ and ω scans to fill Ewald sphere	$\theta_{\text{max}} = 25.1^\circ$
7662 measured reflections	$h = 0 \rightarrow 14$
4117 independent reflections	$k = -15 \rightarrow 14$
3301 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.5467P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
4117 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
420 parameters	
All H-atom parameters refined	

The positions of all H atoms were found from a difference Fourier map. H atoms were included in the refinement without constraints and with isotropic displacement factors. The range and the average value of the refined C—H distances were 0.94 (2)–1.05 (3) and 0.98 (5) Å, respectively.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1999); software used to prepare material for publication: SHELXL97.

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Table 1

Selected geometric parameters (Å, °).

O1—C1	1.4372 (19)	C4—C5	1.515 (2)
O2—C2	1.4508 (19)	C5—C7	1.511 (2)
O3—C3	1.442 (2)	C5—C6	1.530 (2)
O4—C4	1.434 (2)	C6—C7	1.508 (2)
O1—C11	1.3794 (19)	C11—C12	1.397 (2)
O2—C21	1.3788 (18)	C12—C22	1.492 (2)
O3—C31	1.3818 (19)	C21—C22	1.395 (2)
O4—C41	1.3840 (18)	C31—C32	1.397 (2)
C1—C6	1.515 (2)	C32—C42	1.489 (2)
C2—C6	1.511 (2)	C41—C42	1.397 (2)
C3—C5	1.507 (2)		
C1—O1—C11	117.84 (12)	C6—C6—C7	59.63 (10)
C2—O2—C21	116.51 (12)	C5—C7—C6	60.91 (10)
C3—O3—C31	117.02 (12)	O1—C11—C12	116.33 (14)
C4—O4—C41	118.12 (12)	O2—C21—C22	118.64 (13)
C3—C5—C4	112.69 (14)	O3—C31—C32	117.11 (14)
C6—C5—C7	59.46 (10)	O4—C41—C42	116.97 (13)
C1—C6—C2	113.03 (13)		
C11—O1—C11—C6	69.83 (17)	C1—O1—C11—C12	−135.47 (14)
C21—O2—C21—C6	119.68 (15)	O1—C11—C12—C22	5.5 (2)
C31—O3—C31—C5	121.57 (14)	C2—O2—C21—C22	−114.57 (15)
C41—O4—C41—C5	73.82 (18)	O2—C21—C22—C12	2.0 (2)
O3—C3—C5—C4	−82.14 (16)	C11—C12—C22—C21	61.5 (2)
O4—C4—C5—C3	42.80 (18)	C3—O3—C31—C32	−119.37 (15)
O2—C2—C6—C1	−86.08 (17)	O3—C31—C32—C42	6.8 (2)
O1—C1—C6—C2	47.21 (19)	C4—O4—C41—C42	−133.13 (14)
C3—C5—C6—C2	−0.4 (2)	O4—C41—C42—C32	3.0 (2)
C4—C5—C6—C1	3.2 (2)	C31—C32—C42—C41	58.1 (2)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1148). Services for accessing these data are described at the back of the journal.

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