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Bis(1,3-dioxan-2-yl)arenes: precursors to linked porphyrins

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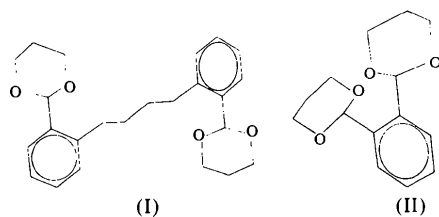
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Abstract

The crystal structures of two linked-porphyrin precursors have been determined. In the crystalline state, 1,4-bis[2-(1,3-dioxan-2-yl)phenyl]butane, $C_{24}H_{30}O_4$, (I), exists in a stair-like conformation with dioxane rings in chair conformations. The molecule is positioned on an inversion center. In the crystalline state, 1,2-bis(1,3-dioxan-2-yl)benzene, $C_{14}H_{18}O_4$, (II), is arranged in zigzag chains. In each chain, molecules of (II) are tilted $106.2(1)^\circ$ relative to each other. They are also oriented to form a weak C—H \cdots O contact (H \cdots O 2.43 Å).

Comment

Considerable effort (Kadish *et al.*, 1998, and references therein) has been devoted to model systems, especially linked porphyrins, for photosynthetic reaction centers for *Rhodospseudomonas viridis* and *Rhodobactersphaeroides* (Clement *et al.*, 1998). The crystal structures of two precursors for diporphyrin systems are detailed here, namely 1,4-bis[2-(1,3-dioxan-2-yl)phenyl]butane, (I), and 1,2-bis(1,3-dioxan-2-yl)benzene, (II). The syntheses of compounds of this type have been published previously (Sessler *et al.*, 1990).



Compound (I) (Fig. 1) is a precursor for a flexibly connected diporphyrin system, 1,4-diporphyrinpropane. Selected geometrical data are given in Table 1. The molecule sits on an inversion center. The benzene ring is planar with a maximum deviation from its mean plane of 0.0022 (14) Å for atom C5. The two benzene rings are parallel by symmetry. These rings are separated by 8.96 (1) Å, measured from the centroid of each ring. Since the C1—C6—C7—C8 torsion angle is $101.2(2)^\circ$ and the C6—C7—C8—C8' torsion angle is $-175.1(2)^\circ$, the overall conformation is stair-like. Molecules stack in an offset manner. The distance between equivalent benzene rings in neighboring molecules is 4.69 (1) Å. Closest contacts are H \cdots H non-bonded interactions between the propyl arms of adjacent molecules. The dioxane rings assume chair conformations.

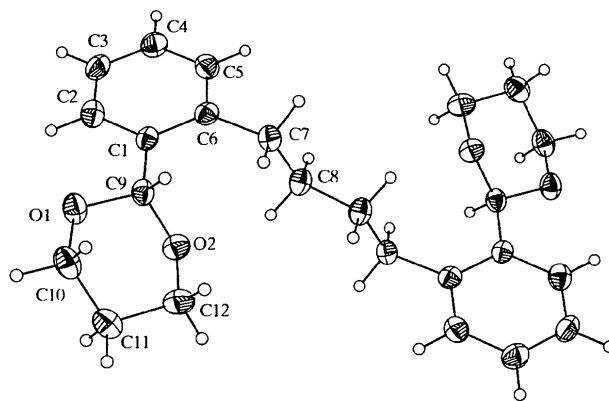


Fig. 1. The structure of compound (I). Symmetry-generated atoms are shown without labels. Displacement ellipsoids are shown at the 50% probability level.

Compound (II) (Fig. 2) is a precursor for the rigidly connected system *o*-diporphyrinbenzene. In Table 2, similar bond lengths and angles are listed in pairs. The benzene ring is planar with a maximum deviation from its mean plane of 0.0037 (17) Å for atom C5. The two dioxane rings adopt chair conformations. The orientation of the dioxane rings does not seem to be determined by inter-ring contacts. The shortest atom-to-atom distance is 2.32 Å between H7A of one ring and H11A of the other ring. Molecules of (II) are tilted $106.2(1)^\circ$ relative to each other (measured as the dihedral angle between mean benzene planes of adjacent molecules). There is a close interaction (H4A \cdots O2 = 2.43 Å) between molecules at (x, y, z) and $(x, 1-y, -\frac{1}{2}+z)$. The fixed C4—H4A distance is 0.95 Å, the C4 \cdots O2 distance is 3.354 (3) Å and the C4—H4A \cdots O2 angle is 164.8° . In the crystal structure, molecules of (II) form zigzag chains seemingly determined by this contact. The acetal C—O bond lengths in (I) and (II) are

equal within experimental error [average 1.415 (6) Å]. This is consistent with the lack of hydrogen bonds to the acetal O atoms (Gandour *et al.*, 1986). These C—O bonds average 1.407 (10) Å in other reported unsubstituted (2,6-dioxahexyl)arenes (Gandour *et al.*, 1986; De & Kitagawa, 1991). Both in those compounds and in the present study, the 2,6-dioxahexyl rings have the chair conformation.

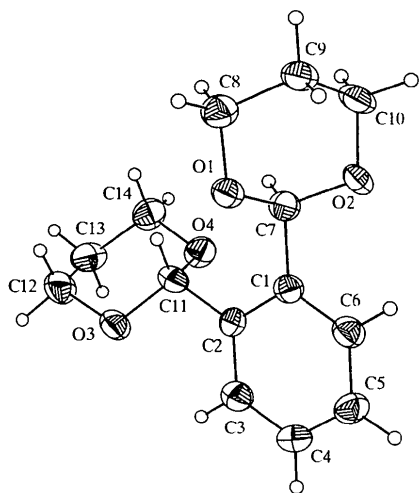


Fig. 2. The structure of compound (II). Displacement ellipsoids are shown at the 50% probability level.

ω scans

Absorption correction:
face-indexed numerical
(Sheldrick, 1997)
 $T_{\min} = 0.979$, $T_{\max} = 0.997$
5153 measured reflections
1887 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.090$
 $S = 0.81$
1887 reflections
127 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0375F_o^2)^2]$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 25.50^\circ$
 $h = -16 \rightarrow 16$
 $k = -5 \rightarrow 5$
 $l = -13 \rightarrow 19$
Intensity decay: <2%

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

C6—C7	1.511 (3)	C10—O1	1.434 (2)
C7—C8	1.534 (3)	C10—C11	1.510 (3)
C8—C8'	1.515 (4)	C11—C12	1.511 (3)
C9—O1	1.411 (2)	C12—O2	1.437 (2)
C9—O2	1.421 (2)		
C1—C6—C7	122.69 (19)	O1—C10—C11	110.17 (18)
C6—C7—C8	112.66 (17)	C10—C11—C12	109.23 (17)
C8'—C8—C7	112.7 (2)	C11—C12—O2	109.32 (17)
O2—C9—O1	110.62 (15)	C12—O2—C9	109.91 (15)
C9—O1—C10	110.28 (16)		
C2—C1—C9—O1	-2.7 (3)	C12—O2—C9—O1	-64.3 (2)
C9—O1—C10—C11	-57.9 (2)	O2—C9—O1—C10	63.3 (2)
O1—C10—C11—C12	53.4 (2)	C6—C7—C8—C8'	-175.1 (2)
C10—C11—C12—O2	-54.1 (2)	C5—C6—C7—C8	-77.6 (2)
C11—C12—O2—C9	59.3 (2)	C1—C6—C7—C8	101.2 (2)

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

Experimental

Both precursor compounds may be prepared by standard synthetic techniques. However, the complete diporphyrin syntheses are demanding and are described elsewhere in detail (Sessler *et al.*, 1990, and references therein).

Compound (I)

Crystal data

C₂₄H₃₀O₄
 $M_r = 382.48$
Monoclinic
 $P2_1/c$
 $a = 13.979 (3) \text{ Å}$
 $b = 4.689 (1) \text{ Å}$
 $c = 16.239 (3) \text{ Å}$
 $\beta = 107.279 (4)^\circ$
 $V = 1016.5 (3) \text{ Å}^3$
 $Z = 2$
 $D_x = 1.250 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ Å}$
Cell parameters from 1032 reflections
 $\theta = 1.53\text{--}25.50^\circ$
 $\mu = 0.084 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$
Square prism
 $0.42 \times 0.05 \times 0.05 \text{ mm}$
Colorless

Data collection

Bruker SMART-1000 CCD diffractometer
982 reflections with $I > 2\sigma(I)$

Compound (II)

Crystal data

C₁₄H₁₈O₄
 $M_r = 250.28$
Monoclinic
 $C2/c$
 $a = 26.064 (5) \text{ Å}$
 $b = 8.696 (2) \text{ Å}$
 $c = 11.943 (2) \text{ Å}$
 $\beta = 103.604 (4)^\circ$
 $V = 2630.9 (8) \text{ Å}^3$
 $Z = 8$
 $D_x = 1.264 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Bruker SMART-1000 CCD diffractometer
 ω scans
Absorption correction:
face-indexed numerical
(Sheldrick, 1997)
 $T_{\min} = 0.988$, $T_{\max} = 0.997$
6995 measured reflections
2453 independent reflections

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ Å}$
Cell parameters from 638 reflections
 $\theta = 1.61\text{--}25.50^\circ$
 $\mu = 0.092 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$
Notched square plate
 $0.17 \times 0.14 \times 0.03 \text{ mm}$
Colorless

1007 reflections with

$I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\max} = 25.50^\circ$
 $h = -31 \rightarrow 31$
 $k = -9 \rightarrow 10$
 $l = -14 \rightarrow 12$
Intensity decay: <2%

RefinementRefinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.041$$

$$wR(F^2) = 0.077$$

$$S = 0.72$$

2453 reflections

163 parameters

H atoms: see below

$$w = 1/[\sigma^2(F_o^2) + (0.0190F_o^2)^2]$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.19 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 2. Selected geometric parameters (Å , $^\circ$) for (II)

O1—C8	1.448 (3)	O2—C10	1.441 (3)
O4—C14	1.442 (3)	O3—C12	1.430 (3)
C8—C9	1.515 (3)	O2—C7	1.409 (3)
C13—C14	1.512 (3)	O3—C11	1.419 (2)
C9—C10	1.505 (3)	O1—C7	1.416 (3)
C12—C13	1.506 (3)	O4—C11	1.411 (2)
O1—C8—C9	109.9 (2)	O3—C12—C13	110.1 (2)
C8—C9—C10	108.7 (2)	C12—C13—C14	108.3 (2)
C9—C10—O2	109.6 (2)	C13—C14—O4	110.2 (2)
C7—O2—C10	110.9 (2)	C14—O4—C11	110.7 (2)
O2—C7—O1	111.5 (2)	O4—C11—O3	111.2 (2)
C7—O1—C8	111.3 (2)	C11—O3—C12	111.2 (2)
C6—C1—C7—O1	-102.2 (3)	C10—O2—C7—O1	-61.5 (2)
C6—C1—C7—O2	19.1 (3)	O2—C7—O1—C8	60.1 (3)
C1—C2—C11—O3	-156.9 (2)	C11—O3—C12—C13	58.4 (3)
C1—C2—C11—O4	82.4 (3)	O3—C12—C13—C14	-54.7 (3)
C3—C2—C11—O3	25.7 (3)	C12—C13—C14—O4	54.5 (3)
C7—O1—C8—C9	-56.5 (3)	C13—C14—O4—C11	-58.0 (3)
O1—C8—C9—C10	54.2 (3)	C14—O4—C11—O3	60.9 (3)
C8—C9—C10—O2	-55.5 (3)	O4—C11—O3—C12	-61.4 (3)
C9—C10—O2—C7	59.4 (3)		

For both compounds, the crystal-to-detector distance was 5.023 cm. Data were collected in groups of 606, 435, and 230 frames at ϕ settings of 0, 90, and 180°, respectively. Each exposure covered -0.3° in ω for 30 s for compound (I) and 20 s for compound (II). Crystals of compound (I), immersed in Krytox oil, were cut to appropriate dimensions with a razor. H atoms were placed at calculated positions and refined with a riding model (methylene C—H = 0.99, methine C—H = 1.00 and aromatic C—H = 0.95 Å). The U_{iso} value for each H atom was set at 1.2 times the equivalent isotropic displacement value of the C atom to which it is attached.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1997); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTLIPC* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTLIPC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1202). Services for accessing these data are described at the back of the journal.

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Absolute configuration of isocurcumenol†

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Abstract

The absolute configuration of isocurcumenol, $\text{C}_{15}\text{H}_{22}\text{O}_2$ was determined as $(3\alpha, 3\alpha, 6\alpha, 8\alpha\beta)$. The C=C double bonds in the 5-isopropylidene and 8-methylene groups were confirmed. The molecules are arranged by intermolecular hydrogen bonds between the hydroxyl groups to form helices about 3_2 screw axes.

Comment

Isocurcumenol is a sesquiterpene found in *Curcuma sp.* (Zingiberaceae). It was isolated from *Curcuma zedoaria* Roscoe (Hikino *et al.*, 1969; Shiobara, Asakawa *et al.*, 1985), but was also found in *Curcuma kwangsiensis* S. G. Lee & C. F. Liang (Chen *et al.*, 1983), *Curcuma heyneana* Valetton & van Zijp (Firman, Kinoshita, Itai & Sankawa, 1988; Firman, Kinoshita & Sankawa, 1988), *Curcuma aeruginosa* Roxburgh (Zhang *et al.*, 1986; Zwaving & Bos, 1992), *Curcuma cochinchinensis* Gagnepain (Dung *et al.*, 1996), *Curcuma harmandii* Gagnepain (Dung *et al.*, 1997) and *Curcuma phaeo-caulis* Valetton (Hou *et al.*, 1997). Crystals which deposited from zedoary oil were first reported by Haensel

† CAS Registry Number [24063-71-6]; CAS name: 3S-(3 α ,3 α ,6 α ,8 $\alpha\beta$)-octahydro-3-methyl-8-methylene-5-(1-methylethylidene)-6H-3a,6-epoxyazulen-6-ol. IUPAC name: (3 α ,3 α ,6 α ,8 $\alpha\beta$)-5-isopropylidene-3-methyl-8-methylene-3a,6-epoxyperhydroazulen-6-ol.