Supplementary Material for:

Unexpected formation of tubular architecture by optically active pure

organic calixsalen

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Experimental details

NMR data was collected using a Bruker 400 MHz or Bruker 300 MHz at ambient temperature. All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CDCl₃ (7.27 ppm) and DMSO (2.50 ppm). All ¹³C NMR spectra were reported in ppm relative to residual CDCl₃ (77.0 ppm) and DMSO (39.52 ppm) and were obtained with ¹H decoupling. Data was manipulated directly using TopSpin (version 2.1) or Mnova (version 6.0.2). Mass spectra were run on a MaldiSYNAPT G2-S HDMS. Infrared data was collected using a Nicolet iS50 FT-IR machine as a thin film unless otherwise stated. Flash column chromatography was performed on Merck Kieselgel type 60 (250 - 400 mesh). Merck Kieselgel type 60F₂₅₄ analytical plates were employed for TLC. Melting points were measured on Büchi Melting Point B-545 and uncorrected.

Time-dependent NMR analysis

Solution of *trans*-(1*R*,2*R*)-diaminocyclohexane (5.4 mg, 0.047 mmol) in 0.6 mL DMSO- d_6 was added to dialdehyde **3** (7.9 mg, 0.047 mmol). The mixture was rapidly mixed, immediately moved to NMR probe and measured.

All known compounds were identified by spectroscopic comparison with authentic samples. 5-methoxy-2-hydroxyisopthalaldehyde (2) was synthesized according to the known procedure.[1]

2,5-dihydroxyisophthalaldehyde 3: 2-Hydroxy-5-methoxyisophthalaldehyde (0.5 g, 2.8 mmol) was suspended in 35 mL of dry dichloromethane and the mixture was cooled to -50 °C. Then 1M tribromoborane solution (11.4 mL, 11.4 mmol) was added drop-wise and the mixture was slowly warmed to 0 °C. The reaction was quenched by the slow addition of water (10 mL), followed by extraction with EtOAc (3×40 mL). The organic layer was washed with saturated solution of sodium thiosulfate (2×40 mL), water, brine and dried over Na₂SO₄. The solvent was evaporated under vacuum and the brown solid product was obtained. Purification by column chromatography on silica gel (1% methanol in dichloromethane) and then crystallization from ethanol-water gave 0.390 mg of

the title aldehyde (85% yield); m.p. 183-185 °C; HRMS (ESI) calcd. for $C_8H_6O_4$ [M-H]⁻ 165,0193; found 165,0173; ¹H NMR (300 MHz, DMSO) δ 10.95 (s, 1H, -OH), 10.20 (s, 2H, -CHO), 9.80 (s, 1H, -OH), 7.43 (s, 2H, *Ar*).; ¹³C NMR (75 MHz, DMSO) δ 192.34 (-CHO), 156.08 (C-OH), 150.73 (C-OH), 124.74 (*Ar*), 123.01 (*Ar*); FTIR (ATR): $\tilde{\nu}$ = 3258, 2886, 1680, 1667, 1602, 1451, 1387, 1306, 1196, 978 cm⁻¹.

(41R,42R,101R,102R,161R,162R,2E,5E,8E,11E,14E,17E)-3,5,9,11,15,17-hexaaza-1,7,13(1,3)-

tribenzena-4,10,16(1,2)-tricyclohexanacyclooctadecaphane-2,5,8,11,14,17-hexaene-

12,15,72,75,132,135-hexaol – **Calixsalen 1:** To *trans*-(1*R*,2*R*)-diaminocyclohexane (114 mg, 1 mmol) dissolved in 20 mL of dry DMSO, the dialdehyde **3** (166 mg, 1 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 24 hours under argon atmosphere. The solvent was evaporated under vacuum and the yellow solid product was obtained. The crude product contains 5% of contracted [2+2] macrocycle was crystallized from ethanol-water mixture of solvents to provide dark brown crystals of **1**. M.p. >300 °C (dec.); HRMS (ESI) calcd. for C₄₂H₄₈N₆O₆ [M+H]⁺ 733.3708; found 733.3715; ¹H NMR (300 MHz, DMSO) δ 13.59 (s, 1H, -OH), 8.93 (s, 1H, -OH), 8.53 (s, 1H, -N=CH-), 8.37 (s, 1H, -N=CH-), 7.24 (s, 1H, *Ar*), 6.83 (s, 1H, *Ar*), 3.35 (s, 2H, –CHN=), 1.74 (s, 3H, *Cy*), 1.61 (s, 3H, *Cy*), 1.41 (s, 2H, *Cy*); ¹³C NMR (101 MHz, DMSO) δ 164.80 (-N=CH-), 154.54 (-N=CH-), 153.82 (C-OH), 149.36 (C-OH), 123.47 (*Ar*), 121.08 (*Ar*), 119.83 (*Ar*), 115.62 (*Ar*), 75.02 (-CHN=), 72.81 (-CHN=), 33.47 (*Cy*), 24.37 (*Cy*), 24.19 (*Cy*) ppm; FTIR (ATR): \tilde{v} = 3431, 3233, 2937, 2861, 1633, 1536, 1451, 1327, 1208, 1141, 1024 cm⁻¹.

Crystal structure of 1

Crystals of 1 suitable for single-crystal X-ray diffraction were obtained from the slow evaporation of a mixture of ethanol and water in ratio *aprox*. 9:1. Reflection intensities were measured on a SuperNova diffractometer equipped with Cu microfocus source (λ =1.54178 Å) and 135 mm Atlas CCD detector. The temperature of the crystal (130K) was controlled with an Oxford Instruments Cryosystem cold nitrogen-gas blower. Data reduction and analysis were carried out with the CrysAlisPro software. The structures were solved by direct methods using SIR-2011[2] and refined by the full-matrix least-squares techniques with SHELXL-2014.[3] All heavy atoms were refined anisotropically. The hydrogen atoms of the macrocycle were placed at calculated positions and refined using the riding model, and their isotropic displacement parameters were assigned a value 20% higher than the isotropic equivalent for the atom to which they were attached. The hydrogen atoms attached to the oxygen atoms were determined on the basis of the likely hydrogen bond scheme and refined with their $U_{150's}$ constrained to 1.5· U_{eq} of the carrier O atoms. No H atoms bonded to O with site occupancy factor 0.5 were present.

In one of the two symmetry independent molecules, one aromatic ring displays a disorder where three carbon atoms and oxygen atom at C5 position are split up into two positions. The occupancies for these positions were refined to 0.6 and 0.4. In another symmetry independent molecule the hydrogen atom of one hydroxyl group is disordered over two positions. The site occupancy factors for these positions were refined to 0.5. Where necessary, restraints for the 1,2-and 1,3-distances were applied.

In the crystal structures of **1** solvent molecules (ethanol and water molecules) were highly disordered and could not be properly modeled therefore their contributions were removed from the diffraction data using SQUEEZE as implemented in Platon.[4] The estimated electron count is 2266 in an accessible void volume of 10162.8 Å³.

The relevant crystal data and refinement parameters are listed in Table ESI_1.

Graphical images were produced in Xseed[5] using Pov-Ray[6] and Mercury[7] programs.

CCDC 1568645 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data%5Frequest/cif

Calculations details

Starting geometry of macrocycle **1** was obtained from crystallographic data and pre-optimized at the PM6 level. The optimized structure of homochiral, monomeric **1** was used as the starting point for construction of dimers **A-C**.

The initial structures of dimers and monomeric **1** were optimized at first with the use of PM6 semiempirical method, then at the B3LYP/6-311G(d,p) level together with empirical D3 version of Grimme's dispersion with Becke-Johnson damping (D3BJ), using Gaussian09 package.[8,9] The Boys and Bernardi counterpoise correction has been utilized to precise calculation of interaction energies between monomers involved in dimers.[10]

	1				
Chemical formula	$C_{84}H_{104}N_{12}O_{17.50}$				
<i>M</i> _r	1561.79				
Crystal system,	Tetragonal, 14 ₁ 22				
space group					
Temperature (K)	130				
a, c (Å)	33.5891 (7), 35.8422 (9)				
<i>V</i> (Å ³)	40438 (2)				
Ζ	16				
Radiation type	Cu Ka				
μ (mm ⁻¹)	0.59				
Crystal size (mm)	$0.34 \times 0.29 \times 0.19$				
Diffractometer	SuperNova				
Absorption	Multi-scan				
correction	CrysAlis PRO 1.171.38.42b (Rigaku Oxford Diffraction, 2015)				
T _{min} , T _{max}	0.899, 1.000				
No. of measured,	125458,				
independent and	21208,				
observed $[l > 2\sigma(l)]$	18491				
reflections					
R _{int}	0.032				
(sinϑ/λ _{max} (Å⁻¹)	0.632				
$R[F^2 > 2\sigma(F^2)],$	0.059, 0.176, 1.05				
wR(F ²), S					
No. of reflections	21208				

Table ESI_1. Crystal data, structure refinement parameters for compound 1.

No. of parameters	1079
No. of restraints	36
H-atom treatment	H-atom parameters constrained
Δho_{\max} , Δho_{\min} (e Å ⁻³)	0.62, -0.34
Absolute structure	0.07 (4)
parameter	Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).

Table ESI_	2 . Geometrical pa	rameters of O-H	.O, O-HN and	C-HO hydrog	en bonds in the	e crystals
of 1 .						

	D-H (Å)	HA (Å)	DA (Å)	D-HA (°)	Symm
O2-H2O4	0.84	1.83	2.583(4)	149	-y+1, -x+1, -z
O4-H4O4S	0.84	1.87	2.642(4)	152	
O6-H6O3S	0.84	1.85	2.651(5)	159	
O6-H22O6	0.84	1.89	2.694(6)	160	-y+1, -x+1, -z
O8-H8O10	0.84	1.89	2.728(5)	175	-y+1/2, -x+1/2, -z+1/2
010-H1007S	0.84	1.79	2.625(8)	175	y-1/2, x+1/2, -z+1/2
012_b-	0.78	2.03	2.610(14)	131	-y+1/2, -x+1/2, -z+1/2
H12_bO12					
O2S-H4SO2	0.81	1.90	2.703(5)	172	
O3S-H5SO6S	0.85	1.89	2.654(8)	149	
O4S-H7SO5S	0.83	1.91	2.667(10)	151	
O4S-H7SO5S	0.83	2.11	2.747(11)	133	у, х, -z
O1-H1N3	0.84	1.87	2.599(3)	144	
O3-H3N5	0.84	1.82	2.559(3)	146	
O5-H5N1	0.84	1.83	2.584(4)	148	
O7-H7N9	0.84	1.83	2.571(4)	145	
O9-H9N11	0.84	1.82	2.551(4)	145	
O11-H11N7	0.84	1.81	2.564(4)	148	
O1S-H2SN12	0.82	2.01	2.814(4)	164	
O1S-H1SN8	0.83	2.01	2.819(5)	165	y, -x+1/2, z+1/4
O1S-H2SN12	0.82	2.01	2.814(4)	164	

O2S-H3SN2	0.86	1.98	2.832(4)	178	-x+1/2, y, -z-1/4
O3S-H6SN6	0.92	1.95	2.824(4)	158	x, -y+3/2, -z+1/4
O4S-H8SN4	0.77	2.03	2.802(4)	176	-x+1, -y+1, z
C2-H18O7	1.00	2.55	3.487(4)	155	
C13-H13O2S	0.95	2.62	3.543(5)	163	-x+1/2, y, -z-1/4
С30-Н30О9	1.00	2.58	3.540(4)	161	
C44-H44O1	1.00	2.60	3.545(5)	157	
C55-H55O1S	0.95	2.62	3.534(5)	160	-y+1/2, x, z-1/4
C56-H56O7S	0.95	2.55	3.271(8)	133	
C57-H57O7S	1.00	2.59	3.332(9)	131	
C58-H58O5	1.00	2.62	3.569(5)	157	
C69-H69O7S	0.95	2.59	3.270(9)	129	y-1/2, x+1/2, -z+1/2
С72-Н72ОЗ	1.00	2.66	3.594(4)	156	

Table ESI_3. Calculated at the B3LYP-GD3BJ/6-311G(d,p) level total energies (*E*, in Hartree), relative energies (ΔE , kcal mol⁻¹) and dimerization energies with and without counterpoise correction (E_{dim} , $E_{dim_{CP}}$, in kcal mol⁻¹) for **A-C** dimers of calixsalen **1**.

Dimer	Ε	ΔΕ	E _{dim}	E _{dim_CP}
Α	-2410.081111	0.18	-53.37	-40.34
В	-2410.077739	2.29	-59.06	-46.06
С	-2410.08139	0.00	-63.66	-49.55



Figure ESI_1. Traces of ¹H NMR spectra measured at time intervals for the reaction between (R,R)-DACH and **3**.



Figure ESI_2. An overlay of the molecules (a), the capsule dimers (b) and the hourglass dimers (c) obtained from the crystal structure of **1** (magenta) and the gas phase calculations (black).



Figure ESI_3. The cavity volume of the capsule (a) and the hourglass (b) motifs. The solvent accessible volume of 42 Å³ in the capsule and 84 Å³ in the hourglass dimmer is shown as pink Connolly surfaces[11] using a probe radius of 1.5 Å.



Figure ESI_4. 3-D Diamondoid-like channel network in the crystals of 1.



Figure ESI_5. Calculated at the B3LYP-GD3BJ/6-311G(d,p) level structures of macrocycle **1** a) and its dimeric forms **A** b), **B** c) and **C** d).

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