

SUPPORTING INFORMATION FOR THE MANUSCRIPT ***** to be completed

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Figure S3. Stereoview illustrating the C-H \cdots π bonds (1-2) and short H \cdots C_{ar} contacts (3-6) that stabilize the axial conformer of 4-methylcyclohexanone in the crystal of 1·5.

Table S1. Crystal data, data-collection and refinement parameters for the crystals of (a) TETROL-3-methylcyclohexanone 1·4 and (b) TETROL-4-methylcyclohexanone 1·5.

(a) Crystal Data and Details of the Structure Determination for Compound 1·4

<i>Crystal Data</i>	
Formula	C ₂₈ H ₂₆ O ₄ , C ₇ H ₁₂ O
Formula Weight	538.65
Crystal System	Monoclinic
Space group	P2 ₁ (No. 4)
a, b, c [Å]	12.4493(6), 8.2368(4), 13.9466(7)
α, β, γ [°]	90, 95.843(2), 90
V [Å ³]	1422.69(12)
Z	2
D _{calc} [g/cm ³]	1.257
μ(MoKα) [mm ⁻¹]	0.083
F(000)	576
Crystal Size [mm]	0.19 x 0.47 x 0.53
<i>Data-collection</i>	
Temperature (K)	200(2)
Radiation [Å]	MoKα, 0.71073
θ _{min, max} [°]	2.1, 28.3
Dataset	-16: 16 ; -10: 11 ; -18: 18
Tot., Uniq. Data, R(int)	26618, 6823, 0.014
Observed data [I > 2.0 σ(I)]	6031
<i>Refinement</i>	
N _{ref} , N _{par}	6823, 399
R, wR2, S	0.0459, 0.1354, 1.04
w	1/[σ ² (F _o ²)+(0.0759P) ² +0.2752P], P=(F _o ² +2F _c ²)/3
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å ³]	-0.27, 0.28

(b) Crystal Data and Details of the Structure Determination for Compound 1·5

<i>Crystal Data</i>	
Formula	C ₂₈ H ₂₆ O ₄ , C ₇ H ₁₂ O
Formula Weight	538.65
Crystal System	Triclinic
Space group	P1 (No. 1)
a, b, c [Å]	8.181(2), 9.952(3), 10.163(3)
α, β, γ [°]	79.296(6), 68.813(5), 65.825(5)
V [Å ³]	703.2(3)
Z	1
D _{calc} [g/cm ³]	1.272
μ(MoKα) [mm ⁻¹]	0.084
F(000)	288
Crystal Size [mm]	0.09 x 0.20 x 0.32
<i>Data-collection</i>	
Temperature (K)	173(2)
Radiation [Å]	MoKα, 0.71073
θ _{min, max} [°]	2.2, 27.1
Dataset	-10: 10 ; -12: 12 ; -13: 13
Tot., Uniq. Data, R(int)	9415, 9403, 0.000
Observed data [I > 2.0 σ(I)]	5729
<i>Refinement</i>	
N _{ref} , N _{par}	9403, 366
R, wR2, S	0.0515, 0.1338, 0.945
w	1/[σ ² (F _o ²)+(0.0540P) ²], P=(F _o ² +2F _c ²)/3
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å ³]	-0.25, 0.26

Table S2. Host-guest interactions (hydrogen bonds, (guest)C-H $\cdots\pi$ and (guest)C-H \cdots C_{ar} interactions). Serial numbers refer to the labelled interactions in the supporting figures.

Compound **1·4**: Host- (R)-enantiomer

D-H \cdots A	D-H /Å	H \cdots A	D \cdots A	D-H \cdots A (°)
O16-H16 \cdots O39A	0.84	1.91	2.621(2)	141
1. C35A-H35A \cdots Cg(C27-C32) ^a	1.00	2.87	3.789(3)	153
2. C38A-H38C \cdots Cg(C1-C6) ^a	0.99	2.75	3.584(6)	142
3. C37A-H37C \cdots Cg(C7-C12) ^b	0.99	2.83	3.732(3)	151
4. C40A-H40E \cdots C25 ^a	0.98	2.76	3.731(3)	171

Compound **1·4**: Host- (S)-enantiomer

D-H \cdots A	D-H /Å	H \cdots A	D \cdots A	D-H \cdots A (°)
O16-H16 \cdots O39B	0.84	2.36	3.125(8)	152
1. C38B-H38A \cdots Cg(C1-C6) ^b	0.99	2.49	3.31(1)	140
2. C38B-H38B \cdots Cg(C7-C12) ^b	0.99	2.91	3.84(2)	156
3. C40B-H40B \cdots Cg(C27-C32) ^a	0.98	3.08	3.87(2)	139
4. C36B-H36A \cdots C30 ^a	0.99	2.90	3.84(1)	159
5. C40B-H40A \cdots C25 ^a	0.98	2.98	3.60(1)	122
6. C37B-H37A \cdots C2 ^b	0.99	2.86	3.41(1)	116

Compound **1·5**: Host- guest

D-H \cdots A	D-H /Å	H \cdots A	D \cdots A	D-H \cdots A (°)
O16-H16 \cdots O39	0.84	1.94	2.713(4)	152
1. C34-H34B \cdots Cg(C7-C12) ^c	0.99	2.66	3.607	159
2. C38-H38B \cdots Cg(C27-C32) ^d	0.99	2.96	3.747	137
3a. C38-H38A \cdots C5	0.99	3.00	3.917(6)	154
3b. C38-H38A \cdots C6	0.99	2.99	3.955(6)	164
4. C40-H40C \cdots C23 ^d	0.98	2.90	3.829(6)	158
5. C40-H40B \cdots C4 ^c	0.98	2.93	3.764(6)	144

Symmetry code: ^a 1-x, ½+y, 1-z; ^b 1-x, ½+y, 2-z; ^c -1+x, y, 1+z; ^d x, -1+y, z

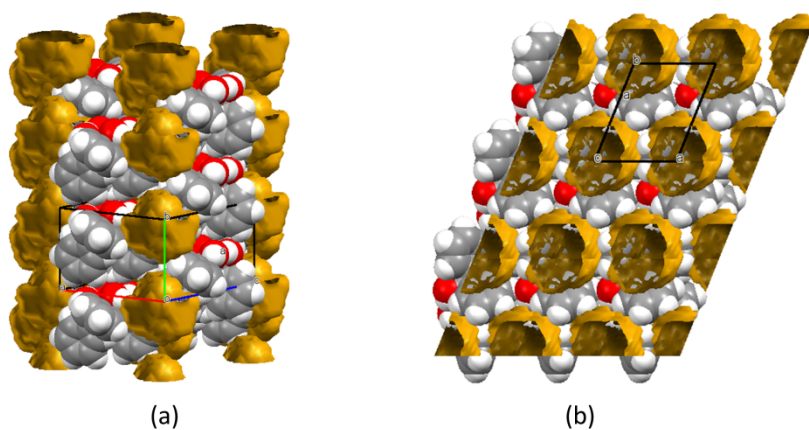


Figure S1. Isolated cavities that accommodate guest molecules in the crystals of (a) TETROL·3-methylcyclohexanone (1·4), (b) TETROL·4-methylcyclohexanone (1·5).

Voids mapped using contact surfaces with program Mercury CSD 3.3 (Build RC5), 2013, with a 1.5 Å probe radius and a grid spacing of 0.5 Å.

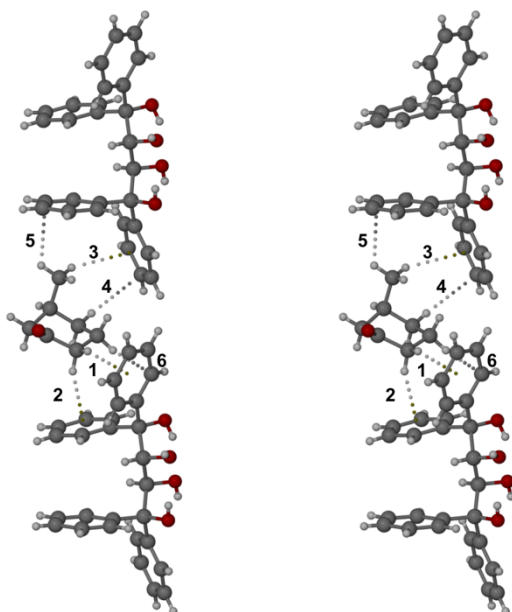


Figure S2: Stereoview illustrating the C-H... π bonds (1-3) and short H...C_{ar} contacts (4-6) that stabilize the axial conformer of the minor guest component ((S)-enantiomer of 3-methylcyclohexanone) in the crystal of 1·4.

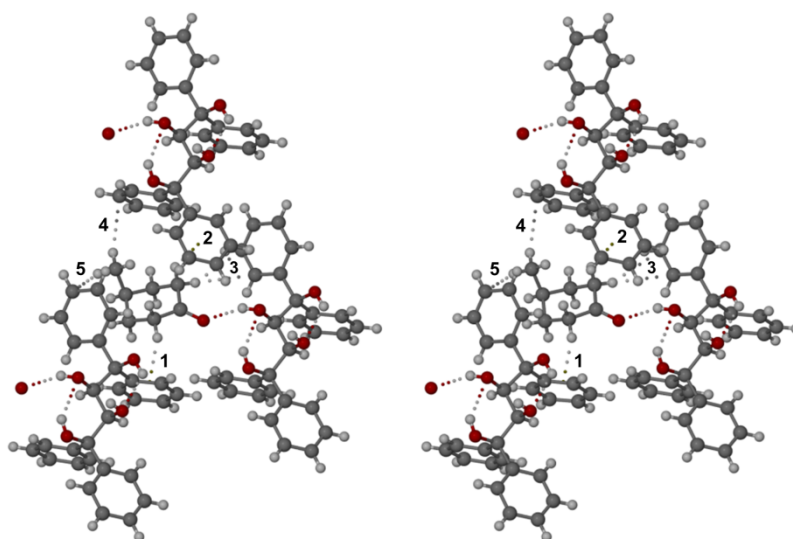
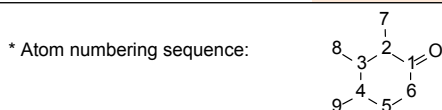


Figure S3: Stereoview illustrating the C-H... π bonds (1-2) and short H...C_{ar} contacts (3-6) that stabilize the axial conformer of 4-methylcyclohexanone in the crystal of 1·5.

Table S3. Comparative crystal structural and theoretical [G3(MP2) composite method] bond lengths, distances, torsion angles and angles for equatorial 2-methylcyclohexanone 3eq, axial 3-methylcyclohexanones 4ax, and axial 4-methylcyclohexanone 5ax.

		3eq			4ax			5ax		
		Theor.	Exp.	Theor-Exp	Theor.	Exp.	Theor-Exp	Theor.	Exp.	Theor-Exp
Bond length/Å	O-C1*	1.23	1.25	-0.02	1.23	1.21	0.02	1.23	1.23	-0.01
	Ha-C8				1.09	0.98 [¶]	–			
	Hb-C8				1.10	0.98 [¶]	–			
	Hc-C8				1.09	0.98 [¶]	–			
	Ha-C9							1.09	0.98 [¶]	–
	Hb-C9							1.09	0.98 [¶]	–
	Hc-C9							1.09	0.98 [¶]	–
Distance/Å	C8-C1				3.06	3.04	0.02			
	C8-Pt4				2.91	2.73	0.19			
	C8-O				3.63	3.74	-0.11			
	Ha(C8)-C1				2.73	2.63 [¶]	–			
	Ha(C8)-Pt4 [§]				2.84	2.83 [¶]	–			
	Ha(C8)-O				3.07	3.13 [¶]	–			
	Ha(C8)-H _{ax} (C6)				2.30	2.38 [¶]	–			
	Hb(C8)-H _{ax} (C6)				3.07	2.74 [¶]	–			
	Hc(C8)-H _{ax} (C6)				3.86	3.71 [¶]	–			
	Ha(C9)-C1							3.35	3.21 [¶]	–
	Ha(C9)-Pt4							3.94	3.78 [¶]	–
	Ha(C9)-O							4.53	4.37 [¶]	–
	C9-C1							3.70	3.62	0.08
	C9-Pt4							4.31	4.23	0.08
	C9-O							4.93	4.84	0.08
	Ha(C9)-H _{ax} (C2)							2.31	2.38 [¶]	–
	Ha(C9)-H _{ax} (C6)							2.31	2.27 [¶]	–
Torsion angle/°	O-C1-C2-C3	-124.0	-127.2	3.2	-122.0	-135.4	13.4	126.7	135.6	-8.9
	C1-C2-C3-C4	-54.1	-55.0	0.9	-55.3	-48.6	-6.6	53.5	53.2	0.2
	C2-C3-C4-C5	57.2	57.6	-0.4	56.7	54.3	2.3	-55.7	-58.1	2.3
	C3-C4-C5-C6	-56.3	-56.0	-0.3	-55.3	-54.8	-0.5	55.7	55.0	0.7
	C4-C5-C6-C1	54.1	52.9	1.2	52.1	46.2	5.9	-53.5	-48.8	-4.7
	C5-C6-C1-C2	-54.7	-53.8	-0.9	-54.0	-42.6	-11.4	51.9	45.4	6.5
	C6-C1-C2-C3	54.0	54.5	-0.6	55.9	44.7	11.2	-51.9	-47.0	-4.9
	C5-C6-C1-O	123.2	127.9	-4.7	123.9	137.5	-13.6	-126.7	-137.2	10.5
	C1-C2-C4-C5	1.4	1.3	0.1	0.0	4.0	-4.0	-2.3	-4.4	2.1
	C2-C3-C5-C6	0.1	1.1	-1.0	1.8	1.3	0.5	0.0	-2.3	2.3
	C3-C4-C6-C1	-1.5	-2.3	0.8	-1.7	-5.8	4.1	2.3	6.6	-4.3
	C7-C2-C3-C4	-178.7	178.2	0.6						
	C7-C2-C1-C6	179.0	-178.6	-0.5						
	Ha-C7-C2-H	-179.6	-177.7	-1.9						
	Hb-C7-C2-C1	178.3	179.8	-1.5						
	Hc-C7-C2-C3	-179.7	-175.6	-4.1						
	C7-C2-C1-O	1.1	-0.2	1.3						
	C8-C3-C2-C1				69.3	74.0	-4.7			
	C8-C3-C4-C5				-66.8	-66.9	0.1			
	Ha-C8-C3-H				-175.1	-163.7	-11.5			
Hb-C8-C3-C2				-178.1	-165.7	-12.4				

		3eq			4ax			5ax		
		Theor.	Exp.	Theor-Exp	Theor.	Exp.	Theor-Exp	Theor.	Exp.	Theor-Exp
Hc-C8-C3-C4					-174.8	-163.0	-11.8			
C9-C4-C3-C2								70.0	66.6	3.4
C9-C4-C5-C6								-70.0	-69.9	-0.2
Ha-C9-C4-H								180.0	-179.3	-0.8
Hb-C9-C4-C3								177.6	179.0	-1.4
Hc-C9-C4-C5								-177.6	-177.3	-0.3
Angle/°	C2-C1-C6	115.2	115.7	-0.5	114.5	117.3	-2.8	114.9	116.3	-1.4
	O-C1-Pt2 [†]	178.3	178.5	-0.2	178.3	179.8	-1.6	178.8	177.6	1.2
	C1-Pt2-Pt3 [‡]	129.9	130.1	-0.2	129.8	139.9	-10.1	132.6	137.9	-5.3
	C4-Pt3-Pt2	128.9	128.9	0.1	129.0	131.3	-2.2	130.3	129.6	0.7



[†] In the crystal structures, H atoms were placed in idealized positions in a riding model [C-H (Å): methylene 0.99, tertiary 1.00, methyl 0.98]. Calculated differences in distances between the theoretical and experimental structures involving H atoms are hence uncertain.

[‡] Pt4: centroid (O C1). [†] Pt2: centroid (C2 C6). [‡] Pt3: centroid (C3 C5).

Experimental Section

Synthesis of (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol **1**

This compound was synthesized according to a published procedure.¹ This afforded a gum which was crystallized and recrystallized from CH₂Cl₂/hexane/MeOH to afford (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol **1** as a white solid (45 %), mp 147-149 °C (lit.², mp 150-151 °C); [α]_D²³ +166° (c = 9.32, CH₂Cl₂) {lit.², [α]_D²⁵ +154° (c = 1.2, CHCl₃)}; ν_{max}(solid)/cm⁻¹ 3440 (br, OH), 3294 (br, OH), 3057 (Ar), 3033 (Ar), 1598 (Ar) and 1494 (Ar); δ_H(CDCl₃) 3.86 (2H, d, 2COH), 4.44 (2H, d, 2HCOH), 4.72 (2H, s, 2CPh₂OH) and 7.2-7.4 (20H, m, Ar); δ_C(CDCl₃) 72.11 (HCOH), 81.71 (CPh₂OH), 124.97 (Ar), 126.05 (Ar), 127.15 (Ar), 127.27 (Ar), 128.10 (Ar), 128.37 (Ar), 128.55 (Ar), 130.08 (Ar), 143.85 (quaternary Ar) and 144.16 (quaternary Ar).

Preparation of inclusion complexes

The complexes of **1** with cyclohexanone **2** and the methylcyclohexanones **3-5** were prepared by dissolving **1** in each of the cyclohexanones with heating, followed by slow evaporation of the latter at ambient temperature and pressure. ¹H NMR analysis revealed that each guest compound was included with a 1:1 host-guest ratio.

Single crystal X-ray Diffraction

The structures were determined from X-ray data collected on Bruker diffractometers with the crystals of **1-4** and **1-5** cooled to 200(2) and 173(2) K respectively. Crystals of **1-5** showed persistent non-merohedral twinning, but the correct unit cell and orientation matrix were successfully determined from a twinned crystal using the program CELL_NOW³ The structures were solved by direct methods and refined by full-matrix least-squares.⁴ Non-H atoms refined anisotropically, except for the minor guest component in **1-4** where isotropic refinement was employed and the refined *U*_{iso} values were in the range 0.04-0.07 Å². H atoms were located in difference Fourier syntheses and were subsequently placed in idealized positions in a riding model [C-H (Å): methylene 0.99, tertiary 1.00, methyl 0.98] with *U*_{iso} values in the range 1.2-1.5 times those of their parent atoms.

Computational studies

Calculations were performed using SPARTAN '10 for Windows [build 1.1.0 (Mar 20 2011)] software, supplied by Wavefunction Inc. Energies of the respective conformers were calculated using the G3(MP2) composite method.⁵

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