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Selectivity of a Resorcinarene Host for Pentanol Isomers

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The resorcinarene host H = 1^4,1^6,5^4,5^6-tetrahydroxy-2,4,6,8-tetrapentyl-3^4,3^6,7^4,7^6-tetra(*p*-toluenesulfonyloxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane was found to form inclusion compounds with seven pentanol isomers, namely 1-pentanol (H·2(1PENT)), 2-pentanol (H·2(2PENT)), 3-pentanol (H·2(3PENT)), 2-methyl-1-butanol (H·2(2M1B)), 3-methyl-1-butanol (H·2(3M1B)), 2-methyl-2-butanol (H·2(2M2B)) and 3-methyl-2-butanol (H·2(3M2B)). These compounds were characterized by thermal analysis, which showed that they all have host–guest (H:G) ratios of 1:2, and their structures were elucidated and compared. Competition experiments were carried out to investigate the selectivity of this host for some of the pentanol guests and thereby investigate the capability of this host for the separation of pentanol isomers.

Keywords: Resorcinarene; pentanol isomers; selectivity

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INTRODUCTION

The chemistry of resorcinarenes, including synthesis, conformational behaviour and complexation properties, has been studied extensively and is well established [1]. The use of resorcinarenes in supramolecular host–guest chemistry is developing rapidly and *C*-methylcalix[4]resorcinarene has been found to act as a suitable building block for a wide variety of supramolecular complexes. Many inclusion compounds have been formed with this host, including host–guest compounds containing small organic guests only [2–6], as well as inclusion compounds with additional spacers linking the resorcinarene host molecules together [7–10], sometimes resulting in the formation of capsules in which the guest molecule is completely enclosed [11–17].

C-methylcalix[4]resorcinarene can be modified by substitution at the upper and lower rim [18–24] or by extending the upper rim using various pillars [25–27] in order to increase the size of the cavity in which guests can be situated or even by covalently linking neighbouring hydroxyl groups to form cavitands [28].

Studies of the selectivity of resorcinarene hosts for various guests have been carried out. Examples include the selectivity of a hydrogen-bonded molecular capsule for benzene, *p*-xylene and toluene [29] and selectivity of a resorcinarene host with long alkyl chains for several cyclohexanediols [30].

In this work we have investigated a resorcinarene host with four substituted tosylate groups on the upper rim and with pentyl groups on the lower rim, namely 1^4,1^6,5^4,5^6-tetrahydroxy-2,4,6,8-tetrapentyl-3^4,3^6,7^4,7^6-tetra(*p*-toluenesulfonyl-oxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane, and have elucidated and compared the structures of the host–guest compounds formed with this host and the seven pentanol isomers. Competition experiments were also carried out with pairs of guests to study the selectivity of this host for some of the pentanol isomers. The structural formula of the host, with its atomic nomenclature, as well as that of the various guests is shown in Scheme 1.

RESULTS AND DISCUSSION

The results of the thermal analysis for H·2(3PENT) are shown in Fig. 1. The TG trace shows a one step desolvation, with a corresponding endotherm in the DSC trace followed by a second endotherm due to the melting of the host. Similar curves were obtained for all the remaining inclusion compounds and in

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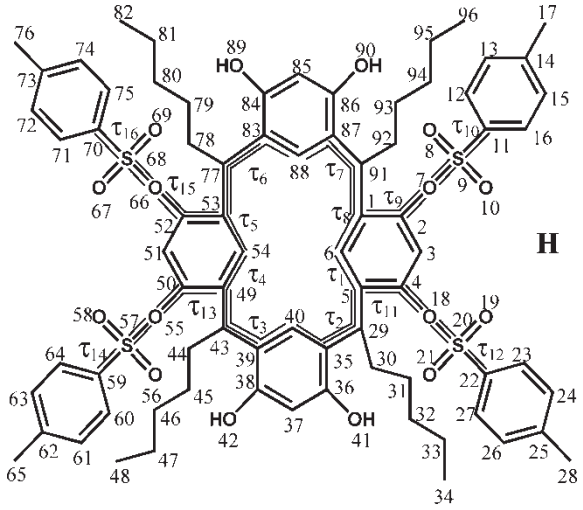

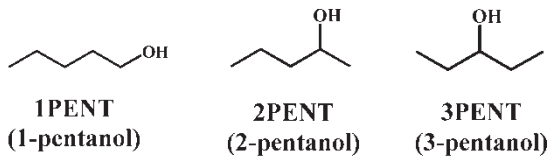

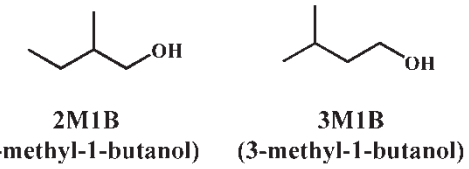

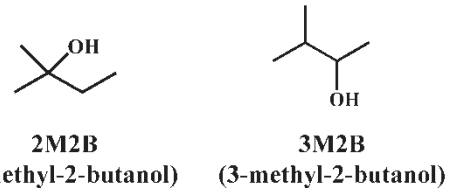

SCHEME 1

each case the observed mass losses from the TG traces are in good agreement with the calculated value for a host:guest ratio of 1:2.

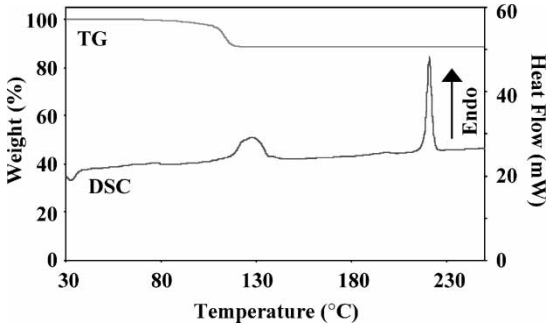

FIGURE 1 TG and DSC traces of H·2(3PENT).

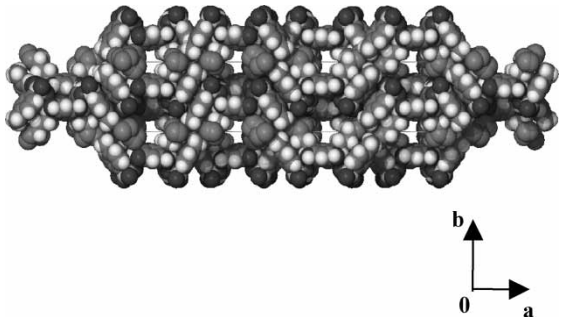

FIGURE 2 View down the channels of H·2(3M1B) along [001] with guest molecules omitted and host molecules represented with van der Waals radii.

H·2(1PENT), H·2(2PENT), H·2(2M1B) and H·2(3M1B) were all found to crystallize in the orthorhombic crystal system in the space group *Pcca* with $Z = 8$. They are isostructural with respect to the host molecules and in each case both the host molecules and guest molecules are located in general positions. The host molecules pack to form undulating channels along [001] as shown in Fig. 2. These channels have a maximum cross-section of approximately 7.6 × 8.0 Å and a minimum cross-section of approximately 5.7 × 3.8 Å and are located at $y = 0$ and $x = 0.12$, 0.36, 0.63 and 0.88. The crystal packing of H·2(2PENT) viewed along [010] is shown in Fig. 3 as an example.

In each of these structures both guest molecules are hydrogen bonded to the host molecule via (Host)-O-H···OH(Guest). The structure is also stabilized by hydrogen bonding that occurs between the host molecules from the hydroxyl groups that are not hydrogen bonded to the guests, to one of the oxygen atoms on the tosyl group of the next host. This hydrogen bonding pattern is exhibited by all seven of the inclusion compounds and Fig. 4 shows the hydrogen bonding in H·2(3PENT) as an example. The hydrogen bonding details for all of the structures are given in Table I. In addition to these hydrogen bonds there are weaker interactions

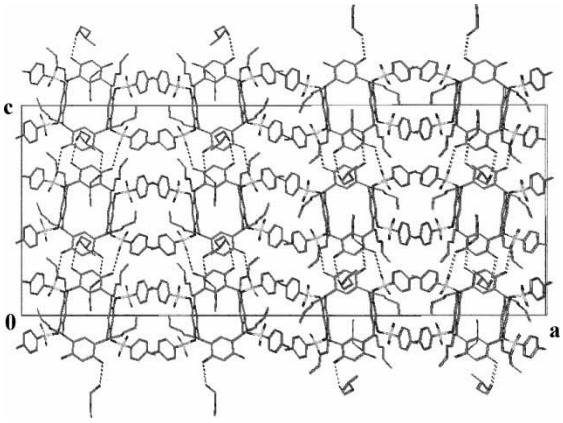

FIGURE 3 Packing diagram of H·2(3M1B) viewed along [010].

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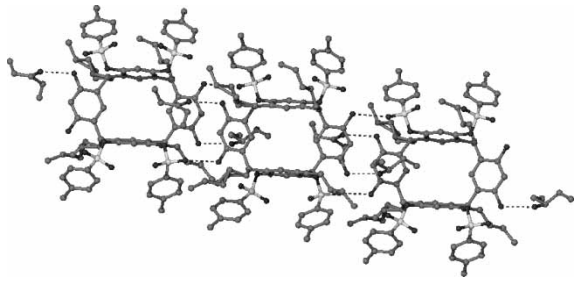

FIGURE 4 Hydrogen bonding in H·2(3PENT).

between the guest oxygen atoms and oxygen atoms in the tosyl groups.

H·2(3PENT) and H·2(2M2B) both crystallize in the monoclinic crystal system in the space group $P2_1/n$ with $Z = 4$. They are isostructural with respect to the host molecules and in both cases both the host molecules and guest molecules are located in general positions. The host molecules pack together resulting in the formation of cavities in which the guest molecules are located. These cavities have dimensions $4.0 \times 11.2 \times 13.7$ Å and four of these cavities are located in each unit cell, with each cavity containing two guest molecules. The crystal packing of H·2(3PENT) viewed along [100] is shown in Fig. 5.

H·2(3M2B) crystallizes in the monoclinic crystal system in the space group $P2/n$ with $Z = 2$. The host molecules are located on twofold axes at Wyckoff position *f* and the guest molecules are located in general positions. The host molecules pack to form very narrow channels along [101] that widen into cavities that extend alternately above or below the channel. These channels are shown in Fig. 6. The dimensions of these cavities extending from the channels are $4.6 \times 9.6 \times 13.5$ Å, and the guests are located in these cavities. The crystal packing viewed along [010] is shown in Fig. 7.

The torsion angles defining the conformation of the host molecule are given in Table II and the conformation of the host molecule in H·2(3M1B) is shown in Fig. 8 as an example. The stereochemistry of resorcinarenes can be defined by the conformation of the macrocyclic ring (crown, boat, chair, diamond and saddle) combined with the relative and individual configurations of the substituents at the methylene bridges. In each of the structures the resorcinarene host has an all-*cis* and all-*axial* arrangement of the pentyl groups with the macrocyclic ring in a boat-like conformation.

The boat conformation occurs when two opposite benzene rings are coplanar with the main macrocyclic plane and the other two are perpendicular to the plane. In this case the two unsubstituted resorcinol rings are nearly coplanar with the macrocyclic ring, while the tosylated resorcinol units are perpendicular to the plane. The tosyl groups are oriented outwards from the centre and bent in a downward direction. Similar boat-like conformations have been reported

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TABLE I Hydrogen bonding details

Compound	D–H···A	D–H (Å)	D···A (Å)	D–H–A (°)
H·2 (1PENT)	O41–H41···O8*	0.970(1)	2.753(6)	171(9)
	O42–H42···O1G	0.980(1)	2.715(6)	160(5)
	O89–H89···O58†	0.971(4)	2.788(6)	158(8)
	O90–H90···O8G	0.984(8)	2.681(6)	134(7)
H·2 (2PENT)	O41–H41···O8*	0.960(1)	2.773(5)	157(5)
	O42–H42···O1G	0.980(1)	2.716(7)	173(6)
	O42–H42···O2G	0.980(1)	2.689(9)	150(5)
	O89–H89···O58†	0.970(1)	2.763(4)	156(6)
	O90–H90···O11G	0.970(1)	2.744(6)	166(6)
	O90–H90···O12G	0.970(1)	2.73(1)	149(6)
H·2 (2M1B)	O41–H41···O8†	0.972(5)	2.763(6)	151(4)
	O42–H42···O1G	0.980(1)	2.672(7)	174(6)
	O89–H89···O58*	0.960(1)	2.872(6)	160(4)
	O90–H90···O11G	0.981(3)	2.675(6)	153(7)
H·2 (3M1B)	O41–H41···O8*	0.970(1)	2.758(5)	157(5)
	O42–H42···O1G	0.980(1)	2.702(6)	172(6)
	O89–H89···O58†	0.960(1)	2.810(5)	166(8)
	O90–H90···O7G	0.980(1)	2.681(5)	175(6)
H·2 (3PENT)	O41–H41···O8‡	0.960(1)	2.869(3)	165(3)
	O42–H42···O1G	0.980(1)	2.679(3)	166(4)
	O89–H89···O58¶	0.970(1)	2.740(3)	176(5)
	O90–H90···O6G	0.980(1)	2.709(4)	147(3)
H·2 (2M2B)	O41–H41···O8‡	0.960(1)	2.800(3)	143(4)
	O42–H42···O1G	0.980(1)	2.688(3)	161(3)
	O89–H89···O58¶	0.960(1)	2.850(2)	162(3)
	O90–H90···O7G	0.980(1)	2.700(3)	162(3)
H·2 (3M2B)	O41–H41···O8§	0.960(1)	2.792(3)	143(4)
	O42–H42···O1G	0.980(1)	2.672(3)	159(4)

Symmetry codes: * $x, -y+1, z+1/2$. † $x, -y+1, z-1/2$. ‡ $x-1/2, -y+3/2, z-1/2$. ¶ $x+1/2, -y+3/2, z+1/2$. § $x-1/2, -y+2, z$.

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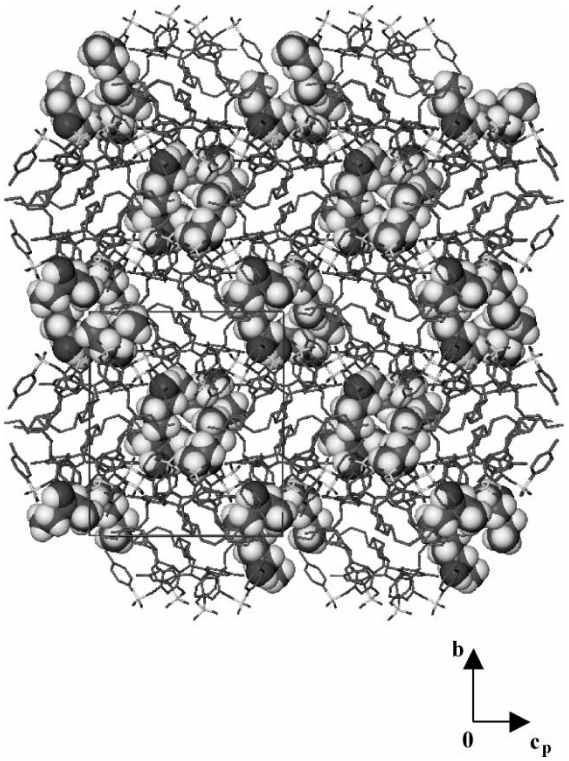

FIGURE 5 Packing diagram of H·2(3PENT) viewed along [100] with the guest molecules represented with van der Waals radii.

for the X-ray crystal structures of bis-benzoxazine derivatives of tetratosylate [19], a resorcinarene tetratosylate bis(triethylammonium) dichoride clathrate [24], as well as for a variety of tetrasulfonates [21], although in each of these cases the tosylated resorcinol units are the coplanar units and the unsubstituted resorcinol rings are nearly parallel.

The selectivity of the host for some of the pentanol isomers was established by carrying out

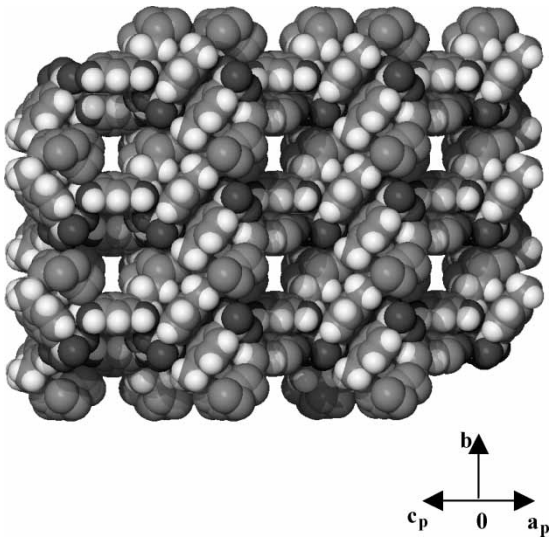

FIGURE 6 View down the channels of H·2(3M2B) along [101] with guest molecules omitted and host molecules represented with van der Waals radii.

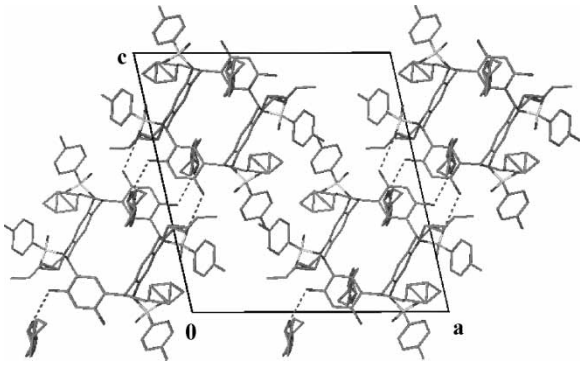

FIGURE 7 Packing diagram of H·2(3M2B) viewed down [010].

competition experiments between pairs of guests. The results of the competition experiments are illustrated in Fig. 9. Each graph shows the mole fraction X of one of the guests in the initial solution versus the mole fraction Z of the same guest included by the host. It can be seen from Fig. 9a that the host does not show any preference for either 2PENT or 3PENT. Following Pivovar *et al.* [31], we have calculated the selectivity constant for each of the competition experiments, which is defined as $K_{A:B} = Z_A/Z_B \times X_B/X_A \quad (X_A + X_B = 1)$. For the 2PENT versus 3PENT competition experiment in which the host shows no selectivity, $K_{2PENT:3PENT} \approx 1$. For the 3M1B versus 2PENT competition experiment, we note (Fig. 9b) that 3M1B is enclathrated preferentially to 2PENT over the whole concentration range and $K_{3M1B:2PENT} = 2.2$. 3M1B is also enclathrated preferentially to 3PENT, although only when the mole fraction of 3PENT is less than or equal to 0.7 (Fig. 9c) and within this range $K_{3M1B:3PENT} = 4.0$. For mole fractions of 3PENT above 0.7, the host shows a slight preference for 3PENT.

From DSC data, the ratio of the onset temperature (T_{on}) and the normal boiling point of the guest (T_b) has been found to be a measure of the stability of an inclusion compound [32]. These ratios have been determined for each of the inclusion compounds and the results are given in Table III. These compounds given in order of decreasing stability are: H·2(3M2B) > H·2(2M2B) > H·2(3M1B) > H·2(2M1B) > H·2(1PENT) > H·2(2PENT) > H·2(3PENT). These stabilities correspond to the results of the competition experiments as they show that the preferentially included guest forms the more stable inclusion compound in each case.

CONCLUSIONS

The structures of the host–guest complexes formed with a resorcinarene host and the seven pentanol isomers were elucidated and compared. These

TABLE II Torsion angles (°) describing host conformation

	H·2 (1PENT)	H·2 (2PENT)	H·2 (2M1B)	H·2 (3M1B)	H·2 (3PENT)	H·2(2M2B)	H·2(3M2B)
τ_1	−103.0(6)	−102.1(5)	−102.4(6)	−102.9(5)	−101.9(3)	−93.6(3)	−101.6(3)
τ_2	53.5(7)	54.1(6)	53.2(7)	54.4(6)	51.6(4)	52.0(3)	53.4(4)
τ_3	−53.5(8)	−52.5(6)	−52.3(9)	−52.2(7)	−59.3(3)	−54.1(3)	
τ_4	109.3(6)	108.5(5)	108.1(7)	106.6(6)	111.2(3)	112.3(3)	
τ_5	−103.2(6)	−102.7(5)	−102.5(7)	−102.2(5)	−95.7(3)	−101.2(2)	
τ_6	48.5(8)	51.9(6)	48.7(7)	48.8(6)	51.3(4)	50.4(3)	
τ_7	−50.2(7)	−52.7(6)	−49.0(8)	−49.1(6)	−54.9(4)	−57.7(3)	
τ_8	104.2(6)	103.7(5)	105.0(7)	103.1(6)	112.2(3)	106.1(2)	106.1(4)
τ_9	−115.4(5)	−116.1(4)	−117.2(6)	−116.3(4)	−117.7(3)	−114.2(2)	−116.5(3)
τ_{10}	67.5(4)	67.9(3)	66.4(4)	67.1(4)	67.1(2)	60.7(2)	57.8(3)
τ_{11}	112.0(4)	111.6(4)	110.8(5)	111.4(4)	115.4(2)	110.2(2)	114.0(3)
τ_{12}	−67.7(4)	−66.5(3)	−69.5(4)	−67.4(4)	−60.7(2)	−77.4(2)	−80.3(2)
τ_{13}	−116.4(5)	−116.6(4)	−116.1(6)	−114.9(5)	−114.7(3)	−118.2(2)	
τ_{14}	60.3(5)	58.8(4)	59.6(5)	59.6(4)	59.3(2)	67.5(2)	
τ_{15}	113.6(5)	113.8(4)	112.0(6)	112.6(5)	110.0(3)	115.9(2)	
τ_{16}	−77.9(5)	−78.8(4)	−77.5(5)	−77.9(4)	−78.9(2)	−61.1(2)	

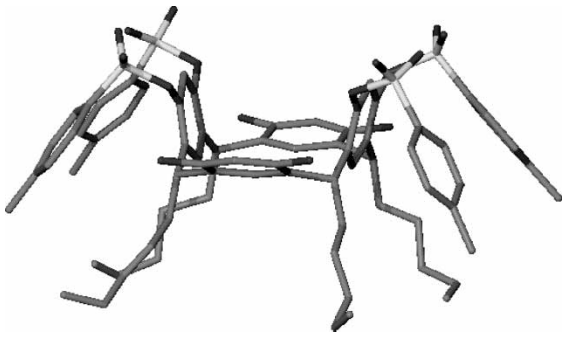

FIGURE 8 Conformation of host molecule in H·2(3M1B).

compounds form three types of structures and in each of the structures the guests are captured between the molecules of resorcinarene rather than within the cavity of the resorcinarene. Competition experiments established that the host exhibits selectivity between certain pairs of pentanol isomers and the results of these competition experiments were correlated with the thermal stabilities of the host–guest systems.

EXPERIMENTAL

General

The host compound was prepared according to a method described in the literature [33]. Suitable crystals of the inclusion compounds were formed by stirring a solution of 30 mg of host in a minimum amount of solvent at approximately 80°C. Once dissolution had occurred, the solution was filtered through a 0.5 μm syringe filter and then left to evaporate slowly at room temperature.

TG experiments were performed on a Mettler Toledo TGA/SDTA 851e under N_2 gas purge (flow rate 30 mL/min). The samples were crushed and blotted dry and the experiments were performed at a heating rate of 20 K/min over the temperature range 30–300°C.

DSC experiments were performed on a Perkin-Elmer PC-7 series thermal analysis system under N_2 gas purge (flow rate 40 mL/min). The samples were crushed, blotted dry and placed in crimped but vented aluminium pans. The experiments were performed over the temperature range 30–300°C at a heating rate of 20 K/min.

Competition experiments were carried out with pairs of guests as follows. A series of mixtures of two guests was prepared such that the mole

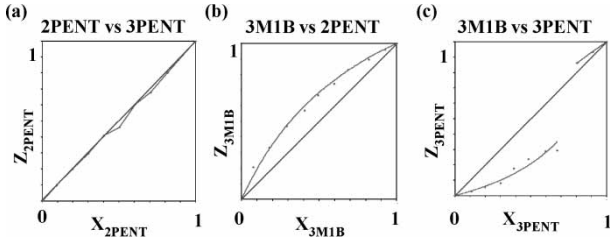

FIGURE 9 Results of the competition experiments of the host with (a) 2PENT vs. 3PENT, (b) 3M1B vs. 2PENT and (c) 3M1B vs. 3PENT.

TABLE III Ratio of onset temperature of guest release (T_{on}) and boiling point of guest (T_b)

Inclusion compound	Onset temperature, T_{on} (K)	Boiling point, T_b (K)	T_{on}/T_b
H·2 (1PENT)	389.9	410.7	0.949
H·2 (2PENT)	371.2	392.5	0.946
H·2 (2M1B)	389.3	401.2	0.970
H·2 (3M1B)	394.6	405.2	0.974
H·2 (3PENT)	358.4	388.8	0.922
H·2 (2M2B)	368.0	375.7	0.980
H·2 (3M2B)	390.8	386.2	1.012

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TABLE IV Crystal data, experimental and refinement parameters

	H·2 (1PENT)	H·2 (2PENT)	H·2 (2M1B)	H·2 (3M1B)	H·2 (3PENT)	H·2 (2M2B)	H·2 (3M2B)
Molecular formula	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$	$C_{76}H_{88}O_{16}S_4{\cdot}2(C_5H_{12}O)$
Guest	1-Pentanol	2-Pentanol	2-Methyl-1-butanol	3-Methyl-1-butanol	3-Pentanol	2-Methyl-2-butanol	3-Methyl-2-butanol
Host:guest ratio	1:2	1:2	1:2	1:2	1:2	1:2	1:2
M/g mol^{-1}	1562.08	1562.08	1562.08	1562.08	1562.08	1562.08	1562.08
Crystal symmetry	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pcca*	*Pcca*	*Pcca*	*Pcca*	$P2_1/n$	$P2_1/n$	$P2/n$
a/Å	60.711(1)	61.1635(6)	60.926(1)	61.0866(7)	19.3857(2)	19.2199(1)	19.2340(2)
b/Å	11.4430(2)	11.4335(1)	11.1517(2)	11.4465(1)	22.3884(2)	22.3700(2)	11.2713(2)
c/Å	24.3637(5)	24.3952(2)	24.4772(7)	24.4263(2)	19.7808(3)	19.9958(2)	19.9335(3)
α/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β/°	90.00	90.00	90.00	90.00	101.634(1)	101.870(1)	102.640(1)
γ/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Z	8	8	8	8	4	4	2
V/Å^3	16,925.7(6)	17,059.9(3)	16,630.4(7)	17,079.5(3)	8408.8(2)	8413.3(1)	4216.7(1)
μ(Mo–Kα)/mm^{-1}	0.178	0.177	0.181	0.177	0.179	0.184	0.179
Temperature/K	293	203	213	203	173	173	203
Range scanned, θ/°	2.21–25.47	2.22–21.94	1.79–25.02	3.15–23.22	2.68–27.88	1.34–28.29	2.77–27.87
Index range	$73 \geq h \geq 0$, $13 \geq k \geq 0$, $29 \geq l \geq 0$	$64 \geq h \geq -63$, $12 \geq k \geq -12$, $25 \geq l \geq -25$	$71 \geq h \geq -71$, $13 \geq k \geq 0$, $28 \geq l \geq -28$	$66 \geq h \geq -65$, $12 \geq k \geq -12$, $27 \geq l \geq -27$	$25 \geq h \geq -25$, $29 \geq k \geq -29$, $26 \geq l \geq -26$	$25 \geq h \geq -25$, $29 \geq k \geq -29$, $26 \geq l \geq -26$	$25 \geq h \geq -25$, $14 \geq k \geq -14$, $26 \geq l \geq -26$
No. reflections collected	14,590	15,464	29,303	19,023	38,696	40,462	18,920
No. unique reflections	14,590 ($R_{int} = 0.0000$)	9145 ($R_{int} = 0.0162$)	11,039 ($R_{int} = 0.0928$)	10,817 ($R_{int} = 0.0353$)	19,912 ($R_{int} = 0.0770$)	20,714 ($R_{int} = 0.0481$)	9932 ($R_{int} = 0.0449$)
No. reflections with $I > 2\sigma I$	5783	7823	5615	7138	9805	12,131	5306
Data/restraints/parameters	14,590/4/954	9145/4/962	11,039/30/959	10,817/4/977	19,912/4/1002	20,714/4/1001	9932/2/486
Final R indices ($I > 2\sigma I$)	$R_1 = 0.0934$ $wR_2 = 0.2569$	$R_1 = 0.0780$ $wR_2 = 0.2130$	$R_1 = 0.0921$ $wR_2 = 0.2498$	$R_1 = 0.0801$ $wR_2 = 0.2093$	$R_1 = 0.0706$ $wR_2 = 0.1760$	$R_1 = 0.0668$ $wR_2 = 0.1770$	$R_1 = 0.0776$ $wR_2 = 0.2146$
R indices (all data)	$R_1 = 0.2118$ $wR_2 = 0.3321$	$R_1 = 0.0890$ $wR_2 = 0.2239$	$R_1 = 0.1896$ $wR_2 = 0.3053$	$R_1 = 0.1255$ $wR_2 = 0.2375$	$R_1 = 0.1613$ $wR_2 = 0.2121$	$R_1 = 0.1253$ $wR_2 = 0.2070$	$R_1 = 0.1464$ $wR_2 = 0.2562$
Largest diff. peak and hole/e Å^{-3}	0.522; −0.379	0.511; −0.478	0.817; −0.499	0.518; −0.410	0.536; −0.440	0.668; −0.569	0.568; −0.448

fraction of a given guest varied from 0 to 1. The host compound was then added to these mixtures, with a total guest:host ratio of 450:1, and dissolved by heating and stirring the solutions. The solutions were then filtered through a 0.5 μm syringe filter and left to evaporate slowly at room temperature, resulting in the formation of crystals. The crystals were then filtered, dried and placed in air-tight glass vials with silicone seals incorporated into the screw-on lids. The vials were heated to induce desorption of the guests in the form of vapour. These vapours then condensed on the sides of the vials as the vials cooled and the resulting drops were extracted, dissolved in acetone and analysed by gas chromatography using a Varian 3400 gas chromatograph equipped with a polar, carbowax column (25 m length, 0.25 mm diameter).

Single Crystal X-ray Analyses

Cell dimensions were established from the intensity data measurements on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation for each of the inclusion compounds. The strategy for the data collections was evaluated using the COLLECT [34] software. For all structures, data were collected by the standard phi- and omega-scan techniques, and were scaled and reduced using DENZO-SMN [35] software. Crystallographic data, experimental and refinement parameters are given in Table IV. The structures were solved by direct methods using SHELX-86 [36] and refined by least-squares with SHELX-97 [37], refining on F^2. The program X-Seed [38,39] was used as a graphical interface for structure solution and refinement using SHELX, and also to produce the packing diagrams.

In each of the structures the positions of all non-hydrogen host atoms were obtained by direct methods and the non-hydrogen guest atoms were located in difference electron density maps. The hydroxyl hydrogens on the host molecule were located in the difference electron density maps and were refined with bond length constraints. The rest of the hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors. In each of the structures there are some atoms in the alkyl chains of the host molecule as well as some atoms in the guest molecules that are disordered over two positions. In each case the temperature factors of the two partial atoms were forced to refine to the same value. This value was then fixed and the site occupancy factors were allowed to refine to give a total site occupancy factor of one. The refined site occupancy factors were then fixed and the isotropic temperature factors of the two partial atoms were allowed to refine independently. In most cases, the site occupancy factors of a disordered atom vary from 0.35 to 0.65, with a maximum variation of 0.18 to 0.82 occurring in a carbon atom of one of the alkyl chains of the host molecule in H·2(3PENT).

CCDC-233960 to -233966 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing . E-mail: data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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