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ARTICLE

Multifold Ring Closing Metathesis Reactions in the Formation of Resorcin[4]arene Cavitands

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The formation of the resorcin[4]arene cavitands using the ring closing metathesis reaction (RCM) in perallylated resorcin[4]arenes was investigated. The formation of resorcinarene cavitands offer unique molecular platforms for host-guest chemistries, sensor development, metal complexation, as well as new polymers and self-assembled systems, and as potential reaction sites, and novel catalytic platforms. In this manuscript we show that the cavitand formation by the RCM reaction depends, to a large extent, on the conformation and the substituents on the upper and lower rim of the perallylated resorcin[4]arenes. The perallylation of the octahydorxy compounds disrupted the intramolecular hydrogen bonds causing a dynamic shift in the conformer equilibrium.

Introduction

Encapsulating molecules in closed surface spherical molecules was proposed by D. J. Cram in 1982.[1] Calix- and resorcin[4]arene cavitands have since been used as precursors to carceplexes, carcerands, hemicarcerands and for encapsulating guest molecules and ions, largely because of their rigidity, enforced cavities and synthetic viability. The ability of resorcin[4]arenes to act as a platform for the synthesis of a multitude of supramolecular structures has been of growing interest.[2] Consequently, resorcin[4]arenes and their derivatives have been used as metal complexing agents, sensors, receptors, molecular reaction vessels and catalytic chambers.[3]

The conformation of the resorcin[4]arenes can be rigidified into a crown conformation by bridging the hydroxyl groups of the upper rim to a cavitand structure leading up to a conformationally locked encapsulating platform.[4] The covalent linkage of the phenolic groups on the adjacent phenyl rings is generally exploited for synthesis of the rigid 'bowl' shaped cavity. The methylenedioxy bridged cavitand, formed by the treatment of the octahydroxy resorcin[4]arene with excess CH_2ClBr in the presence of a base, is the most common covalent linkage reported.[2] The ethylene-, propylene-, dialkylsilicon-, phosphoryl-, heterophenylene-, phosphonate- and quinoxaline-bridged cavitands have also been reported (Figure 1).[5-8] Clearly the bridging reaction can be used to manipulate the cavity size and hence can be used to alter the properties of the cavitand.[9]

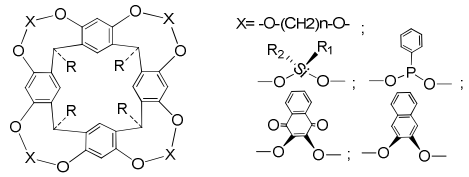
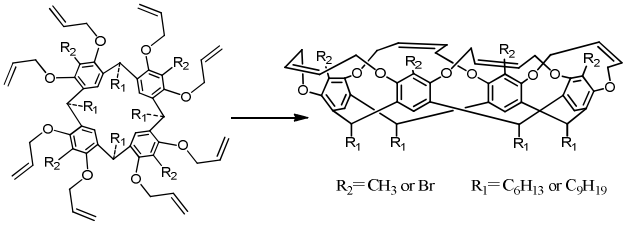


Figure 1. Bridged-resorcin[4]arenes.

Ring-closing metathesis (RCM) has been rapidly established as an efficient methodology for synthesis of medium to large ring systems.[10] Remarkable functional group tolerance, high stability, and commercial availability of the catalyst and the operational simplicity have greatly contributed to the popularity of the RCM reaction. Consequently, it has found applicability in the synthesis of novel macrocyclic hosts[11] and also in the construction of supramolecular assemblies with specific structures.[12] However, the examples of multifold metathesis reactions are still limited for their synthetic challenges.[10–12]

We reported the synthesis and X-ray crystal structure of the first resorcin[4]arenes cavitand by ring closing metathesis (RCM) reaction.[2a] The ring closing metathesis reaction on perallylated resorcin[4]arenes, where allyl groups on adjacent phenyl rings serve as acyclic diene precursors for RCM, led to the formation of ethenylenedioxy-bridged resorcin[4]arene cavitands (Scheme 1).[2a] In this manuscript we report our finding on the multifold RCM reaction with different groups on the upper and lower rim of the resorcin[4]arenes to investigate the formation of the resorcin[4]arene cavitands. Interestingly, the multifold metathesis reaction were dependent on the conformation and the substituents on the upper and lower rim of the resorcin[4]arene.



Scheme 1 Ring-Closing metathesis of allyloxy resorcin[4]arene to bridged resorcin[4]arene cavitands.[2a]

Results and Discussion

Octaallyl resorcin[4]arenes precursors- Condensation of resorcinol, 2-methyl resorcinol or 2-bromo resorcinol with ethanal, 2-ethylbutanal, n-heptanal, n-decanal, benzaldehyde, and 4-bromobenzaldehyde in a refluxing 1:1 mixture of ethanol and HCl (37% water) afforded 48-90% yield of the corresponding octahydroxy resorcin[4]arenes, **1**-**14**.[2b] Resorcin[4]arenes were characterized from their NMR and mass spectral analysis, and whenever possible with the data reported in the literature.[4b,8]

Although, the resorcin[4]arenes can have four stereoisomers, namely, cis-cis-cis (Crown, *rccc, C_{4v})*, cis-trans-trans (chair, *rctt, C_{2h})*, cis-cis-trans (diamond, *rcct, C_s)*, and trans-cis-trans (saddle, *rtct, D_{2d})* (Figure 2),[4b] only two, *rccc* and *rctt*, are predominantly formed. Compounds **1**, **3**, **4**, **7**, **9**, **10, 13** and **14** were isolated as the *rccc* isomers and compounds **5**, **6**, **11**, and **12** were isolated as the *rctt* isomers. The resorcin[4]arenes **2** and **8**, (resulting upon condensation of 2-ethylbutanal with resorcinol or methyl resorcinol) were observed in the *rcct* conformation, which has only been reported sparsely in the literature.[13] The isomeric forms (*rccc, rctt* and *rcct*) were distinguished upon comparison of their ^{1}H-NMR spectra.[8] For example, the ^{1}H-NMR spectrum of the *rccc* isomers showed characteristic single resonance for the resorcin[4]arene aromatic hydrogens while the *rctt* isomers had two resonances for the resorcin[4]arene aromatic hydrogens. Figure 3 below shows the representative spectra for compound **1, 5** and **2** which adopt the crown, the chair and the diamond conformations, respectively.

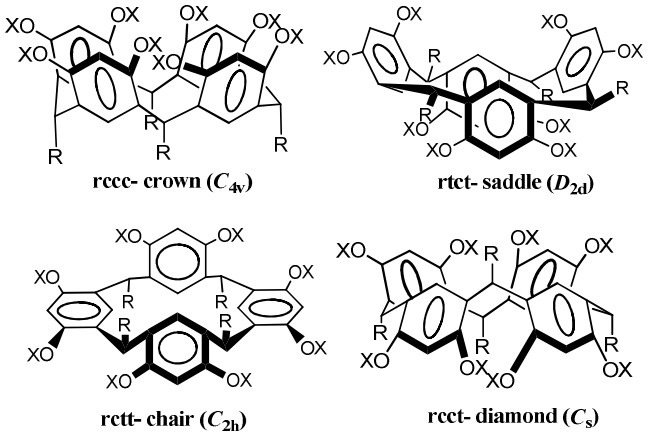


Figure 2 Stereoisomers of resorcin[4]arenes.

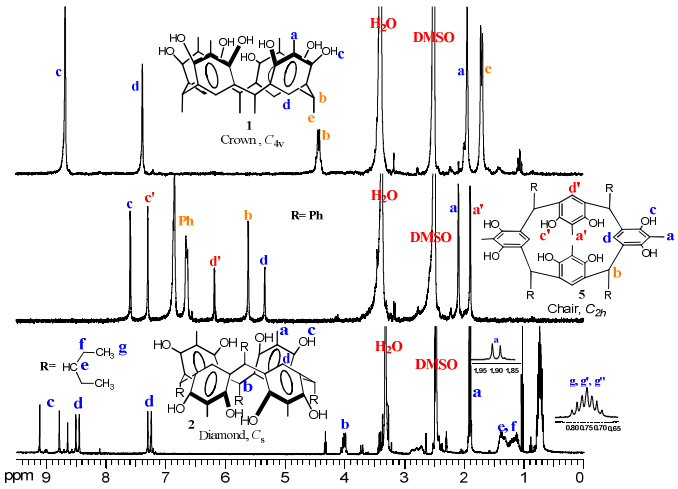
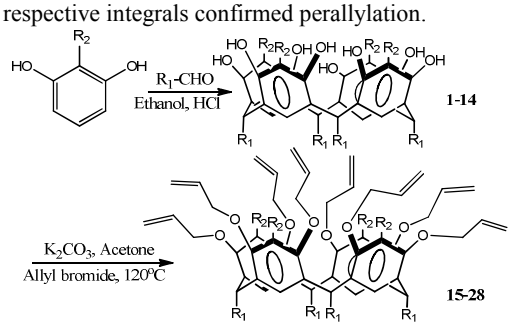


Figure 3 ^{1}H-NMR (250 MHz, DMSO-d_6) spectra for conformationally different resorcin[4]arenes **1,5** and **2**.

Perallylation of the resorcin[4]arenes- The perallylation of the octahydroxy resorcin[4]arenes was carried out to yield 20-78% of the perallylated products (Scheme 2, Table 1). Importantly, the perallylation in acetone or DMF with allyl bromide using potassium carbonate as a base, under standard reflux conditions did not always give the best yield. The allylation reaction performed in a pressure vessel at increased reaction temperature (120 ^{o}C) and pressure gave improved yields. The perallylated compounds **15-28** were characterized from their ^{1}H-, ^{13}C- NMR, and mass spectral analysis. In the ^{1}H-NMR spectra, the allyl group resonances were quantified and the respective integrals confirmed perallylation.



Scheme 2 Perallylation of the resorcin[4]arenes.

Cram et. al.[3a] have previously described the conformational dynamics of alkylated resorcin[4]arenes. In hydroxy resorcin[4]arenes the intramolecular hydrogen bonds rigidify the conformer but in perallylated compounds, which lack intramolecular hydrogen bonds, the flexibility of the skeleton increases and an equilibrium exists between the conformers, e.g., for the C_{4v} (crown) and C_{2v} (boat) symmetries, the barrier to interconversion is reportedly 17-19 kcal/mol,[3a] increasing with the bulkier alkyl substituents on the lower rim. For example, perallylated resorcin[4]arenes **18** preferred the boat (C_{2v}) conformer in solution ($CDCl_3$); in its ^{1}HNMR spectrum two sets of aromatic resonances at 6.5 and 7.6 ppm were observed (Figure 4). The single crystal X-ray analysis showed that perallylated resorcin[4]arene **28** exists, in the solid state, in a C_{2v} 'boat' conformation.[2a]

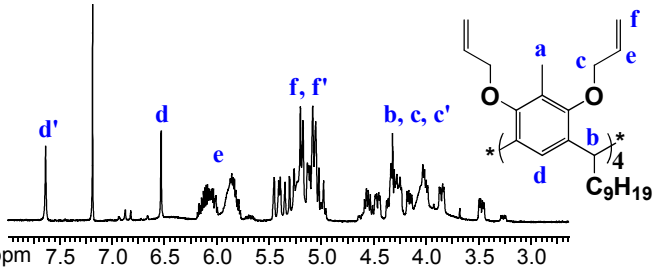


Figure 4 Partial ^{1}H-NMR (250 MHz, $CDCl_3$) of compound **18**.

Compound **5**, **6**, **11**, and **12**, which exist in the chair conformation (C_{2h});[2b] upon perallylation yielded compounds **19, 20, 25** and **26**, respectively, which were analyzed from their NMR and mass spectral data and their chair conformation was evident in their ^{1}H NMR spectrum where two resonances for benzylic protons were observed in accordance with C_{2h} symmetry. The X-ray crystal structure of compound **20** confirmed its chair conformation (C_{2h}).[2a] Likewise, perallylation of the resorcin[4]arenes **2** and **8**, resulted in compounds **16** and **22**, respectively which maintained the diamond, *rcct* configuration.

The RCM reaction- The RCM reactions on octaallyl resorcin[4]arenes **15-28** were investigated using 5-10 mole % of generation-I Grubb's catalyst. The reaction was carried out under nitrogen atmosphere in dry dichloromethane as a solvent at room temperature. The reactions were slow and the effect of upper and lower rim resorcin[4]arene substituents was significant on the RCM reaction (Table 1). With progression of the RCM reaction, thin layer chromatography (ethyl acetate and hexane, 1:4) showed the appearance of product(s) at lower R_f value compared to the starting perallylated resocin[4]arene. The product was separated using silica gel column chromatography using an ethyl acetate/hexane gradient

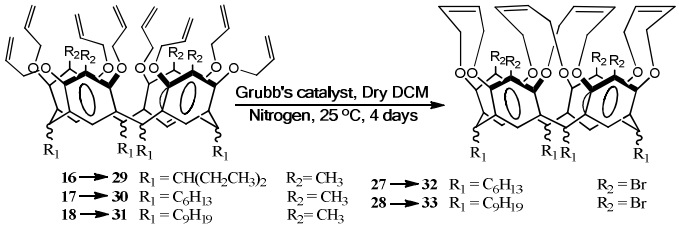
Table 1 RCM reaction on perallylated resorcin[4]arenes.

Resorcinol	Aldehydes	Octahydroxy Resorcinarenes	Allyl resorcin-arenes[#]	RCM product[+]		
				4-bridge	2-bridge	1-bridge
2-Methyl resorcinol	Ethanal	**1** (67%)	**15** (70%)			**38** (13%)
	2-Ethylbutanal	**2** (80%)	**16** (40%)	**29** (35%)		
	Heptanal	**3** (88%)	**17** (60%)	**30** (59%)		
	Decanal	**4** (85%)	**18** (55%)	**31** (61%)		
	Benzaldehyde	**5** (88%)	**19** (48%)			**39** (10%)
	Bromobenzaldehyde	**6** (90%)	**20** (68%)			**40** (10%)
Resorcinol	Ethanal	**7** (48%)	**21** (78%)			
	2-Ethylbutanal	**8** (57%)	**22** (15%)			
	Heptanal	**9** (78%)	**23** (22%)		**34** (32%)	
	Decanal	**10** (62%)	**24** (20%)		**35** (35%)	
	Benzaldehyde	**11** (56%)	**25** (46%)		**36** (22%)	
	Bromobenzaldehyde	**12** (67%)	**26** (65%)		**37** (17%)	
2-Bromo resorcinol	Heptanal	**13**	**27**(68%)	**32**(23%)		
	Decanal	**14**	**28**(35%)	**33**(32%)		

[#]Acetone/K_2CO_3 at reflux in a sealed tube. [+]Isolated yield in parenthesis.

system with increasing ethyl acetate in the eluent (6%-10%) and isolated products were analyzed by ^{1}H- and ^{13}C- NMR, 2D-NMR spectral data and mass spectrometric measurements.

Formation of the four bridge cavitand- Intramolecular ring closing metathesis in perallylated resorcin[4]arenes **16, 17, 18, 27** and **28** at 25 ^{o}C for 96 h using 5 mol % of Grubb's catalyst led to the product cavitands **29-33** in 35-61 % yield with all four 2-butylene bridges formed on the upper rim (Scheme 3). Reactions repeated with higher amount of catalyst (up to 8 mole %) did not lead to higher product yield. In a batch addition experiment, an additional amount (5 mol %) of catalyst was added after 48 h, but without higher conversion. The respective four bridge cavitands **29-33** were the only products isolated and the unreacted substrate perallylated resorcin[4]arene **17** was recovered after column chromatography to be reused in the reaction to increase overall yield of the cavitand.



Scheme 3 Ring closing metathesis for formation of four bridge cavitands.

The structure of the cavitand **29-33** was established from detailed analysis of the ^{1}H- and ^{13}C- NMR data. In the ^{1}H NMR spectrum, the resonances for the terminal vinylic protons (CH=C*H*$_2$) observed in the ^{1}H NMR of the starting perallylated resorcin[4]arene were replaced by the resonance of the bridge alkene protons (*H*C=C*H*) (Figure 5). In the ^{13}C NMR spectrum, the resonances that appeared at 116.0-118.0 ppm for terminal vinylic carbons (CH=*C*H$_2$) disappeared while new resonances for the formed bridge (H*C*=*C*H) were at 125.0-130.0 ppm after ring-closing metathesis. The presence of one resonance for a set four carbons in the ^{13}C-NMR spectrum suggested a C_{4v} symmetric crown conformation for the compounds **30-33**. The mass spectrum confirmed the molecular integrity of the resulting cavitands. In compound **29**, the unsymmetrical conformation was evident in the NMR and the disappearance of the vinylic CH$_2$ in the DEPT NMR and the molecular weight confirmed the formation of the four bridged cavitand.

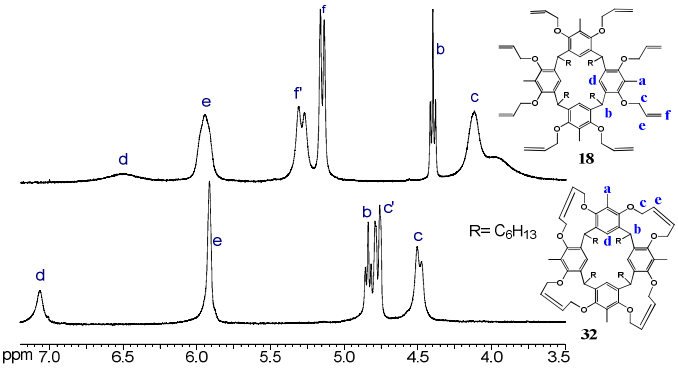


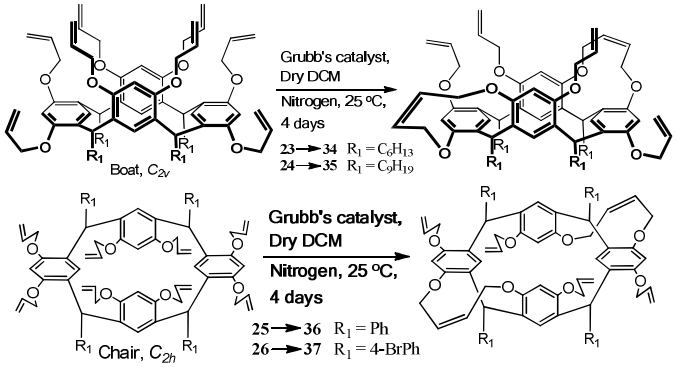
Figure 5 ^{1}H-NMR (250 MHz, $CDCl_3$) of compounds **32** and **18**.

The compound **30** could be crystallized from a methanol and ethyl acetate (70:30) solvent system. The crystal structure showed the formation of all four bridges in the upper rim and confirmed the tetrameric rigid structure with crown conformation (C_{4v} symmetry) and the *cis*-geomerty of the double bond.[2a] The crystal structure of compound **30** also confirmed that RCM reaction involved two allyl groups on the adjacent phenyl rings rather than those on the same phenyl ring.[2a] Molecular weight of the compound **30** was determined to be 1032 g/mol [Observed m/z = 1033 (M+H$^+$)] from it APCI MS analysis.

Formation of the two bridge compounds- RCM reaction catalyzed by the Grubb's generation I catalyst in compounds **23-26** led to partially bridged products **34-37**, respectively, with 17-35% yield (Scheme 4). Even at higher concentration of the Grubb's catalyst (8-10 mole %), formation of only two bridges was observed after 4 days of reaction monitoring. Unreacted starting compound could be recovered during column chromatographic separation/isolation and reused to increase the overall yield.

Compounds **23** and **24**, which lack a substituent on the upper rim led to partially bridged products **34** and **35**, respectively with 32-35% yield. The structures of compounds **34** and **35** were established by ^{13}C- and DEPT NMR data. The molecular weight of compound **34** was determined to be 1088 g/mol [Observed *m/z* = 1089 (M+H$^+$)]

and that of compound **35** was determined to be 1256 g/mol [Observed *m/z* = 1257 ($M+H^+$)] from APCI MS analysis.



Scheme 4 Ring closing metathesis for formation of A,C- di-bridged cavitands.

In ^{1}H-NMR spectra of **35** (Figure 6), two different alkene proton resonances originating from unreacted allyl groups (5.1-5.4 ppm for the =C*H*$_2$; 6.1 ppm for the =C*H*) and the alkene bridge (5.9 ppm for *H*C=C*H*) were observed. The appearance of only two sets of resonances for the alkenyl protons (unreacted and in the bridge) suggested a two-fold symmetry in compounds **34** and **35**. Also, the appearance of only one sharp resonance for the upper rim Ar-H (H_a; 6.4 ppm) confirmed its chemical shift equivalence and the proposed structure as **35**. Similar observations could also be made in the ^{13}C NMR data of compound **35**, in which the two sets of resonances were observed for the alkenyl carbons (115.0 ppm for the =*C*H$_2$; 133.0 ppm for the =*C*H from unreacted allyl group; 127.0 ppm *C*=*C* in the bridge) further establishing a two-fold symmetry in the compounds. Thus it was concluded that the compounds **34** and **35** were A,C- di-bridged, *i. e.*, two bridges formed opposite to each other on the upper rim side. Interestingly, Cram *et. al.* [5c] reported that bridging reaction of an octa hydroxyl resorcinol, prepared from condensation of resorcinol and hexanal, using CH_2ClBr- K_2CO_3-$(CH_3)_2SO$, led to the formation of the A,B-di-bridged tetraol along with other mono-, tri- and tetra-bridged compounds but no A,C-di-bridged compound was reported. The A,B-di bridged, as expected and unlike **34** and **35**, showed multiple resonances for the upper and lower rim Ar-H owing to its asymmetry.[5c]

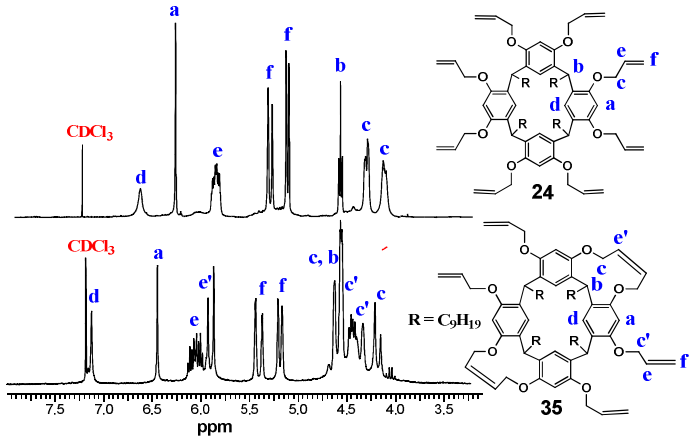
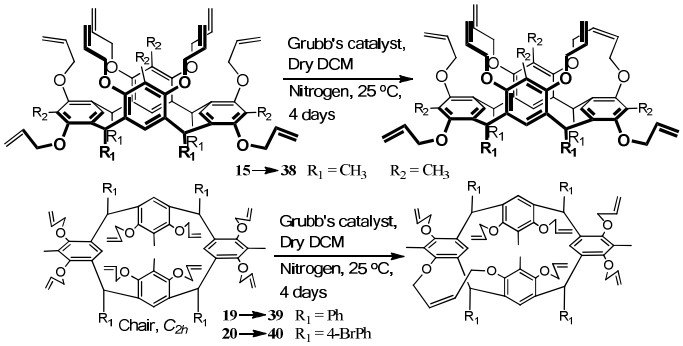


Figure 6 Regions of the ^{1}H NMRs (250 MHz, $CDCl_3$) of A-C di-bridged compound **35** and its precursor **24.**

Perallylated compounds **25** and **26** also led to the formation of two bridges in products **36** and **37** in 17-22% yield. Compounds **25** and **26** prefer the chair conformation (C_{2h} symmetry) in which two adjacent phenyl rings have equatorial orientation and while the other two phenyl rings have axial orientation.[2a] The chair conformation (C_{2h} symmetry) of the compounds seems to have had significant effect on the ring closing metathesis. Although, the bowl shaped cavitand formation has been accomplished for the compound existing in the chair conformation by the methylenedioxy bridge,[4b] the steric strain seems to have prevented the formation of a bowl cavitand in the RCM condition investigated in here. The reactions repeated with higher concentration of Grubb's catalyst (10 mole %) only resulted in the two bridge formation even after 4 days (Scheme 4). Unreacted starting compounds **25** and **26** were recovered during column chromatographic separation/ isolation. ^{13}C NMR data of **36** and **37** showed that bridged alkene carbons (*C*H=*C*H) appeared at 130.0 ppm. Two resonances for the aromatic carbon C_a were observed between 95.0-100.0 ppm and those for C_d were observed between 132.0-133.0 ppm. Unreacted vinylic carbons (-*C*H= and =*C*H$_2$) showed resonances at 125.0 ppm and 116.0 ppm respectively. The resonances for allylic carbon (O-*C*H$_2$-CH=) was observed between 65.0-75.0 ppm. It was concluded that compounds **36** and **37** had two intramolecular 2-butylene bridges but in opposite rim sides of the resorcin[4]arene cavity retaining their chair conformation (C_{2v} symmetry). The molecular weight of compound **36** was determined to be 1056 g/mol [Observed *m/z* = 1056 (M^+)] and that of compound **37** was determined to be 1368 g/mol [Observed *m/z* = 1386 ($M+H_2O$)] from MALDI MS analysis.

Formation of one bridge compound- In allyl compounds **15**, **19**, and **20** the RCM reaction led to formation of compounds **38**, **39**, and **40** respectively (Scheme 5) in 10-13% yield. After column chromatography only one compound could be isolated and attempts at increasing the product yield with higher concentration of Grubb's catalyst (10 mole %) and longer reaction times were unsuccessful.



Scheme 5 Ring closing metathesis for formation of mono-bridged cavitands.

The ^{1}H-NMR spectra of the mono-bridged compounds **38-41** revealed the molecular structure as being highly unsymmetrical (Figure 7). We observed four different carbon resonances for the upper rim methyl groups on aromatic ring, and four different resonances for each aromatic H_d proton, two in the shielding zone at 5.6 and 5.8 ppm and two in the deshielding zone at 6.3 and 6.5 ppm. The molecular weight of the compounds also confirmed the formation of the single bridge in compounds **38-41.** Molecular weights of the compounds **38** [Observed m/z = 893 ($M+H^+$)], **39** [Observed m/z = 1163 ($M+Na^+$)]; and **40** [Observed m/z = 1480 ($M+Na^+$)] suggested the formation of a single bridge by reaction of the two allyl groups on the adjacent phenyl rings.

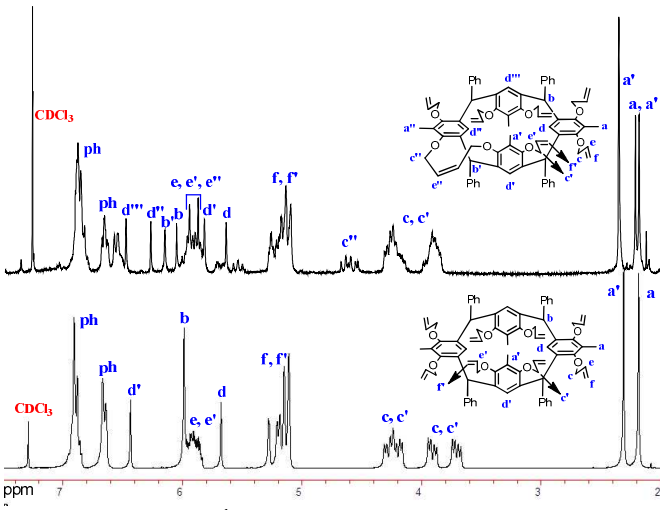


Figure 7 Regions of the ^{1}H-NMR spectra (250 MHz, $CDCl_3$) of mono bridged compound **39** and its precursor **19.**

The RCM reaction on **21** and **22** did not led to the isolation of a well-defined product but the TLC chromatography indicated mostly unreacted starting compound and some compound decomposition (streak). The small alkyl subsequent on the lower rim and lack of a substituent on the upper rim in **21** and **22**, along with the perallylation, may reduce the energy barrier to the conformer equilibrium to an extent that the RCM reaction was not possible.

Conclusions

In this manuscript, we have investigated the formation of the resorcin[4]arene cavitands using the ring closing metathesis reaction (RCM) in perallylated resorcin[4]arenes. The cavitand formation by the RCM reaction is shown to depend, to a large extent, on the conformation and the upper and the lower rim substituents on the resorcin[4]arenes. It was observed that allylation of the octahydorxy compounds disrupted the intramolecular hydrogen bonds between adjacent phenolic hydroxyl and caused a dynamic shift in equilibrium between the crown and boat conformers. The crown conformation with larger alkyl substituents (pentyl, hexyl or nonyl) on the lower rim and a methyl or bromo substituent on the upper rim were a prerequisite for formation of the tetra bridged bowl shaped cavitand, e.g. **29-33**. In compounds with hydrogen (no CH_3 or Br) on the upper rim but with longer alkyl chains on the lower rim (hexyl and nonyl) it was observed that only di-bridged compounds could be formed, e.g., **34** and **35**. For resorcin[4]arenes with lower rim aromatic substituents, which exist in the chair (C_{2h}) conformation, the crown conformers are energetically much less favored because of the repulsion between equatorial aryl ring and the allyloxy groups. The RCM reaction in the perallyalated *chair*-resorcin[4]arenes with hydrogen on the upper rim resulted in the AC-di-bridged resorcin[4]arenes **36** and **37**, while a CH_3 on the upper rim only resulted in a mono-bridged resorcin[4]arenes, *i.e.*, **39** and **41**. Though tetra-bridged cavitand formation has been reported in *chair*-resorcin[4]arenes, most probably a result of ring-inversion to the corresponding cone conformation which is stabilized by the intramolecular hydrogen bonds,[4b] but such ring inversion in perallyated *chair*-resorcin[4]arenes is not possible due the size of the allyoxy group. For perallyated compounds with CH_3 group on the lower rim the dynamic equilibrium between the conformers appear to quite rapid in the solution and only mono bridged compound (**38**) could be synthesized when the upper rim had a methyl subsequent; with a hydrogen on the upper rim, i.e., **21** and **22**, no well-defined RCM product could be isolated.

Experimental

General information

All solvents and reagents were commercially available. Heptanal was purified by distillation. NMR spectra were recorded on 250 MHz and 400 MHz spectrometers at 398 K. Mass spectra were recorded in APCI mode and MALDI. Compounds **1**, **3-7**, **9-14**, **17-20**, **27**, **28**, **30-33**, and **41** have previously been reported in the literature.[2a, 2b, 2i, 4a, 5a]

Synthesis of octahydroxy resorcin[4]arene (1-14)

Following the literature methods the hydroxy resorcin[4 arenes were synthesized. In a typical procedure, resorcinol, 2-methylresorcinol or 2-Bromo resorcinol (8 mmol) was dissolved in anhydrous ethanol (775 mL/mol) and 37% aqueous HCl (185 mL/mol). The solution was cooled in an ice bath and the aldehyde (8.1 mmol) was added to above solution slowly over a period of 30 min. Then the mixture was allowed to warm to room temperature. The reaction was then maintained at temperature of 80^{o}C for nearly 12 hrs after which the precipitate was filtered through Buchner funnel and washed several times until it turned neutral to pH paper. It was dried and the NMR spectrum was taken and the date was compared with that in reported literature.

Compound (2): 80%; ^{1}H NMR (250 MHz, DMSO-d6) δ 0.77 (m, 24H), 1.22 (m, 16H), 1.35 (m, 4H), 1.93 (s, 12H), 1.95 (s, 6H), 3.99 (m, 4H), 7.27 (s, 2H), 7.33 (s, 2H), 8.48 (s, 2H), 8.54 (s, 2H), 8.82 (s, 4H), 9.14 (s, 4H); ^{13}C NMR δ in ppm 9.9, 10.9, 21.5, 22.0, 56.0, 112.3, 112.6, 123.9, 124.7, 125.1, 129.2, 149.5, 149.9, 150.5. ESI-MS (*m/z*): M + Na^{+}, found 847.517. $C_{52}H_{72}O_8Na$ requires 847.511.

Compound (8): 57%; ^{1}H NMR (250 MHz, DMSO-d6) δ 0.76 (m, 24H), 1.10-1.47 (m, 20H), 3.91-4.05 (m, 4H), 6.09 (s, 2H), 6.18 (s, 2H), 7.34 (s, 2H), 7.44 (s, 2H), 8.85 (s, 2H), 8.93 (s, 2H), 9.10 (s, 2H), 9.25 (s, 2H), 9.59 (s, 2H); DEPT NMR (DMSO-d6) δ in ppm 9.9, 10.8, 21.6, 21.9, 38.2-40.9, 56.2, 103.6-104.3, 129.3, 133.6. ESI-MS (*m/z*): M + H^{+}, found 769.466. $C_{48}H_{65}O_8$ requires 769.467.

Synthesis of octaallyloxy resorcin[4]arene: -

Method A- 1.0 g of Octahydroxy compound was dissolved in acetone (20 ml/mol) in a round-bottomed flask. The reaction mixture was cooled to 0 ^{o}C in an ice bath and potassium carbonate (30eq) was slowly added over a period of half an hour during which the solution changed color to purple. Then the reaction mixture was brought to room temperature and allyl bromide (30eq) was added. The reaction mixture was refluxed and monitored using TLC. Upon completion, the reaction mixture was filtered and the filtrate was concentrated *in vacuo* to yield the crude product. Recrystallization from a mixture of acetone and methanol (50:50) resulted in the pure perallylated product.

Method B- 1.0 g of Octahydroxy compound was taken into high pressure reaction tube and dissolved in acetone (20 ml/mol). Then potassium carbonate (30eq) was added to the reaction tube; the solution color changed to purple and then allyl bromide (30eq) was added and the reaction tube was sealed with a threaded Teflon plug. The high pressure reaction tube was then heated to temperature of 80^{o}C in an oil bath for 24-48 hrs. Upon completion, the reaction mixture was filtered and the filtrate was concentrated *in vacuo* to yield the crude product. Recrystallization from a mixture of acetone and methanol (50:50) resulted in the pure perallylated product.

Compound (15): 60%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.45 (t, 12H, *J* = 6.6 Hz), 1.85 (bs, 6H), 2.24 (bs, 6H), 3.41 (bs, 8H), 3.82 (bs, 8H), 4.44 (bs, 4H), 4.46-4.51 (m, 8H), 5.01-5.18 (m, 8H), 5.48 (s, 2H), 6.07 (s, 2H); ^{13}C NMR ($CDCl_3$) δ in ppm 10.5, 20.9, 32.8, 73.2,

90.5, 116.12, 123.6, 133.0, 134.5, 155.0. ESI-MS (*m/z*): M + Na^+, found 943, $C_{60}H_{72}O_8Na$ requires 943.

Compound (16): 40%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.21 (t, 6H, *J* = 6.6 Hz), 0.58-0.89 (m, 24H), 1.09-1.74 (m, 14H), 2.13 (s, 6H), 2.20 (s, 6H), 3.62-3.69 (m, 2H), 3.96-4.03 (m, 2H), 4.10-4.33 (m, 6H), 4.38-4.56 (m, 5H), 4.67-4.72 (m, 4H), 4.97-5.55 (m, 18H), 5.85-6.29 (m, 8H), 6.72 (s, 2H), 7.85 (s, 2H). ^{13}C NMR δ in ppm 10.4, 11.2, 11.3, 12.7, 22.3, 23.5, 24.3, 36.5, 37.4, 40.3, 45.1, 48.3, 73.1, 73.5, 116.3, 116.5, 116.6, 116.8, 125.9, 127.4, 125.9, 127.4, 134.4, 134.8, 135.1, 135.2. ESI-MS (*m/z*): M + H^+, found 1145.779. $C_{76}H_{105}O_8$ requires 1145.

Compound (21): 78%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89-1.57 (m, 44H), 2.16 (s, 6H), 2.67 (s, 6H), 3.11-4.86 (m, 20H), 4.89-5.51 (m, 16H), 5.72-6.64 (m, 8H), 6.98 (s, 4H); DEPT NMR ($CDCl_3$) δ in ppm 20.9, 32.8, 73.2, 116.1, 123.7, 134.5.

Compound (22): 15%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.77 (m, 24H), 1.12-1.61 (m, 16H), 1.88-2.37 (m, 4H), 4.22-4.54 (m, 19H), 5.06-5.47 (m, 16H), 5.84-6.18 (m, 8H), 6.20-6.39 (m, 5H), 7.01-7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ in ppm 9.0-11.0, 44.1, 44.6, 68.8-69.9, 73.9, 98.1-99.7, 101.2-101.4, 115.9-117.8, 127.8, 129.8-130.8, 134.0-135.7. ESI-MS (*m/z*): M + H^+, found 1089. $C_{72}H_{97}O_8$ requires 1089.

Compound (23): 22%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.73 (t, 12H, *J* = 7.2 Hz), 1.12-1.23 (m, 32H,), 1.72 (m, 8H), 4.11 (d, 8H, *J* = 12.0 Hz), 4.28 (d, 8H, *J* = 12.0 Hz), 4.51 (t, 4H, *J* = 4.0 Hz), 5.11 (d, 8H, *J* = 8.0 Hz), 5.29 (d, 8H, *J* = 16.0 Hz), 5.82 (m, 8H), 6.11 (s, 4H,), 6.52 (s, 4H); ^{13}C NMR δ in ppm 14.1, 22.8, 28.3, 29.7, 31.9, 34.7, 35.8, 69.6, 99.3, 116.1, 125.9, 126.8, 134.1, 154.8. ESI-MS (*m/z*): M + H^+, found 1145. $C_{76}H_{105}O_8$ requires 1145.

Compound (24): 20%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (t, 12H, *J* = 7.2 Hz), 1.26-1.31 (m, 56H), 1.85 (m, 8H), 4.13 (d, 8H, *J* = 12.0 Hz), 4.31 (d, 8H, *J* = 12.0 Hz), 4.59 (t, 4H, *J* = 4.0 Hz), 5.13 (d, 8H, *J* = 8.0 Hz), 5.31 (d, 8H, *J* = 16.0 Hz), 5.94 (m, 8H), 6.35 (s, 4H), 6.65 (s, 4H); ^{13}C NMR δ in ppm 14.1, 22.9, 28.3, 29.4, 29.8, 30.1, 31.9, 34.7, 35.7, 36.8, 69.6, 99.3, 116.1, 126.3, 126.8, 134.1, 154.7. ESI-MS (*m/z*): M + Na^+, found 1335, $C_{88}H_{128}O_8Na$ requires 1335.

Compound (25): 46%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.81-4.33 (m, 16H), 4.95-5.20 (m, 16H), 5.53-5.76 (m, 8H), 5.76-5.81 (m, 4H), 5.91 (m, 4H), 6.13-6.17 (d, 2H, *J* = 9.6 Hz), 6.30 (s, 2H), 6.73-6.77 (m, 16H), 6.89-6.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ in ppm 69.5, 116.2, 125.3, 125.6, 127.7, 128.9, 133.9, 143.5, 155.6. ESI-MS (*m/z*): M + H^+, found 1113, $C_{76}H_{73}O_8$ requires 1113.

Compound (26): 65%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.32-4.62 (m, 16H), 4.99-5.33 (m, 16H), 5.62-5.93 (m, 8H), 6.11-6.23 (m, 4H), 6.29-6.36 (m, 4H), 6.45-6.62 (m, 8H), 6.64-6.73 (m, 4H) 7.10-7.31 (d, 8H, *J*=7.0Hz); DEPT NMR ($CDCl_3$) δ 42.7, 69.0, 69.3, 69.6, 116.5, 130.5, 130.7, 132.9, 133.3, 133.5. ESI-MS (*m/z*): M + H^+, found 1425, $C_{76}H_{69}Br_4O_8$ requires 1425.

Ring closing metathesis reaction synthesis of bridged-resorcin[4]arene:- To a stirred solution of octaallyloxy resorcin[4]arene (1.0 g, 1.086 mmole) in dry methylene chloride (114 ml) was added Grubb's catalyst (8 mole%, 0.071 gm, 0.087 mmol) in dry methylene chloride (25ml) at room temperature. The reaction mixture was stirred and monitored by TLC. When no increase in the amount of the product was observed over 8 hrs, the reaction mixture was concentrated *in vacuo* to remove solvent. The crude product was column chromatographed over silica gel using ethyl acetate : hexane (1:9) eluent.

Compound (29): 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (t, 6H, *J* = 7.3 Hz), 0.68 (m, 18H), 0.94 (t, 6H, *J* = 7.5 Hz), 1.25-1.31 (m, 10H), 1.47 -1.74 (m, 4H), 2.20 (s, 6H), 2.28 (s, 6H), 4.08-4.16 (m, 4H), 4.37-4.48 (m, 4H), 4.54-4.57 (m, 4H), 4.70-4.86 (m, 6H), 5.24 (t, 2H, *J* = 8.4 Hz), 5.63-5.73 (m, 2H), 5.92-6.21 (m, 7H), 7.00 (s, 2H), 8.02 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ in ppm 8.8, 8.9, 9.2, 10.4, 10.5, 10.6, 10.7, 20.3, 20.8, 21.2, 21.9, 22.2, 36.4, 40.3, 42.2, 43.5, 48.6, 50.5, 67.2, 67.3, 67.9, 72.3, 122.5, 122.6, 122.7, 124.4, 126.6, 129.9, 130.0, 131.0, 131.4, 132.0, 131.1, 132.6, 153.6, 153.8, 154.1, 154.6, 155.0; ESI-MS (*m/z*): M + H^+, found 1033, $C_{68}H_{89}O_8$ requires 1033.

Compound (34): 32%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.77 (t, 12H, *J* = 6.2 Hz), 1.13-1.73 (m, 32H), 1.85 (m, 8H), 4.25 (m, 16H), 4.55 (d, 2H, *J* = 2.5 Hz), 4.62 (s, 2H), 5.18 (dd, 4H, *J* = 1.2 Hz, *J* = 10.5 Hz), 5.41 (dd, 4H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.86 (s, 2H), 5.93 (s, 2H), 6.12 (m, 4H), 6.45 (s, 4H), 7.12 (s, 4H); ^{13}C NMR ($CDCl_3$) δ in ppm 13.0, 21.7, 27.2, 28.7, 30.9, 33.4, 34.5, 63.6, 68.9, 96.8, 98.2, 115.3, 122.3, 125.3, 125.6, 127.0, 128.2, 133.3, 152.0, 153.1; ESI-MS (*m/z*): M + H^+, found 1090, $C_{72}H_{97}O_8$ requires 1089.

Compound (35): 35%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.79 (t, 12H, *J* = 6.2 Hz), 1.12-1.75 (m, 56H), 1.98 (m, 8H), 4.34 (m, 16H), 4.68 (s, 2H), 4.77 (s, 2H), 5.19 (dd, 4H, *J* = 1.2 Hz, *J* = 10.2 Hz), 5.43 (dd, 4H, *J* = 1.5 Hz, *J* = 17.0 Hz), 5.88 (s, 2H), 5.95 (s, 2H), 6.11 (m, 4H), 6.45 (s, 4H), 7.12 (s, 4H); ^{13}C NMR ($CDCl_3$) δ in ppm 13.0, 21.6, 27.2, 28.3, 28.7, 29.0, 30.9, 33.4, 34.4, 34.5, 63.5, 68.9, 96.8, 98.1, 115.3, 122.7, 125.3, 125.6, 127.0, 128.7, 133.3, 152.0, 153.2; ESI-MS (*m/z*): M + H^+, found 1257, $C_{84}H_{121}O_8$ requires 1257.

Compound (36): 22%; H-NMR (250 MHz, $CDCl_3$) δ in ppm 4.22-4.62 (m, 16H), 5.04-5.20 (m, 12H), 5.72-5.91 (m, 10H), 6.16-6.25 (m, 4H), 6.44 (s, 2H), 6.83-7.03 (m, 22H); C-NMR ($CDCl_3$) δ in ppm 41.8, 63.8, 68.6, 96.2, 101.2, 115.3, 124.4-125.9, 126.8, 127.3, 127.9, 128.1, 132.1, 132.7, 140.9, 141.7, 143.1, 143.9, 151.8, 154.4; DEPT NMR ($CDCl_3$) δ in ppm 41.8, 63.8, 68.6, 96.2, 98.9, 115.3, 124.3, 126.6, 126.8, 127.3, 127.9, 128.1, 132.1, 132.7, 140.9, 141.7, 151.8, 154.4; ESI-MS (*m/z*): M + H^+, found 1057, $C_{72}H_{65}O_8$ requires 1057.

Compound (37): 17%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19-4.71 (m, 16H), 4.87-5.31 (m, 8H), 5.53-5.84 (m, 6H), 5.98-6.24 (m, 4H), 6.39 (s, 2H), 6.52-6.71 (m, 8H), 7.21-7.56 (m, 16H). DEPT NMR ($CDCl_3$) δ in ppm 41.2, 63.8, 68.3, 96.4, 98.1, 115.5, 123.3, 123.5, 127.2, 127.3, 129.7, 130.2, 131.5, 132.4, 140.9, 141.7, 151.8, 154.4; ESI-MS (*m/z*): M^+ + H_2O, found 1385 (100%), 1386 (80 %), $C_{72}H_{62}Br_4O_9$ requires 1386.

Compound (38): 13%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.6 Hz), 1.26-1.37 (m, 9H), 1.78-2.38 (m, 12), 4.16 (m, 2H), 4.22-4.64 (m, 16H), 4.82 (m, 2H), 4.99-5.34 (m, 12H), 5.62-6.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 10.2, 20.2-23.8, 29.8, 32.1, 69.2, 69.9, 71.8, 72.4, 115.9-116.4, 122.0,-126.0, 130.1, 132.2, 134.4, 136.2; MALDI *m/z* 893 (M+H^+), $C_{58}H_{69}O_8$ requires 893.

Compound (39): 10%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.15 (s, 3H), 2.29 (s, 6H), 3.80-3.96 (m, 6H), 4.10-4.28 (m, 6H), 4.49-4.65 (m, 4H), 5.08-5.26 (m, 12H), 5.62 (s, 1H), 5.81 (s, 1H), 5.83-5.99 (m, 8H), 6.05 (s, 1H), 6.15 (s, 1H), 6.26 (s, 1H), 6.48 (s, 1H), 6.50-6.57 (m, 3H), 6.63-6.68 (m, 4H), 6.80-6.93 (m, 12); ^{13}C NMR ($CDCl_3$) δ in ppm 10.8, 10.9, 24.9, 36.8, 44.7, 44.9, 73.3, 73.4,

73.7, 73.9, 116.4, 116.6, 116.8, 117.0, 123.8, 124.1, 125.3, 125.8, 125.9, 126.3, 127.4, 127.8, 128.3, 129.0, 129.2, 130.1, 131.2, 132.7, 132.8, 133.1, 133.2, 134.1, 134.2, 134.3, 134.4, 141.4, 143.6, 154.3, 154.8, 154.9, 155.0. ESI-MS (*m/z*): M + Na^+, found 1163. $C_{78}H_{76}O_8Na$ requires 1163.

Compound (40): 10%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.16 (s, 6H), 2.27 (s, 6H), 3.81-3.97 (m, 6H), 4.08-4.34 (m, 6H), 4.40-4.65 (m, 4H), 5.10-5.29 (m, 12H), 5.52 (s, 1H), 5.67 (s, 1H), 5.79 (s, 1H), 5.82-5.96 (m, 6H), 6.00 (s, 1H), 6.09 (s, 1H), 6.12 (s, 1H), 6.37-6.53 (m, 8H), 7.04-7.13 (m, 8H); ^{13}C NMR ($CDCl_3$) δ in ppm 10.9, 11.0, 14.4, 29.9, 43.7, 44.3, 70.8, 73.5, 73.8, 74.5, 110.0, 116.6, 116.8, 117.3, 117.8, 120.0, 120.1, 124.3, 125.8, 126.4, 128.2, 130.6, 130.9, 131.4, 132.1, 132.4, 132.5, 133.8, 134.0, 140.5, 142.9, 143.6, 154.3, 154.8, 155.0, 155.4. ESI-MS (*m/z*): M + Na^+, found 1479 (100%) 1480 (80%). $C_{78}H_{72}Br_4O_8Na$ requires 1480.

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Notes and references

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Multifold Ring Closing Metathesis Reactions in the Formation of Resorcin[4]arene Cavitands.

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The formation of the resorcin[4]arene cavitands by the ring closing metathesis (RCM) reaction depends, to a large extent, on the conformation and the substituents on the upper and lower rim of the perallylated resorcin[4]arenes.