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ORIGINAL ARTICLE

Synthesis and inclusion properties of pillar[n]arenes

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Abstract A detailed study of the reaction conditions revealed that a quantitative cyclocondensation of 1,4-dialkoxy-2,5-bis(alkoxymethyl)-benzenes to pillar[n]arenes can be achieved by catalysis of *p*-toluenesulfonic acid in CH_2Cl_2. Major product of this new reaction is in each case a cyclopentamer (n = 5), but small amounts of the pillar[n]arenes with n = 6, 7 and 10 can be obtained as well. Different alkoxy groups in 1- and 4-position lead to regioisomers. All cyclooligomers exist in pillar structures as pair of enantiomers, which show a racemisation at room temperature, which is fast in terms of the NMR time scale. The racemisation process occurs by rotation of the 1,4-phenylene segments in the macrocyclic rings. Pillar[n]arenes exhibit novel host–guest behavior.

Keywords Catalysis · Host–guest chemistry · Pillararene · Calixarene · Inclusion

Introduction

Ortho-, meta- and para-cyclophanes, which represent macrocyclic ring systems with 4–6 phenylenemethylene repeat units, are fascinating compounds in theoretical as well as in practical respect. The preparation of the parent hydrocarbons $\mathbf{1^n}$–$\mathbf{3^n}$ (Fig. 1) is laborious and not very efficient: $\mathbf{1^4}$ [1], $\mathbf{1^5}$ [1], $\mathbf{2^4}$ [2], $\mathbf{3^4}$ [3], $\mathbf{3^5}$ [4], $\mathbf{3^6}$ [4].[1] Hydroxy or alkoxy derivatives $\mathbf{4^n}$–$\mathbf{6^n}$, such as the veratrylenes $\mathbf{4^4}$ [5], $\mathbf{4^5}$ [5], $\mathbf{4^6}$ [5], calixarenes $\mathbf{5^4}$ [6], $\mathbf{5^5}$ [7], $\mathbf{5^6}$ [8] and pillararenes $\mathbf{6^5}$ [9–13], are somewhat easier to obtain and are important host systems for host–guest chemistry.

We published recently [14] a short paper on a novel type of cyclocondensation reaction, which provides a facile and efficient preparation of pillar[5]arenes $\mathbf{6^5}$ (Scheme 1).

The reaction $\mathbf{7} \rightarrow \mathbf{6^5}$ is quite unusual since an *ipso*-substitution on benzene rings occurs by an alkylation/dealkylation process. Moreover, CH_2OR^2 and OR^2 are normally not the best leaving groups. We assume a radical-cation mechanism [14]. After a further systematic study, we report here the detailed results, such as the influences of the reaction conditions on the synthetic method, and synthesis of a series of novel pillar[n]arenes by the facile method.

Results and discussion

We studied now the role of the acidic catalysis and the influence of different substituents R^1 and R^2 on this new reaction type. The results are summarized in Table 1.

Entries 1 and 9 with 10–15 mol % *p*-toluenesulfonic acid in CH_2Cl_2 at room temperature proved to be the best variant for $\mathbf{7a} \rightarrow \mathbf{6^5a}$ (yield 89–92 %). Other solvents such as $BrCH_2Cl$, $ClCH_2CH_2Cl$ or $BrCH_2CH_2Br$ (entries 2–5) reduced the yield, requested higher reaction temperatures and/or longer reaction times. The reaction worked to a very low extent or not at all in toluene, CCl_4 or THF. Sulfuric

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[1] The parent compounds $\mathbf{1^6}$, $\mathbf{2^5}$ and $\mathbf{2^6}$ are, to our best knowledge, not known.

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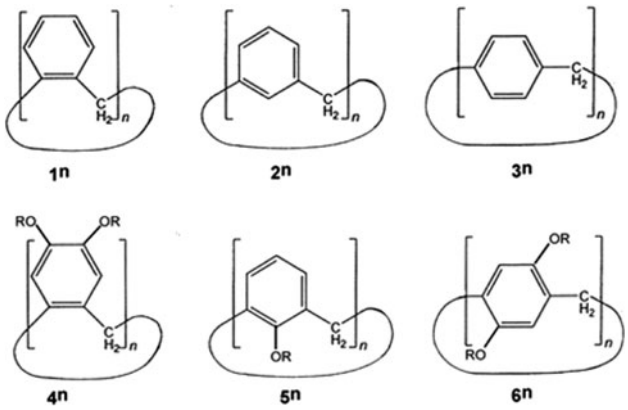
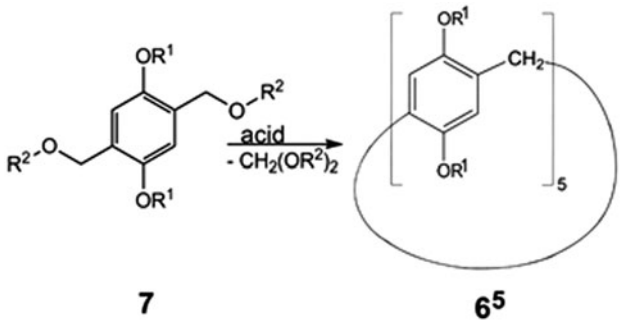


Fig. 1 [1.1.1.1…]Ortho-, meta- and para-cyclophanes $\mathbf{1^n}$–$\mathbf{3^n}$ and their derivatives: veratrylenes $\mathbf{4^n}$, calixarenes $\mathbf{5^n}$ and pillararenes $\mathbf{6^n}$ (n = 4, 5, 6; R = H, alkyl)



Scheme 1 Formation of pillar[5]arenes $\mathbf{6^5}$ by catalytic cyclocondensation reactions of ethers **7** (R^1: alkyl, R^2: H, alkyl, aralkyl)

acid (entry 6) or phosphoric acid (entry 7) could be used instead of *p*-toluenesulfonic acid, but then the reaction was much slower. Non-oxidizing acids or acids with an extremely low oxidizing potential (HCl, HCOOH, H_3CCOOH) gave at most traces of $\mathbf{6^5a}$. Polymerization is the major competing process to cyclo oligomerization.

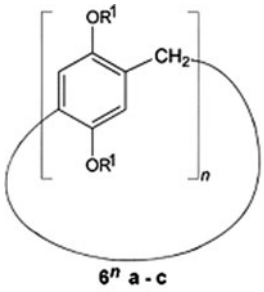
The next question concerned the influence of the leaving groups CH_2OR^2 and OR^2. It turned out that small alkyl groups (R^2 = Me, Et) are best suited. Free hydroxy groups (R^2 = H) or bulkier alkyl groups (R^2 = n-Bu, Bn) gave somewhat lower yields (entries 1, 9–12)—even when higher reaction temperatures and/or longer reaction times were used.

The substituents R^1 of the starting compounds (entries 1, 13 and 14) have a certain influence on the size of the formed macrocycles. A fourfold cyclocondensation was never observed, because the strain of a [1.1.1.1]paracyclophane is too high. The formation of cyclopentamers was in each case the major process but some higher pillar[n]arenes with n = 6, 7 and 10 were minor byproducts. The yields of the larger ring systems (n > 5) are low, but the presently described method represents the first access to these hitherto unknown pillar[n]arenes (Scheme 2).

From the crystal structure of pillar[5]arene $\mathbf{6^5b}$, $\mathbf{6^5a}$ and $\mathbf{6^5c}$ (Fig. 2), we know their cavity is more or less the same, with the length of R^1 increases, the volume of pillar[5]arenes become bigger, so the more solvent molecules included [15]. The details of the X-ray crystal structure analyses of pillar[5]arenes $\mathbf{6^5a}$–$\mathbf{6^5c}$ are summarized in Table 2.

Table 1 Synthetic optimization of the cyclocondensation 7 → 6^5

Entry	Starting compound 7	R^1	R^2	Catalyst	Solvent	Reaction temperature (°C)	Reaction time (h)	Isolated yield (%)
1	7a	Et	Et	TsOH	CH_2Cl_2	rt	3–4	89
2	7a	Et	Et	TsOH	$ClCH_2CH_2Cl$	rt	24	61
3	7a	Et	Et	TsOH	$BrCH_2Cl$	rt	22	18
4	7a	Et	Et	TsOH	$BrCH_2CH_2Br$	rt	48	–
5	7a	Et	Et	TsOH	$BrCH_2CH_2Br$	53	30	25
6	7a	Et	Et	H_2SO_4(98 %)	CH_2Cl_2	rt	27	89
7	7a	Et	Et	H_3PO_4(85 %)	CH_2Cl_2	41	64	19
8	7a	Et	Et	CF_3COOH	CH_2Cl_2	rt	21	14
9	7b	Et	Me	TsOH	CH_2Cl_2	rt	3–4	92
10	7c	Et	H	TsOH	CH_2Cl_2	rt	5–6	84
11	7d	Et	n-Bu	TsOH	CH_2Cl_2	41	24	75
12	7e	Et	Bn	TsOH	CH_2Cl_2	41	28	75
13	7f	Me	Et	TsOH	CH_2Cl_2	rt	3–4	95
14	7g	n-Bu	Et	TsOH	CH_2Cl_2	rt	15	86



6^n	a	b	c
R^1	Et	Me	*n*-Bu
6^5	89	95	86
6^6	8	—	11
6^7	—	2.4	—
6^{10}	—	1.8	—
Total yield (7 → 6^n)	97%	99%	97%

Scheme 2 Yields [%] of pillar[n]arenes $\mathbf{6^n a\text{-}c}$ (entries 1, 13 and 14)

The cyclocondensation of 1,4-dialkoxy-2,5-bis(methoxymethyl)benzenes with different alkoxy groups leads to a mixture of regioisomers [15]. Scheme 3 demonstrates this for the 1-methoxy-4-n-octyloxy compound **7 h**. Product $\mathbf{6^5 d}$ is the regular cyclopentamer with a repeat unit which corresponds to the general formula $\mathbf{6^5}$ in Scheme 1. The other regioisomers $\mathbf{8^5}$, $\mathbf{9^5}$ and $\mathbf{10^5}$ do not have regular repeat units. The statistical ratio of $\mathbf{6^5 d}$:$\mathbf{8^5}$:$\mathbf{9^5}$:$\mathbf{10^5}$ is 1:5:5.2:5.0 (total yield about 84 %). Column chromatography permitted a separation and elution in the sequence $\mathbf{8^5}$, $\mathbf{10^5}$, $\mathbf{9^5}$, $\mathbf{6^5 d}$.

In contrast to the low yields of the originally published mode of preparation [9], Scheme 2 demonstrates that the process **7a** → $\mathbf{6^n a}$ is nearly quantitative (total yield: 97 %). However, **7a** has to be prepared in preceding steps from 1,4-diethoxybenzene **11**. Therefore we tried to improve the procedure (Scheme 4).

When 2.5×10^{-2} M solutions of **11** in CH_2Cl_2 were used, the amount of linear oligomers and polymers is very low compared to the reported results [9]. Thus, the yield of $\mathbf{6^5 a}$ could be improved up to 82 % with $FeCl_3$ as catalyst.

The molecular structure of pillar[n]arenes can be regarded on the basis of two models. Diphenylmethane provides the first model. It accepts a gable conformation with C_{2v} symmetry [16].

Its dehedral angles subtended between the least-squares planes of the two benzene rings and the central plane, defined by the ipso-C atoms and the methylene carbon atom, amount to 90°. The bond angle i-C-C-i-C is about 112° (force field and semiempirical quantum chemical calculations for the free molecule) [16]. This geometry fits excellently to the generation of pillar[5]arenes.

The second model is related to the conformations of cycloalkanes. Instead of the single bonds in cycloalkanes, 1,4-phenylene segments have to be considered (Fig. 3). Cyclopentane has an envelope conformation (C_s) and an energetically slightly higher half-chair conformation (C_2) [17]. Both are not far from planarity. Thus, an essentially planar macrocycle can be assumed for $\mathbf{6^5}$, $\mathbf{8^5}$, $\mathbf{9^5}$ and $\mathbf{10^5}$ in which the benzene rings are perpendicular to the plane of the macrocycle. The crystal structure analyses proved this model [9, 15].

The pillar structures of $\mathbf{6^6}$, $\mathbf{6^7}$, and $\mathbf{6^{10}}$ seem to be more complicated. Planar systems can be excluded because they would have an angle strain. Cyclohexane has a chair conformation (D_{3d}) and two conformations with higher energy which are called boat (C_{2v}) and twisted boat (D_{2d}). Chair (C_s), twisted chair (C_2) and twisted boat (C_2) conformers are discussed for cycloheptane. Finally, boat–chair-boat (C_{2v}), boat–chair-chair (C_2), chair–chair-chair (C_{2v}) and crown conformers (D_{5d}) are relevant for cyclodecane [17].

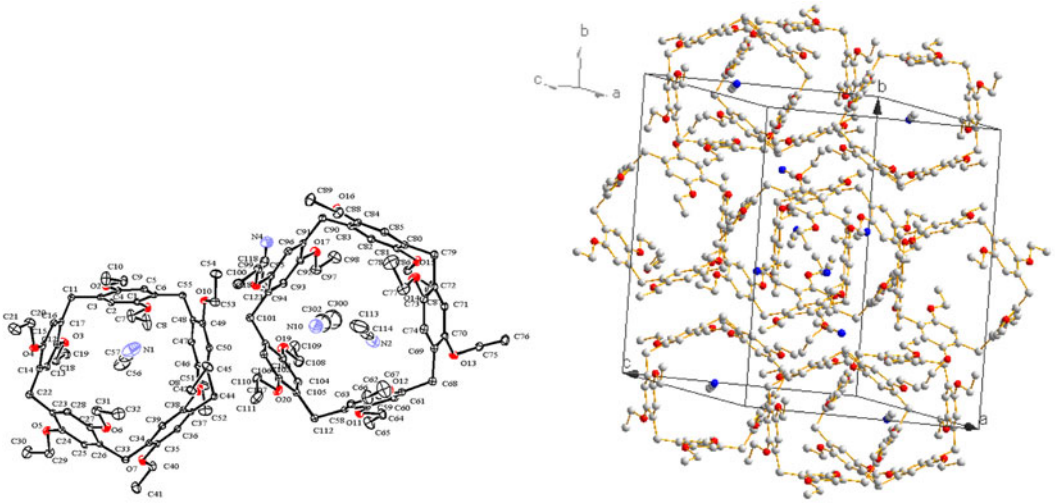
It is not known which conformations of the pillar[n]arenes as "extended cycloalkanes" have the lowest energies, but irrespective of that, the diameter of the interior cavities increases strongly with increasing numbers n of the pillar[n]arenes (Fig. 3). This is an important feature for the encapsulation of guest molecules. Since the energy differences between the different conformers are low, we can assume that host and guest conformers can be adapted to each other.

The alkoxy chains are arranged in the crystals of $\mathbf{6^5}$ so that they avoid an interaction with each other [9–13, 15]. When we consider the diphenylmethane segments, then the two OC_4H_9 chains in the ortho-positions to the CH_2 bridge have always different orientation (up and down). This orientation is also present in solution since the ROESY spectra exclude an alkoxy–alkoxy interaction [15, 18]. Accordingly, just one of four possible pairs of enantiomers is realized in $\mathbf{6^5 a\text{-}d}$. This statement comprises the presence of a C_5 axis. One of 16 possible pairs of enantiomers is populated in each of the non-symmetric systems $\mathbf{8^5}$, $\mathbf{9^5}$ and $\mathbf{10^5}$.

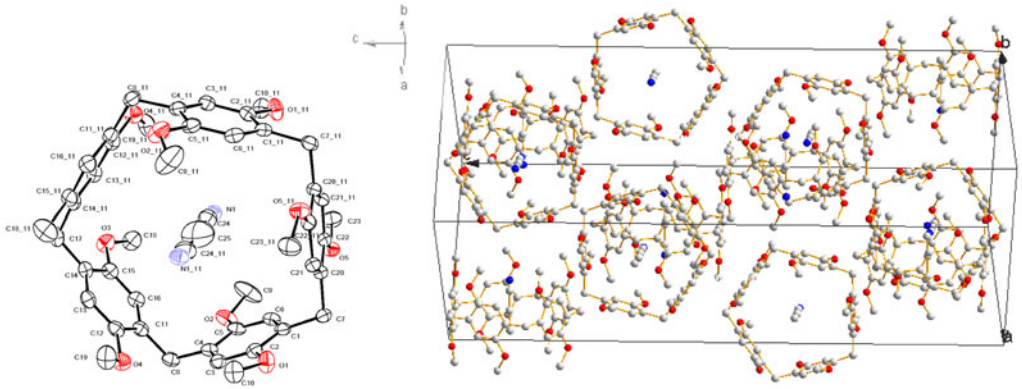
Figure 4 shows the comparison between the ^{1}H NMR spectra of $\mathbf{6^5 d}$ with a C_5 axis and its isomer $\mathbf{10^5}$ without symmetry axis. Instead of two signals (6.860, 6.767 ppm) for the aromatic protons, $\mathbf{10^5}$ has ten partially superimposed signals (6.832, 6.826, 6.810, 6.810, 6.810, 6.800, 6.796, 6.790, 6.790. 6.772 ppm). The CH_2 bridge protons give in $\mathbf{6^5 d}$ one (3.737 ppm) and in $\mathbf{10^5}$ five singlets (3.775, 3.737, 3.737, 3.737, 3.707 ppm).

In general the CH_2 bridges of $\mathbf{6^5 a\text{-}d}$, $\mathbf{8^5}$, $\mathbf{9^5}$, and $\mathbf{10^5}$ give at room temperature in the ^{1}H NMR spectra singlet signals, each. The splitting of these signals of non-symmetric systems up to 110 °C was an error[2] [15, 18]. These geminal protons are homotopic for $\mathbf{6^5 a\text{-}c}$ and enantiotopic for $\mathbf{6^5 d}$, $\mathbf{8^5}$, $\mathbf{9^5}$, and $\mathbf{10^5}$. The latter statement means that the compounds have a de facto symmetry plane, because the rotation of the benzene rings is fast in terms of the NMR time scale. We assume that the OCH_3 groups of the non-symmetric pillararenes $\mathbf{6^5 d}$, $\mathbf{8^5}$, $\mathbf{9^5}$, and $\mathbf{10^5}$ may move through the cavity, because the rotation of the n-octyloxy group through the cavity would be more stericly challenging. The two benzene ring protons are in the "frozen"

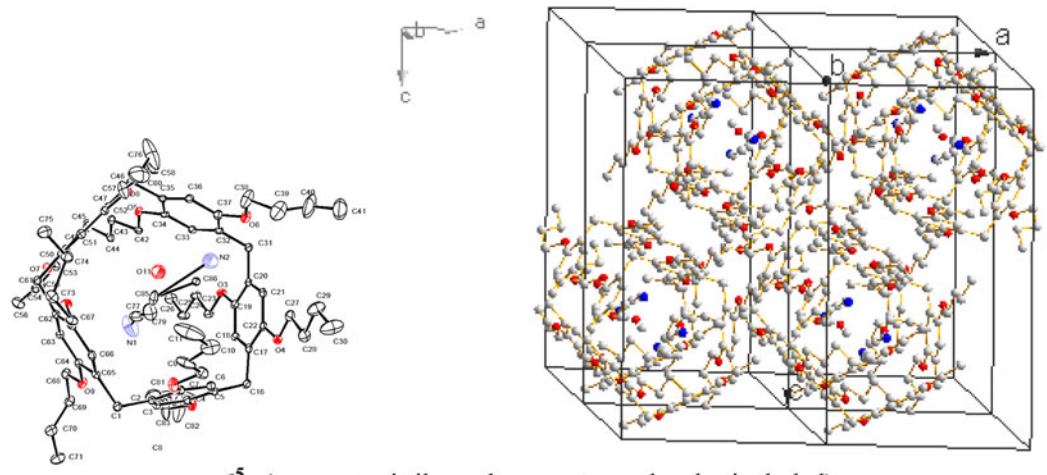
[2] A definite structure proof of the four regioisomers was provided by four crystal structure analyses in the case of the methoxy/n-butoxy compounds [see ref. 15]



6^5a (two acetonitrile molecules included)



6^5b (one acetonitrile molecule included)

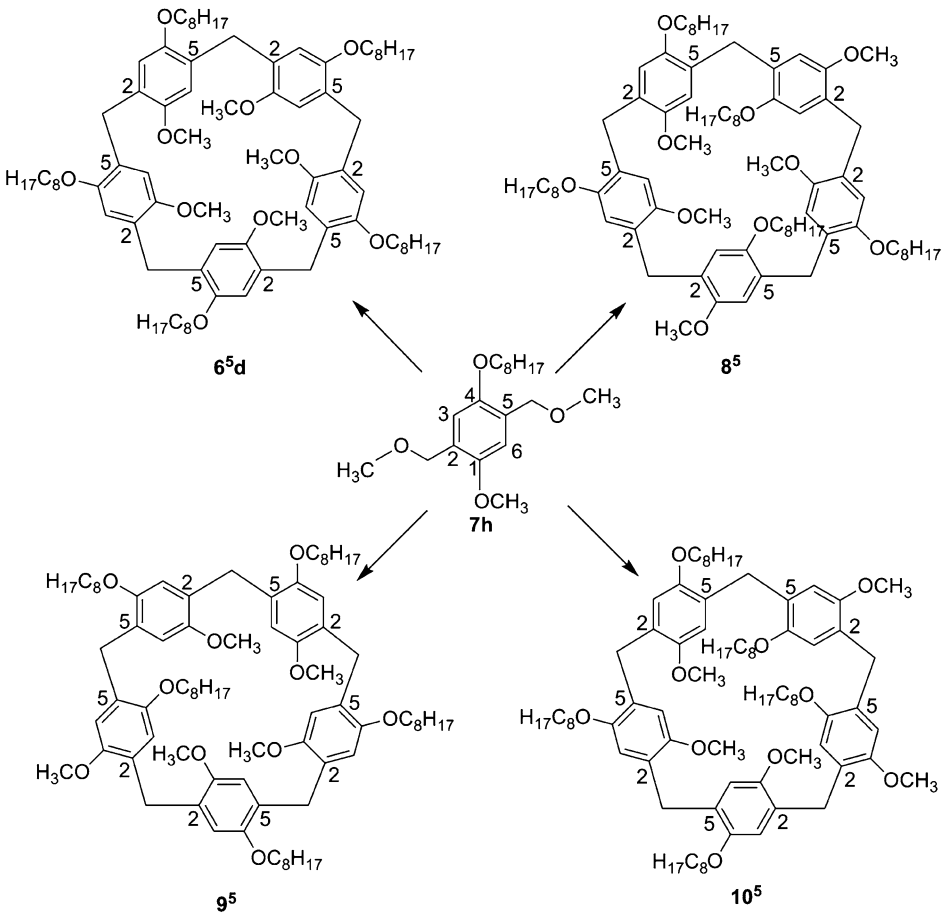


6^5c (two acetonitrile and one water molecules included)

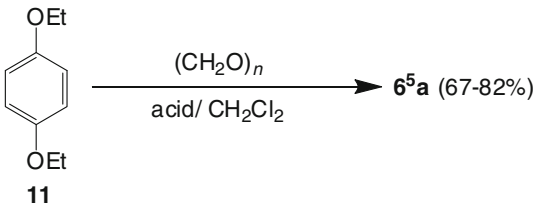
Fig. 2 Crystal structure of pillar[5]arene **6^5b·CH_3CN**, **6^5a·$2CH_3CN$** and **6^5c·$2CH_3CN·H_2O$** (All of them were prepared in acetonitrile) [15]

Table 2 Details of the X-ray crystal structure analyses of pillar[5]arenes $\mathbf{6^5a}$–$\mathbf{6^5c}$

	$\mathbf{6^5a}$	$\mathbf{6^5b}$	$\mathbf{6^5c}$
Empirical formula	$C_{118}\ H_{152}\ N_4\ O_{20}$	$C_{47}H_{50}NO_{10}$	$C_{79}H_{118}N_2O_{11}$
Formula weight	1946.44	788.88	1271.75
Crystal system	Triclinic	Tetragonal	Triclinic
Space group	P-1	*I*41/a	P-1
a/Å	13.3205(16)	14.930(2)	12.1821(16)
b/Å	21.185(3)	14.930(2)	14.6959(19)
c/Å	21.202(3)	39.341(8)	21.725(3)
α/°	77.613(2)	90	89.543(2)
β/°	87.610(2)	90	89.862(2)
γ/°	83.748(2)	90	75.068(2)
V/Å^3	5807.9(12)	8769(2)	3757.9(9)
Z	2	8	2
D_{calcd}/g cm^{-3}	1.113	1.195	1.124
F(000)	2096	3352	1388
θ Range/°	2.61-25.03	3.09-25.19	2.55-25.03
Reflections collected	41982	33531	25979
R(int)	0.0185	0.0959	0.0224
R_1, wR[$I > 2\sigma(I)$]	0.0557,0.1584	0.0694,0.2127	0.1285,0.4368
R_1, wR(all data)	0.0682,0.1693	0.1266,0.2375	0.1445,0.4861



Scheme 3 Formation of regioisomeric pillar[5]arenes from **7h** which bears different alkoxy substituents (the numbers 2 and 5 in the cyclopentamers correspond to the carbon atoms in **7h**)



Scheme 4 Direct preparation of 6^5a from 11 and paraformaldehyde

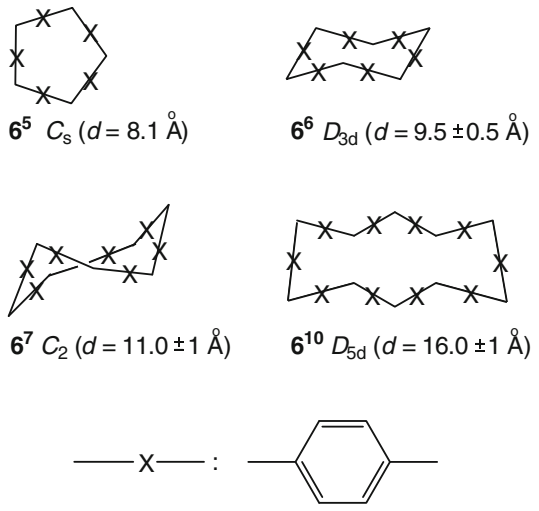


Fig. 3 Selected conformers of $\mathbf{6^5}$ (almost planar), $\mathbf{6^6}$ (chair), $\mathbf{6^7}$ (twisted chair), and $\mathbf{6^{10}}$ (crown). The diameters d[a] of the internal cavities correspond to the crystal structure analysis of $\mathbf{6^5}$ [9, 15] and to model considerations for the higher pillar[n]arenes. [a]The diameter d does not take into account the Van der Waals radii and the torsion of the benzene rings [15]. Thus, the available space for guest molecules is somewhat smaller

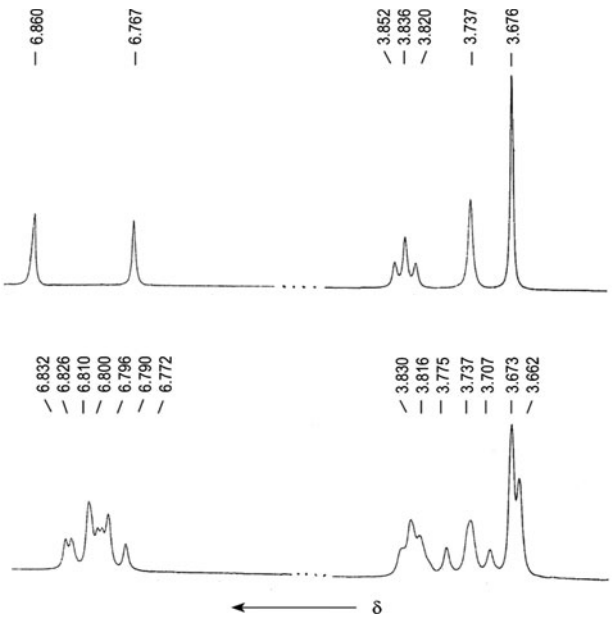


Fig. 4 ^{1}H NMR spectra (low-field part) of $\mathbf{6^5d}$ (*top*) and $\mathbf{10^5}$ (*bottom*) ($CDCl_3$ as solvent, TMS as internal standard)

conformers as well as in the case of fast exchange homotopic for the symmetric and diastereotopic for the nonsymmetric systems. The OCH_2 protons are in the "frozen" conformers diastereotopic and become chemically equivalent in the case of fast exchange. Thus, the OCH_2 groups and in principle also their neighboring CH_2 groups are excellent probes for the benzene ring rotation [18–20]. The chain packing effect [20] at the rim of the pillars is in our opinion a minor effect if present at all. Table 3 summarizes the topicity of several indicative pairs of protons for the corresponding symmetry classes.

An effective symmetry plane, horizontal to the major axis C_n, has for n = 6, 7, 10 two preconditions: the fast inversion of the macrocyclic ring (Fig. 3) and the fast rotation of the benzene rings. Both preconditions are fulfilled for $\mathbf{6^6a}$, $\mathbf{6^6c}$, $\mathbf{6^7b}$ and $\mathbf{6^{10}b}$ at room temperature. These compounds have in the ^{1}H NMR spectra a set of signals which corresponds to the repeat units. The bridge protons as well as the benzene protons give one singlet, each, and the OCH_2 protons provide a triplet. Table 4 summarizes the ^{1}H and ^{13}C NMR data of the pillar[n]arenes with regular repeat units.

Concerning the arrangement of the alkoxy chains in $\mathbf{6^5}$, $\mathbf{6^6}$, $\mathbf{6^7}$ and $\mathbf{6^{10}}$, the preference of one conformer, namely that one with the lowest steric interaction, significates a far-going stereoselectivity, since the theoretical number N of diastereomeric conformers increases strongly with increasing numbers n:

n	5	6	7	8	9	10
N	4	8	9	18	23	46

Pillar[n]arenes as host systems have the possibility to include guests in their cavities. Since pillararenes have high electron density in the pillar structure, electron deficient guests are "welcome". Besides acetonitrile many compounds can also become the guests of pillar[5]arenes, such as ammonium salts [9], dibromoalkanes [13], etc. Due to the different sizes of their cavities, pillar[5]arenes and pillar[6]arenes show specific encapsulations respectively. For example, α,ω-dibromoalkanes are firmly encapsulated in pillar[5]arene $\mathbf{6^5a}$, but not in the larger host pillar[6]arene [25]. The even larger hosts pillar[7]arene and pillar[10]arene might show different host–guest behavior. The study on their host–guest properties is under progress.

Conclusion

We report here on a new type of condensation reaction of ethers $\mathbf{7} \rightarrow \mathbf{6^n}$ (Scheme 1 and 2) which leads to an unexpected *ipso*-substitution on benzene rings by an alkylation/dealkylation process. A detailed study of the reaction conditions revealed that *p*-toluenesulfonic acid in CH_2Cl_2 is the best catalyst for the elimination of CH_2OR^2 and OR^2 groups present in the ethers **7**. A quantitative formation of the

Table 3 Topicity of pairs of protons of 6^5a-d, 8^5, 9^5 and 10^5 and the resulting spin patterns (h: homotopic, e: enantiotopic/chemically equivalent, d: diastereotopic)

Compd.	Symmetry	CH_2 bridges	OCH_2	Ar–H
6^5a-c	D_5	h [A_2, s]	d [AB of ABX_2…]	h [A_2, s]
	D_{5h} (fast exchange)	h [A_2, s]	e [A_2 of A_2X_2…]	h [A_2, s]
6^5d	C_5	d [AB]	d [AB of ABX_2…]	d [AB, 2′s′][a]
	C_{5h} (fast exchange)	e [A_2, s]	e [A_2 of A_2X_2…]	d [AB, 2′s′][a]
8^5, 9^5, 10^5	*C*	d [5AB]	d [5AB of $5ABX_2$…]	d [5AB, 10′s′][a]
	C_s (fast exchange)	e [$5A_2$, s]	e [$5A_2$ of $5A_2X_2$…]	d [5AB, 10′s′][a]

[a] *Para* coupling (^5J) not detectable in 400 MHz spectra

Table 4 ^{1}H and ^{13}C NMR data of **6^5a-d**, **6^6a**, **6^6c**, **6^7b** and **6^{10}b** (δ values in $CDCl_3$, Me_4Si as internal standard)

Compd.		C_qO	C_q	CH	CH_2	OR
6^5a	^{1}H			6.71	3.75	3.81 1.25
	^{13}C	149.8	128.5	115.1	29.8	63.8 15.0
6^5b	^{1}H			6.75	3.76	3.64
	^{13}C	150.7	128.2	113.9	29.6	55.7
6^5c	^{1}H			6.83	3.74	3.84, 1.76, 1.52, 0.96
	^{13}C	149.7	128.1	114.6	29.3	67.9, 32.0, 19.5, 14.0
6^5d	^{1}H			6.86, 6.77	3.74	3.84, 3.68, 1.76, 1.47, 1.30, 1.18, 1.02, 1.02, 0.73
	^{13}C	150.4, 149.8	128.0, 128.0	114.5, 113.8	29.4	68.0, 55.5, 31.5, 29.6, 29.1, 26.2, 22.4, 22.4, 14.0
6^6a	^{1}H			6.68	3.78	3.81 1.27
	^{13}C	150.4	127.8	115.2	30.9	64.0 15.2
6^6c	^{1}H			6.69	3.77	3.74, 1.65, 1.41, 0.89
	^{13}C	150.4	127.8	114.9	30.7	68.2, 31.9, 19.4, 13.9
6^7b	^{1}H			6.61	3.82	3.59
	^{13}C	151.5	127.5	114.0	31.0	56.1
6^{10}b	^{1}H			6.62	3.83	3.63
	^{13}C	151.3	127.6	113.7	30.0	56.1

cyclooligomers **6^n** can be obtained for $R^2 = CH_3$, C_2H_5, n-C_4H_9, whereby cyclopentamers are always the major products (86–95 %). Additionally to this pillar[5]arenes **6^5**, small amounts (2–11 %) of the members of higher pillar[n]arenes **6^n** (n = 6, 7, 10) can be obtained as well. Pillar[n]arenes represent a novel class of host molecules for host–guest chemistry.

Unsymmetrical starting products, such as **7h**, lead to a statistical mixture of regioisomers (Scheme 3), but all reactions **7** → **6^n** are highly stereoselective, in so far as only the conformers with the lowest interaction of the alkoxy side-chains are formed. All systems, which are studied here show a racemization which is fast in terms of the NMR time scale.

The original preparation [9] of **6^5** by the catalytic reaction of 1,4-dialkoxybenzenes **11** and paraformaldehyde could be improved to three fold yield (Scheme 4).

Experimental

Melting points are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DRX 400 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were obtained on the following spectrometers: Agilent-t 5975 (GC–MS), HCT PLUS (APCI), Acquity UPLC-Q-TOF (ESI), Autoflex III Smartbeam (MALDI-TOF). TLC was performed on silica gel plates (Merck GF 254), visualization at 254 nm. SiO_2 (200–300 mesh) was used for the column chromatographies.

1,4-Diethoxy-2,5-bis(ethoxymethyl)benzene (**7a**)

The starting compound **7a** was prepared from 1,4-diethoxy-2,5-bis(chloromethyl)benzene [20, 21] according to ref [20, 22]. Crystallization from ethanol afforded a colorless product. Yield 90 %; mp 70–71 °C (lit [20] 69–70 °C).

1,4-Diethoxy-2,5-bis(methoxymethyl)benzene (**7b**)

A mixture of 1,4-diethoxy-2,5-bis (chloromethyl)benzene (1.58 g, 6.0 mmol) and CH_3ONa (4.32 g, 80 mmol) was vigorously stirred in methanol (50 mL) and refluxed for 3–5 h [23]. The mixture was concentrated, treated with H_2O

and filtered to deliver the crude product. Crystallization from ethanol afforded colorless crystals. Yield 1.34 g (87 %); mp 72 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.36$ (t, $^3J = 6.8$ Hz, 6 H, CH_3), 3.40 (s, 6 H, OCH_3), 4.00 (q, $^3J = 6.8$ Hz, 4 H, OCH_2CH_3), 4.47 (s, 4 H, CH_2O), 6.90 (s, 2 H, 3-H, 6-H). ^{13}C NMR ($CDCl_3$): $\delta = 15.0$ (CH_3), 58.4 (OCH_3), 64.5 (1-OCH_2, 4-OCH_2), 69.2 (2-CH_2O, 5-CH_2O), 112.5 (C-3, C-6), 126.6 (C-2, C-5), 150.3 (C-1, C-4). GC–MS: *m/z* (%) = 254 (100) [M^+], 225 (31), 194 (22), 134 (31), 109 (16), 67 (14). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.01; H, 8.70.

(2,5-Diethoxy-4-hydroxymethyl-phenyl)-methanol (**7c**)

Preparation according to ref [22]. yield: 70 %, mp 167–169 °C.

2,5-Bis(n-butoxymethyl)-1,4-diethoxy benzene (**7d**)

Na (3.3 g, 143 mmol) and n-butanol (50 mL, 40.5 g, 546 mmol) was stirred till Na had completely reacted. 1,4-Diethoxy-2,5-bis (chloromethyl)benzene [20, 21] (1.91 g, 7.26 mmol) was added and refluxed for 3–4 h. The concentrated mixture was treated with ice-water and neutralized with acetic acid. The water layer was separated and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried with Na_2SO_4 and purified by column chromatography (3 × 50 cm SiO_2, petroleum ether (bp 60–90 °C)/ethyl acetate 20:1). Crystallization from EtOH afforded **7d** (2.10 g, 85 %) as colorless crystals, mp 30 °C. ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, $^3J = 7.4$ Hz, 6 H, CH_3), 1.34–1.42 (m, 10 H, CH_3, CH_2), 1.59 (m, 4 H, CH_2), 3.49 (t, $^3J = 6.6$ Hz, 4 H, OCH_2), 3.99 (q, $^3J = 6.8$ Hz, 4 H, OCH_2CH_3), 4.51 (s, 4 H, 2-CH_2O, 5-CH_2O), 6.91 (s, 2 H, 3-H, 6-H). ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 15.0 (CH3), 19.4, 31.9 (CH2), 64.5, 67.2 (OCH_2), 70.4 (2-CH_2O, 5-CH_2O), 112.5 (C-3, C-6), 127.0 (C-2, C-5), 150.3 (C-1, C-4). GC–MS: *m/z* (%) = 338 (100) [M^+], 265 (41), 237 (18), 191 (9), 165 (40), 123 (24), 107 (14), 57 (30), 41 (18). Anal. Calcd for $C_{20}H_{34}O_4$: C, 70.97; H, 10.12. Found: C, 70.67; H, 10.20.

2,5-Bis(benzyloxymethyl)-1,4-diethoxy benzene (**7e**)

A mixture of 2,5-diethoxy-1,4-bis(chloromethyl)benzene [20, 21] (1.86 g, 7.07 mmol), $(n\text{-}Bu)_4NBr$ (142 mg, 0.44 mmol), benzyl alcohol (1.8 mL, 1.88 g, 17.4 mmol), KOH (1.08 g, 15.8 mmol), H_2O (1 mL) and chlorobenzene (40 mL) was stirred vigorously at 75 °C for 48 h. H_2O (50 mL) was added to the mixture. The separated water layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried with Na_2SO_4. After filtration and concentration, the residue was treated with ethanol to give **7e** as colorless solid (2.44 g, yield 85 %); mp 108–109 °C (ethanol). ^{1}H NMR ($CDCl_3$): $\delta = 1.37$ (t, $^3J = 6.8$ Hz, 6 H, CH_3), 4.01 (q, $^3J = 6.8$ Hz, 4 H, OCH_2CH_3), 4.61 s, 4 H/4.62, s, 4 H (CH_2O), 7.00 (s, 2 H, 3-H, 6-H), 7.29–7.41 (m, 10 H, phenyl). ^{13}C NMR ($CDCl_3$): $\delta = 15.0$ (CH_3), 64.5 (1-OCH_2, 4-OCH_2), 66.9 (2-CH_2O), 5-CH_2O), 72.4 (OCH_2Ph), 112.9 (C-3, C-6), 126.8, 127.5, 127.7, 128.3 (C-2, C-5 and CH, phenyl), 138.6 (C_q, phenyl), 150.5 (C-1, C-4). GC–MS: *m/z* (%) = 406 (20) [M^+], 105 (18), 91 (100). Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.75; H, 7.49.

2,5-Bis(ethoxymethyl)-1,4-dimethoxybenzene (**7f**)

Preparation according to ref [20, 22]. yield: 70 %, mp 57–58 °C (lit. 55 °C).

1,4-Di-n-butoxy-2,5-bis(ethoxymethyl)benzene (**7 g**)

Preparation according to ref [20, 22]. yield: 95 %, colorless oil.

1-Methoxy-2,5-bis(methoxymethyl)-4-(n-octyloxy)benzene (**7 h**)

Preparation analogous to the preparation of **7b.** Yield 622 mg (80 %) when 1-methoxy-4-(n-octyloxy)-2,5-bis(chloromethyl)benzene [24] was used (850 mg, 2.55 mmol); mp 44 °C (ethanol). ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, $^3J = 6.8$ Hz, 3 H, CH_3), 1.27–1.31 (m, 8 H, CH_2), 1.43 (m, 2 H, CH_2), 1.74 (m, 2 H, CH_2), 3.40, s, 3 H/3.41, s, 3 H (OCH_3), 3.80 (s, 3 H, 1-OCH_3), 3.92 (t, $^3J = 6.6$ Hz, 2 H, OCH_2), 4.46, s, 2 H/4.48, s, 2 H (2-CH_2O, 5-CH_2O), 6.89, s, 1 H/6.91, s, 1 H (3-H, 6-H). ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 22.7, 26.1, 29.3, 29.3, 29.4, 31.8 (CH_2), 56.1, 58.3, 58.4 (OCH_3), 69.0, 69.2, 69.3 (OCH_2), 111.2, 112.7 (C-3, C-6), 126.2, 126.8 (C-2, C-5), 150.4, 151.0 (C-1, C-4).

GC–MS: *m/z* (%) = 324 (36) [M^+], 180 (100), 150 (60). Anal. Calcd for $C_{19}H_{32}O_4$ (324.5): C, 70.34; H, 9.94. Found: C, 70.21; H, 10.05.

General procedure for the preparation of pillar[n]arenes $\mathbf{6^n}$ from **7** (Entry 1)

Starting compound **7a**, **f–h** (20.6 mmol) and *p*-toluenesulfonic acid monohydrate (500 mg, 2.63 mmol) were stirred in 400 mL CH_2Cl_2 at room temperature for 3–4 h. Then H_2O (100 mL) was added and the water layer separated and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried (Na_2SO_4) and purified by column chromatography (4 × 60 cm SiO_2, gradient

elution, petroleum ether bp 60–90 °C/ethyl acetate from 500:1 to 10:1). Elution yielded two fractions for the reaction of **7a** and **7 g**, three fractions for **7f** and four fractions for **7 h**, which are described below. The chromatography has to be repeated for difficult separations, in particular for the separation of $\mathbf{10}^{\mathbf{5}}$ and $\mathbf{9}^{\mathbf{5}}$.

The entries 2–4 with **7a** (Table 1) and 9–10 with **7b-c** were performed in an analogous mode. Higher temperatures were used for the entries 5 and 7 with **7a**, 11 with **7d** and 12 with **7e**. Slightly higher amounts of catalyst did not significantly enlarge the reaction rates. The reaction times are listed in Table 1. In the entries 6–8 with **7a**, *p*-toluenesulfonic acid as catalyst was replaced by other acids with moderate success. Only conc. H_2SO_4 gave a high yield when a reaction time of 27 h was used at ambient temperatures (Table 1).

Procedure for the Preparation of Pillar[5]arenes $\mathbf{6}^{\mathbf{5}}$**a** from **11** (Scheme 4)

A mixture of **11** (500 mg, 3.0 mmol), paraformaldehyde (270 mg, 9 mmol) and *p*-toluenesulfonic acid monohydrate (86 mg, 0.45 mmol) was stirred in 120 mL CH_2Cl_2 at room temperature for 10–15 h. 50 mL water was added, and the water layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phase was dried (Na_2SO_4) and purified by column chromatography (2 × 20 cm SiO_2, petroleum ether (bp 60–90 °C)/ethyl acetate 30:1), dried under vacuum to give $\mathbf{6}^{\mathbf{5}}$**a** as colorless crystals (358 mg, yield 67 %).

Pillar[5]arene $\mathbf{6}^{\mathbf{5}}$**a**: First fraction, yield: 3.27 g (89 %); colorless crystals, mp 154–156 °C (Ref [19]. mp 157.5 °C). (CH_2Cl_2/petroleum ether)[3]. GC–MS: *m/z* (%) = 890 (100) $[M]^+$, 862 (5), 667 (3), 503 (3), 445 (40), 355 (5), 221 (5), 207 (10). HRMS: m/z calcd for $C_{55}H_{71}O_{10}$: 891.5047 $[M + H]^+$; found 891.5049.

Pillar[6]arene $\mathbf{6}^{\mathbf{6}}$**a**: Second fraction, yield: 294 mg (8 %); colorless crystals, mp 172–173 °C (Ref [25]. mp 172–173 °C). (CH_2Cl_2/petroleum ether) [See foot note 3]. MS (APCI): *m/z* $[M + H]^+$ = 1069.8. MS (MALDI-TOF): *m/z* calcd for $C_{66}H_{84}O_{12}$: 1068.6; found 1069.1; calcd for $[M + Na]^+$: 1091.6; found 1092.1; calcd for $[M + K]^+$: 1107.6; found 1108.0.

Pillar[5]arene $\mathbf{6}^{\mathbf{5}}$**b**: First fraction, yield: 2.94 g (95 %); colorless crystals, mp 194–195 °C (Ref [9]. mp 248.8 °C).(CH_2Cl_2/petroleum ether) [See foot note 3]. MS (MALDI-TOF): *m/z* calcd for $C_{45}H_{50}O_{10}$: 750.3; found 750.3.

Pillar[7]arene $\mathbf{6}^{\mathbf{7}}$**b**: Second fraction, yield: 75 mg (2.4 %); colorless crystals, mp 281–282 °C (CH_2Cl_2/petroleum ether) [See foot note 3]. MS (ESI): *m/z* = 1073.5 $[M + Na]^+$. MS (APCI): *m/z* = 1051.5 $[M + H]^+$. MS (MALDI-TOF):): *m/z* calcd for $[M]^+$ $C_{63}H_{70}O_{14}$: 1050.5; found 1050.6; calcd for $[M + Na]^+$: 1073.5; found 1073.6.

Pillar[10]arene $\mathbf{6}^{\mathbf{10}}$**b**: Third fraction, yield: 56 mg (1.8 %); colorless crystals, mp 249–250 °C (CH_2Cl_2/petroleum ether) [See foot note 3]. MS (APCI): *m/z* = 1537.1 $[M + HCl]^+$. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{90}H_{100}O_{20}$: 1500.7; found 1500.3; calcd for $[M + Na]^+$: 1523.7; found 1523.3; calcd for $[M + K]^+$: 1539.6; found 1539.3.

Pillar[5]arene $\mathbf{6}^{\mathbf{5}}$**c**: First fraction, yield: 4.15 g (86 %) (Ref [19]. mp 131.5 °C); colorless crystals, mp 133–135 °C [See foot note 3]. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{75}H_{110}O_{10}$: 1170.8; found 1170.6; calcd for $[M + Na]^+$: 1193.8; found 1193.6.

Pillar[6]arene $\mathbf{6}^{\mathbf{6}}$**c**: Second fraction, yield: 530 mg (11 %); colorless crystals, mp 87–89 °C (Ref [25]. mp 89–91 °C). (CH_2Cl_2/EtOH) [See foot note 3]. MS (APCI): *m/z* = 1406.2 $[M + H]^+$. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{90}H_{132}O_{12}$: 1405.0; found 1404.9; calcd for $[M + Na]^+$: 1428.0; found 1427.9; calcd for $[M + K]^+$: 1443.9; found 1443.9.

Pillar[5]arene $\mathbf{8}^{\mathbf{5}}$: Isolated as first fraction, yield: 1.22 g (23.8 %); crystallization from ethyl acetate/EtOH gave colorless crystals, mp 103–104 °C. ^{1}H NMR ($CDCl_3$): δ = 0.72–0.82 (m, 15 H, CH_3), 1.01–1.19 (m, 20 H, CH_2), 1.12–1.19 (m, 20 H, CH_2), 1.41 (m, 10 H, CH_2), 1.77 (m, 10 H, CH_2), 3.70 (m, 15 H, OCH_3), 3.75 (m, 10 H, CH_2), 3.83 (m, 10 H, OCH_2), 6.83 (m, 10 H, aromat. H)[4] [30]. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.5, 22.6, 26.3, 26.3, 29.1, 29.2, 29.4, 29.5, 29.8, 29.8, 29.9, 31.4, 31.5, 31.5, 31.7 (CH_2), 55.4, 55.5, 55.6 (OCH_3), 68.3, 68.4 (OCH_2), 113.6, 113.7, 113.8, 113.9, 114.4, 114.5, 114.8 (aromat. CH), 128.0, 128.0, 128.1, 128.2, 128.2 (aromat. C_q), 149.9, 149.9, 150.0, 150.3, 150.4 (C_qO) [30]. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{80}H_{120}O_{10}$: 1240.9; found 1240.8. Calcd for $[M + Na]^+$: 1263.9; found 1263.8. Calcd for $[M + K]^+$: 1279.9; found 1279.8.

Pillar[5]arene $\mathbf{10}^{\mathbf{5}}$: Isolated as second fraction, yield: 1.28 g (25.0 %); crystallization from ethyl acetate/EtOH gave colorless crystals, mp 101–102 °C. ^{1}H NMR ($CDCl_3$): δ = 0.73–0.81 (m, 15 H, CH_3), 1.10–1.27 (m, 40 H, CH_2), 1.48 (m, 10 H, CH_2), 1.76 (m, 10 H, CH_2), 3.67 (m, 15 H, OCH_3), 3.71–3.78 (m, 10 H, CH_2), 3.82 (m, 10 H, OCH_2), 6.77–6.83 (m, 10 H, aromat. H) [See foot note 4]. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.4, 22.5, 26.2, 26.2, 26.3, 29.1, 29.2, 29.2, 29.4, 29.5, 29.6, 29.8, 29.8, 31.5, 31.6 (CH_2), 55.5, 55.6 (OCH_3), 68.3, 68.4, 68.4 (OCH_2), 113.7, 113.9, 114.7, 114.8, 115.0 (aromat. CH), 128.0, 128.1, 128.2, 128.3 (aromat. C_q), 149.9, 150.4 (C_qO) [See

[3] ^{1}H and ^{13}C NMR data are listed in Table 3.

[4] Due to the lack of symmetry, the ^{1}H and ^{13}C NMR signals of the five phenylene methylene subunits are strongly superimposed.

foot note 4]. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{80}H_{120}O_{10}$: 1240.9; found 1240.9. Calcd for $[M + Na]^+$: 1263.9; found 1263.9. Calcd for $[M + K]^+$: 1279.9; found 1279.8.

Pillar[5]arene $\mathbf{9^5}$: Isolated as third fraction, yield: 1.33 g (26.0 %); crystallization from ethyl acetate/EtOH gave colorless crystals, mp 49–51 °C.

^{1}H NMR ($CDCl_3$): $\delta = 0.69$–0.78 (m, 15 H, CH_3), 1.05–1.19 (m, 30 H, CH_2), 1.28 (m, 10 H, CH_2), 1.46 (m, 10 H, CH_2), 1.76 (m, 10 H, CH_2), 3.67 (m, 15 H, OCH_3), 3.74 (m, 10 H, CH_2), 3.84 (m, 10 H, OCH_2), 6.83 (m, 10 H, aromat. H) [See foot note 4]. ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (CH_3), 19.5, 22.4, 22.5, 26.1, 26.3, 29.1, 29.2, 29.3, 29.5, 29.6, 29.6, 29.7, 31.4, 31.6, 31.9, 31.9, 32.0 (CH_2), 55.5, 55.6, 55.7, 55.8 (OCH_3), 67.9, 68.0, 68.2, 68.5 (OCH_2), 113.7, 113.8, 113.9, 114.0, 114.1, 114.5, 114.8, 114.9, 114.9, 115.0 (aromat. CH), 128.0, 128.1, 128.2, 128.3 (aromat. C_q), 149.9, 150.1, 150.5, 150.6 (C_qO) [See foot note 4]. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{80}H_{120}O_{10}$: 1240.9; found 1240.9. Calcd for $[M + Na]^+$: 1263.9; found 1263.9. Calcd for $[M + K]^+$: 1279.9; found 1279.8.

Pillar[5]arene $\mathbf{6^5d}$: Isolated as fourth fraction, yield: 450 mg (8.8 %); crystallization from ethyl acetate/EtOH gave colorless crystals, mp 137–138 °C [See foot note 3]. MS (MALDI-TOF): *m/z* calcd for $[M]^+$ $C_{80}H_{120}O_{10}$: 1240.9; found 1240.8; calcd for $[M + Na]^+$: 1263.9; found 1263.8. Calcd for $[M + K]^+$: 1279.9; found 1279.8.

Preparation of Pillar[5]arene $\mathbf{6^5a}$ from 1,4-Diethoxybenzene (**11**). A mixture of **11** (415 mg, 2.5 mmol), paraformaldehyde (210 mg, 7.0 mmol) and $FeCl_3$ (68.2 mg, 0.42 mmol) was stirred in 100 mL CH_2Cl_2 at room temperature for 2–3 h. Then H_2O (50 mL) was added and the water layer was separated and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and purified by column chromatography (3 × 30 cm SiO2, petroleum ether bp 60–90 °C/ethyl acetate 20:1) to give $\mathbf{6^5a}$ (365 mg, 82 %) as colorless crystals, mp 154–156 °C. The reactions with $SnCl_4$ and *p*-toluenesulfonic acid were performed in the same way, but the reaction time amounted to 6–7 h and 20 h, respectively.

Pillar[5]arene $\mathbf{6^5e}$: To a solution of $\mathbf{6^5b}$ (85 mg, 0.11 mmol) in CH_2Cl_2 (8 mL), BBr_3 (0.5 mL, 1325 mg, 5.3 mmol) was added dropwise at 0 °C. After 45 h stirring at room temperature, 15 mL of petroleum ether (bp 60–90 °C) was added and the formed precipitate was filtered off and washed with acetone (20 mL). The filtrate was concentrated and purified by column chromatography (3 × 40 cm SiO_2, CH_2Cl_2/acetone 50:50). Product $\mathbf{6^5e}$ (49 mg, 70 %) was obtained as a colorless solid [9, 14].

^{1}HNMR (400 MHz, acetone-d6) $\delta = 3.55$ (s, 10H), 6.66 (s, 10H), 8.34(less than one H) (Lit [9].)

The ether cleavage of $\mathbf{6^5a}$ gave under the same conditions a somewhat lower yield. The identification of $\mathbf{6^5e}$ was performed by comparison with an authentic sample [9].

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