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Large parent homooxacalixarenes: formation and transformation

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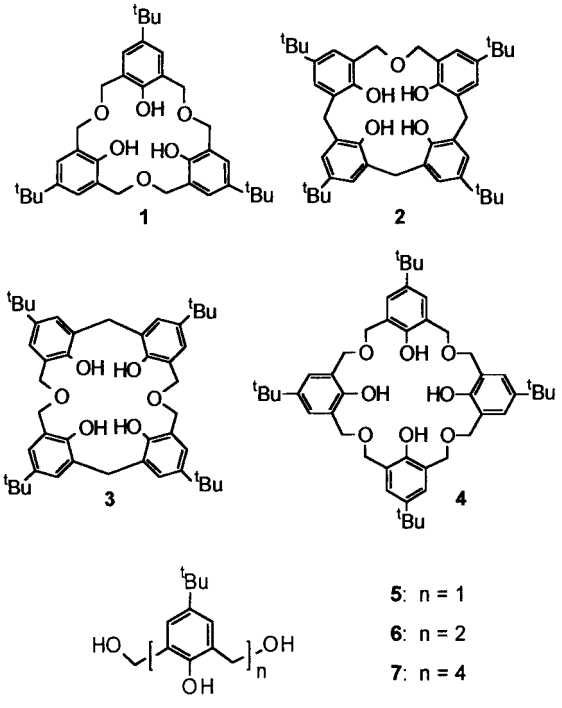
Abstract—The mixtures obtained on thermally dehydrating concentrated solutions of a bishydroxymethylated diphenol could be reliably analysed through the signals of the phenol protons in the ^{1}H NMR spectra. This allowed two oxygenated homologues of calix[6]arene and one homologue of calix[8]arene to be prepared in favourable conditions along with two homooxacalix[4]arenes. The obtained compounds are regular products of a cyclooligomerization reaction, namely dimer, trimer, and tetramer, and modified structures with one CH_2OCH_2 bridge less than expected. The latter compounds and lower regular cyclooligomers appear to be formed when cyclooligomers are thermally decomposed. The thermal lability of the compounds increases along the series dimer, trimer, tetramer. The strict relationship between parent homooxacalixarenes and typical calixarenes becomes increasingly evident in the light of the obtained results.

1. Introduction

Homooxacalixarenes are calixarene[1–6] analogues in which some or all of the CH_2 units bridging the aromatics in the typical series are replaced by CH_2OCH_2 units. Currently investigated homooxacalixarene systems are that of *p-tert*-butyldihomooxacalix[4]arene **2**,[7] and that of *p-tert*-butylhexahomotrioxacalix[3]arene **1** and analogues, the latter system enjoying particular popularity due to its complexation of fullerenes.[8–10] Compounds **1**, **2** and **3** were prepared by Dhawan and Gutsche[11] through thermal dehydration of **5**, **7** and **6**, respectively, in refluxing xylene. Although this is the leading reference for parent homooxacalixarene formation, the thermal dehydration of bishydroxymethylated phenols has been followed to a limited extent in subsequent literature. Compound **2** is now a readily available material through a one-step procedure from *p-tert*-butylphenol,[12] while variable results have been reported for the thermal dehydration leading to **1** so that alternative acid catalysed high-dilution procedures have been developed.[13,14] On the other hand, **3** very seldom occurs in the literature and only the preparation of a small sample has been reported for the fourth known parent homooxacalixarene system, **4**.[15]



As a matter of fact the chemistry of homooxacalixarene as a class is still relatively undeveloped because the parent compounds are not generally available. Our former approach to fill this gap was to obtain ether derivatives of **3**[16] and **4**,[17] by-passing the parent macrocycle. This method has also been extended to obtain ether derivatives in quite new homooxacalixarene systems[18] and the remarkable ligation properties of the whole homooxacalix[4]arene family have been reported.[16,18] However, the chemistry of

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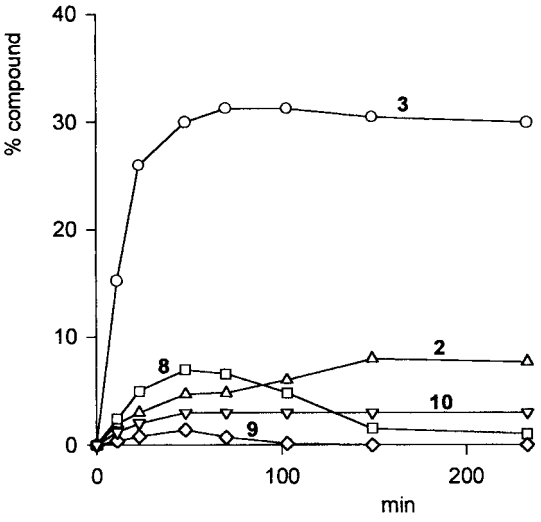


Figure 1. Homooxacalixarene mixture composition at varying times on dehydrating **6** in refluxing 1,1,2,2-tetrachloroethane.

homooxacalixarenes cannot thrive without parent macrocycles and to make them available a deeper knowledge is needed of the dehydration reaction. Our first results in this field are shown in the present paper in connection with the formation of large homooxacalixarenes from a bishydroxymethylated diphenol.

2. Results and discussion

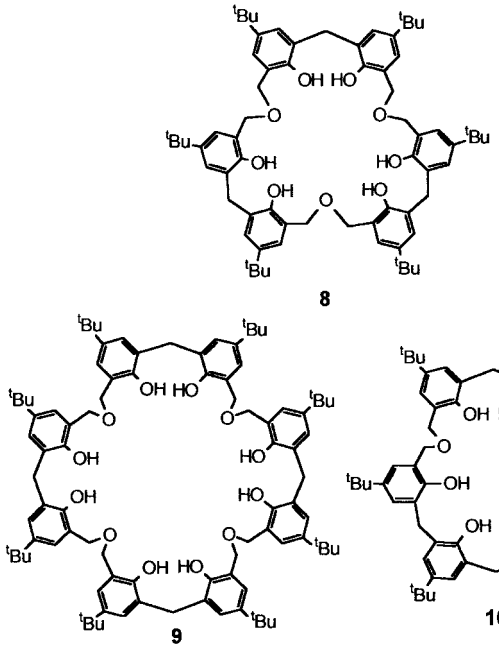
2.1. The products of the dehydration reaction

In this paper, we are concerned with thermal dehydration[11] that in spite of some reported failures[13] is apparently simple and of wide scope. The generally expected trend of cyclooligomerisation reactions prompted us to look for higher cyclooligomers in the mixture obtained on dehydrating **6** according to Ref. 11. Column chromatography did not allow new products to be isolated in pure form although a relatively abundant component could be detected by TLC.

A reliable analysis of the reaction mixtures and of materials to be purified could be carried out through ^{1}H NMR spectra in $CDCl_3$. Namely, although spectra of the several products were largely superposed, singlet signals of ArOH protons were found across a wide range of values (7.5–10.5 ppm) in fixed and characteristic positions for a given component. This is obviously due to strong intramolecular hydrogen bondings in cyclic arrays, analogous to that which occurs in typical calixarenes. Systematic investigation of the signals of the ArOH protons in the ^{1}H NMR spectra allowed suitable conditions for both the formation and purification of several compounds to be found.

The several new ring types can be identified through the sequence of indexes for the length of the CH_2OCH_2 and CH_2 bridges according to cyclophane naming, while such abridged names as tetrahomodioxacalix[4]arene for compound **3** cannot account for possible regioisomers.[18]

The products that have been isolated are the cyclodimer **3**, namely a [3.1.3.1]homooxacalixarene, the cyclotrimer **8** (a [3.1.3.1.3.1]homooxacalixarene), and the cyclotetramer **9** (a [3.1.3.1.3.1.3.1]homooxacalixarene). Two further macrocycles were obtained as by-products, namely the [3.1.1.1]homooxacalixarene **2** and the [3.1.3.1.1.1]homooxacalixarene **10**.



According to the eventually adopted procedure the large homooxacalixarenes were prepared on heating at 120°C concentrated (0.75 mol L^{-1}) solutions of **6** either in 1,1,2,2-tetrachloroethane (TCE) for 310 min or in xylene for 200 min. Lowering the temperature with respect to that of refluxing xylene and strictly controlling the heating time are of fundamental importance to obtain **8** and particularly **9**. A simple procedure based on three selective precipitations and one easy column chromatography step was eventually set-up to obtain in pure form the large homooxacalixarenes. The yields in the dehydrations carried out in TCE were as follows: **3**, 40%; **8**, 10%; **9**, 2.6%; **10**, 2.8%. Only small samples were, on the other hand, isolated in pure form of the well known **2** which is easily available through other procedures.[7] Apart from the important difference in required heating times, strictly similar trends and yields were observed in the two tested solvents, the differences being well below the uncertainties expected in purifying the complicated mixtures with classical techniques. TCE has been used because samples for ^{1}H NMR analysis could be taken from a homogeneous refluxing reaction mixture, but xylene should be preferred due to its apparently more constant quality in commercial samples and, most importantly, its lower toxicity. TCE should be a colourless, high quality, solvent. Markedly different results, which are currently being evaluated for their mechanistic implications, are observed when these dehydration reactions are carried out in lower quality commercial batches of TCE.

2.2. The reaction sequence of cyclooligomerisation

Only three regular cyclooligomer homooxacalixarenes were formed in relevant amounts. At 0.75 mol L^{-1} concentration,

extensive polymerisation with a rather flat distribution of cyclooligomers should be observed in the absence of template effects.[19] Intramolecular hydrogen bonding clearly promotes cyclisation with respect to further intermolecular reaction, analogously to what happens in calixarene formation in alkaline solution,[1–5] and at variance with what is observed in acid catalysed homooxacalixarene formation.[13,14]

The system is actually more complicated than a simple cyclooligomerisation and little is known of unidentified materials that could be in part a linear polymer with a non-reactive terminal group (possibly an aldehyde) or simply linear and cyclic polymers with a broad distribution. Namely it may happen that hydrogen bonding template effects are only favourable for the first possible cyclisation steps, and are absent or unfavourable with higher oligomers.[20] Actually, on extrapolating the observed behaviour of **3**, **8**, and **10** (see below), it seems likely that cyclopentamer and higher cyclooligomers are quite unstable in the reaction conditions and possibly, although formed, they do not accumulate to a significant extent. It should be noted that in the spectra of the final mixtures unresolved signals possibly due to polymers are observed in the region near 7.7 ppm and that some signals of medium to low intensity attributable to aldehydes are observed at about 11 ppm, with associated signals of phenol functions at about 8.90, 8.64, and 9.86 ppm. Removing oxygen from the reaction medium reduced the intensity of the peaks related to aldehydes.

2.3. Modified cyclooligomers

Two homooxacalixarenes have been isolated, namely **2** and **10** which can be formally related to **3** and **8**, respectively, by subtracting a formaldehyde unit in one CH_2OCH_2 bridge. Dhawan and Gutsche[11] had reported that after recovering **3** as a solid from xylene, a small amount of **2** could be detected by TLC in the mother liquors. We had actually isolated it through column chromatography,[21] moreover the analogue of **2** has been obtained also in the case of the *p*-phenyl substituted compounds.[22] Moreover, products with mixed CH_2 and CH_2OCH_2 bridges apparently accompanied the formation of **1** and **4** and their analogues in the acid catalysed dehydration of **5**.[13] Such 'unexpected' compounds actually appear to occur in general in the dehydrated mixtures, so that interesting homooxacalixarenes formed besides regular cyclooligomers can be pursued. Their amount is relatively small in the presently adopted conditions: **2** actually only complicates the isolation of more interesting compounds, **10** is, on the other hand, a compound which is very difficult to obtain otherwise.

2.4. Product decomposition and transformation

The relative abundance of homooxacalixarene products, and particularly of large cyclooligomers, was found to change markedly on changing the dehydration temperature and on prolonging heating times. The finally adopted conditions to prepare the large homooxacalixarenes have been chosen on the basis of several small-scale runs and extensive ^{1}H NMR analysis. In Fig. 1 the results are shown for one of these dehydration runs on **6**, namely in refluxing TCE (bp of the pure solvent 147°C).

The three regular cyclooligomers rapidly reach a maximum concentration that is in all cases lower than that reached at 120°C. After 200 min the concentration of **3** is possibly slightly decreasing, while compound **8** appears to have been largely destroyed. Compound **9** never exceeds 1.4% yield and cannot be practically detected in the mixture after 2 h. Interestingly, the by-product **2** reaches higher percentage values than in the dehydration at 120°C and the apparent trends for **3**, **8**, and **2** suggest possible interconversions. Pure samples of **9**, **8**, and **3** were heated to clarify the latter point and the results were as follows: compounds **3** and **8** were identified among the main products obtained on heating **9**; compounds **3**, **2**, and **10** are obtained on heating **8**; compound **3** is partly converted into **2**. Summing up, the regular cyclooligomers are consumed on heating and partly transformed into lower cyclooligomers and/or modified cyclooligomers. A marked increase in the thermal lability is observed on going from the cyclic dimer to the trimer and to the tetramer. Product decomposition and occurrence of anomalous homooxacalixarenes appear to be related points.

Actually, CH_2OCH_2 bridge decomposition at high temperature with loss of formaldehyde is well known to take place in the hardening of phenol-formaldehyde resins along with dehydration of hydroxymethylphenols.[23] The decomposition as investigated in the 1940s to model the reaction occurring in the curing of Bakelite appeared to be a quite complicated process and several pathways have been proposed to account for the products isolated in the various cases.[23] A satisfactory control of the dehydration and of the decomposition steps to obtain several but separable interesting macrocycles in a non-resinous mixture is what we aimed for in the present investigation.

The relationship between typical calixarenes and homooxacalixarenes is not only a formal one, namely they differ by CH_2O units which correspond to formaldehyde molecules and formaldehyde is reacted with *p-tert*-butylphenol and alkali in the one-step synthesis to give both calixarenes and homooxacalixarene **2**.[12,24] Moreover, we found that CH_2O units can be lost from formed homooxacalixarenes even on simple heating in neutral solution. So the obtained results indicate that homooxacalixarenes should be taken into account, either as true precursors or as collaterals, while studying the intriguing chemogenesis of calixarenes.

3. Conclusion

Just like in the series of typical calixarenes, compounds with more than four aromatic units can also be obtained in the series of parent homooxacalixarenes, and just like in the series of typical calixarenes interconversion among cyclooligomers is found to take place in the series of homooxacalixarenes. Conditions have been found to readily obtain two oxygenated homologues of calix[6]arene and one of calix[8]arene along with two analogues of calix[4]arene. The absolute yields in large homooxacalixarenes are not high on an absolute scale, but they are fairly good when allowance is made for the contemporary formation of 40% dimer. The high precursor concentration used allows 0.25–1.0 g samples of the large homooxacalixarenes to be

available from a reaction carried out on 10 g precursor in 27 mL solvent. The procedure given by Dhawan and Gutsche[11] to prepare **3** is straightforward, namely in the original conditions large homooxacalixarenes are formed to a lower extent or are decomposed after being formed, the higher temperature and/or the prolonged heating time yielding a simpler final mixture with possibly increased concentration of **3** due to transformation of the higher homologues. On adjusting the concentration of **6**, and, most importantly, on regulating the temperature and the heating time, the control has been shifted from a maximum yield of **3** towards a maximum survived of the larger macrocycles. Conformational and structural properties of the three new macrocycles, as well as their binding properties, are currently being investigated. Moreover, preliminary results indicate that interesting chemistry can be carried out at the lower rim of **8**.

4. Experimental

NMR spectra were recorded at 298 K on a Bruker AC 300 spectrometer, using $CDCl_3$ (Merck) with TMS as an internal standard. Infrared spectra were taken on a Nicolet 510 FTIR in $CHCl_3$ solution. Mass spectra were obtained with a Fisons Instruments VG-Platform Benchtop LC–MS (negative ion electrospray mass spectra (ES^-) MS; flow injection analysis in MeOH of samples in MeOH/MeONa). Melting points (uncorrected) were obtained in sealed evacuated capillaries.

Compound **6** was prepared according to the one-pot procedure reported.[11] Xylene was from Carlo Erba or from Merck. TCE (**CAUTION**: very toxic) was either from Aldrich or from Fluka. Column chromatography was carried out on 230–400 mesh silica gel (Merck).

Both in the analytical and in the preparative runs the reactant and solvent mixtures were nitrogen flushed and a nitrogen atmosphere was maintained while heating.

4.1. Analytical dehydration runs

Analytical dehydration runs were carried out in a 10 mL two necked flask fitted with a condenser and with a Teflon coated septum. In a typical run TCE (2 mL) was added to a mixture of **6** (745 mg, 2.00 mmol) and *p-tert*-butylcalix[4]arene (30.0 mg, 0.0462 mmol; internal standard). Samples taken at varying times were ^{1}H NMR analysed after rapid solvent removal. The areas of several ArOH signals and in suitable cases simply their heights, were assumed to be proportional to their concentrations. The signal at δ=8.43 of compound **10** is markedly broader than the other ArOH signals at the temperature of 298 K at which the spectra were taken.

Decomposition runs were carried out by adaptation of the above analytical technique. In a typical run, **9** (24.15 mg, 0.0170 mmol) and *p-tert*-butylcalix[4]arene (6.49 mg, 0.0100 mmol) were heated in TCE (2.5 mL) and samples of about 80 μL were taken at varying times and analysed as before.

4.2. Preparative dehydration runs

A mixture of **6** (10.0 g, 26.8 mmol) and TCE (27 mL) was heated at 120°C and magnetically stirred for 310 min. Heating never exceeded 50°C during the following work-up. TCE was completely removed under vacuum; xylene (100 mL) was added to the residue and the mixture was heated and stirred so that most solid dissolved. Xylene was partly (55 mL) removed under vacuum and the mixture was cooled in an ice-water bath for 30 min and filtered to give **3** (3.78 g, 39.8% yield), more than 99% pure by ^{1}H NMR. Xylene was almost completely removed from the filtrate, acetone was gradually added up to 50 mL while stirring and the solution was left to stand overnight. Filtration of the crystallized material gave 1.5 g of a 4:1 mixture of **8** and **10** according to ^{1}H NMR. The latter compounds could be easily separated by column chromatography (eluent:toluene) to give pure **8** (990 mg, 10.4% yield) and **10** (260 mg, 2.8% yield). Acetone was partly evaporated from the above filtrate and to the residue (12 mL) methanol (25 mL) was gradually added while heating and stirring. At room temperature a precipitate formed (320 mg) that was recrystallised from chloroform–methanol to give **9** (250 mg, 2.6% yield). Column chromatography (eluent: chloroform or toluene) could not effectively separate the small quantities of large homooxacalixarenes in the residue of the above acetone–methanol filtrate, while a small sample of pure **2** was nevertheless obtained.

In the preparative run carried out in xylene at 120°C, heating was stopped after 200 min. Further xylene was added (75 mL), the mixture was heated and stirred, then work-up continued as before. The yields were as follows: **3**, 38.3%; **8**, 10.0%; **10**, 3.1%; **9**, 2.5%.

4.2.1. 7,13,21,27,35,41-hexa-*tert*-Butyl-43,44,45,46,47,48-hexahydroxy-2,3,16,17,30,31-hexahomo-3,17,31-trioxacalix[6]arene (8). White solid, mp 184–186°C; MS (ES^-) *m/z* 1062 $[M-H]^-$ (100), 1084 $[M-2H+Na]^-$ (50); IR: ν_{max} 3330, 2960, 2900, 2870, 1490, 1360 and 1070 cm^{-1}; ^{1}H NMR: δ 1.23 (s, 54H), 4.01(s, 6H), 4.63 (s, 12H), 6.95, (d, *J*=2.4 Hz, 6H), 7.26 (d, *J*=2.4 Hz, 6H), 8.75 (s, 6H); ^{13}C NMR: δ 31.2, 31.5, 33.9, 71.4, 123.4, 124.8, 127.6, 128.1, 143.0, 150.2. Anal. Calcd for $C_{69}H_{90}O_9$: C, 77.93; H, 8.53. Found: C, 77.76; H, 8.84.

4.2.2. 7,13,21,27,35,41,49,55-octa-*tert*-Butyl-57,58,59,60,61,62,63,64-octahydroxy-2,3,16,17,30,31,44,45-octahomo-3,17,31,45-tetraoxacalix[8]arene (9). White solid, mp 224–226°C; MS (ES^-) *m/z* 1438 $[M-2H+Na]^-$ (100), 1470 $[M-H+Na+MeO]^-$ (90); IR: ν_{max} 3330, 2960, 2900, 2870, 1490, 1360 and 1070 cm^{-1}; ^{1}H NMR: δ 1.22 (s, 72H), 4.03 (s, 8H), 4.62 (s, 16H), 6.92 (d, *J*=2.2 Hz, 8H), 7.23 (d, *J*=2.2 Hz, 8H), 9.05 (s, 8H); ^{13}C NMR: δ 31.4, 31.5, 33.9, 71.5, 123.3, 124.5, 127.6, 127.8, 142.7, 150.5. Anal. Calcd for $C_{92}H_{120}O_{12}$: C, 77.93; H, 8.53. Found: C, 77.64; H, 8.76.

4.2.3. 7,13,21,27,33,39-hexa-*tert*-Butyl-41,42,43,44,45,46-hexahydroxy-2,3,16,17-tetrahomo-3,17-dioxacalix[6]arene (10). White solid, mp 221–223°C, (frothing); MS (ES^-) *m/z* 1054 $[M-2H+Na]^-$ (58), 1076 $[M-3H+2Na]^-$ (48), 515.5 $[M-2H]^{2-}$ (100); IR: ν_{max}

3220–3330 flat, 2960, 2900, 2870, 1490, 1360 and 1070 cm^{-1}; ^1H NMR: δ 1.24 (s, 18H), 1.25 (s, 18H), 1.26 (s, 18H), 3.80–4.15 (br, 8H), 4.66 (br s, 8H), 6.97 (d, J= 2.4 Hz, 2H), 7.00 (d, J=2.4 Hz, 2H), 7.17 (app.s, 4H), 7.25 (d, J=2.4 Hz, 2H), 7.34 (d, J=2.4 Hz, 2H), 8.43 (s, 2H), 9.34 (s, 2H), 10.14 (s, 2H); ^{13}C NMR: δ 31.1, 31.5, 31.5, 32.1, 32.8, 33.9, 34.0, 71.6, 71.7, 123.2, 123.6, 124.5, 125.4, 125.8, 127.6, 127.7, 127.9, 128.0, 128.0, 128.5, 143.2, 144.3, 147.0, 150.1, 150.4. Anal. Calcd for $C_{68}H_{88}O_8$: C, 79.03; H, 8.58. Found: C, 78.68; H, 8.86.

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