Downloaded from orbit.dtu.dk on: May 03, 2019

DTU Library

Synthesis and structure of functional organic molecules: Calix[4]arenes, Trioxatriangulenes and Helicenes

Faldt, André

Publication date:
2000

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Faldt, A. (2000). Synthesis and structure of functional organic molecules: Calix[4]arenes, Trioxatriangulenes and Helicenes. Roskilde: Risø National Laboratory. Denmark. Forskningscenter Risoe. Risoe-R, No. 1148(EN)

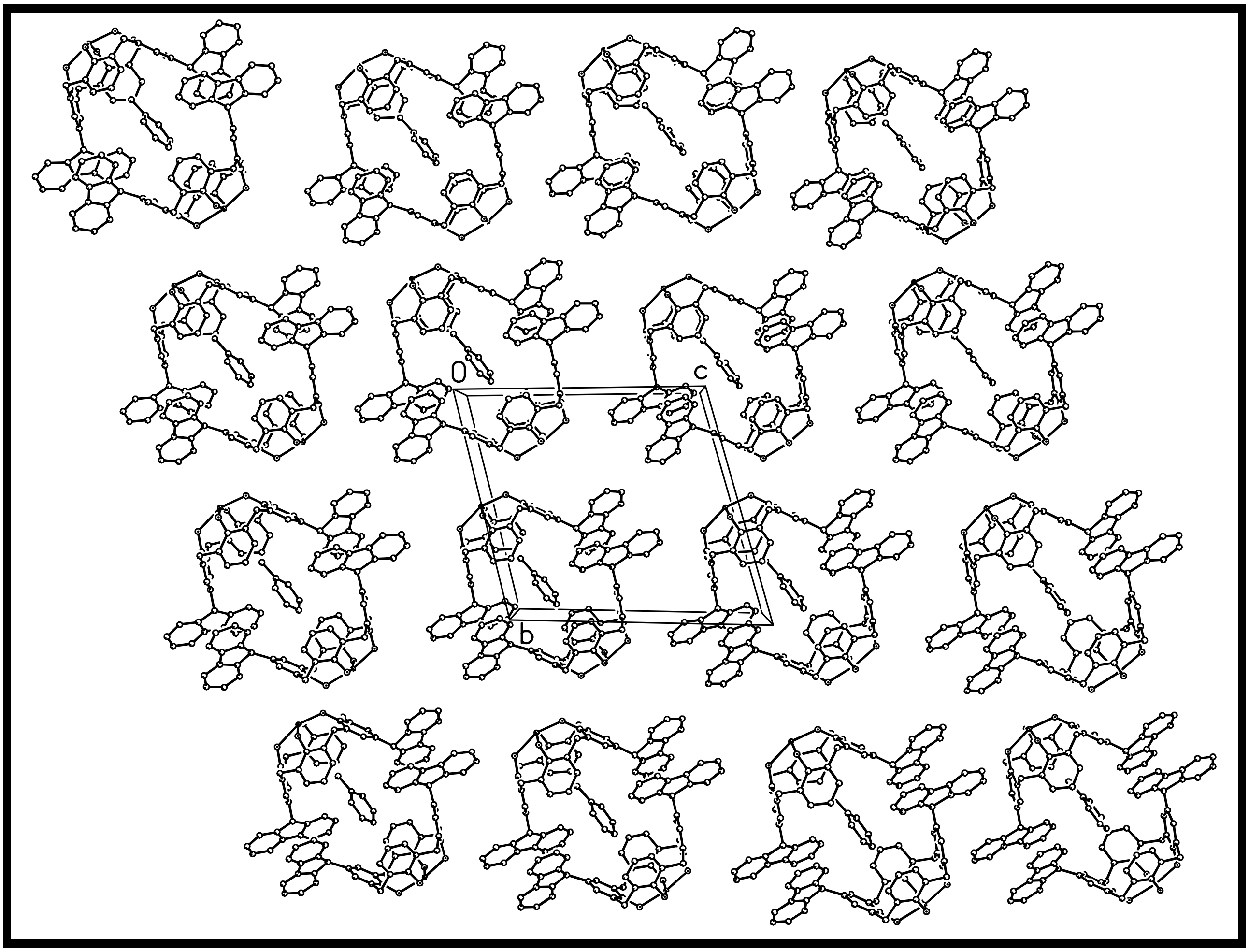
General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Synthesis and structure of functional organic molecules:

Calix[4]arenes, Trioxatriangulenes and Helicenes



Ph.D. Thesis

André Faldt

Risø National Laboratory

and
Department of Chemistry, University of Southern Denmark

February 2000

Abstract: This Ph.D. thesis describes the synthesis and structure of a series of organic and metalorganic molecules. The idea of the project was to combine the supramolecular properties of calix[4]arenes with the catalytic properties of a metallocene. This was attempted by substitution at the *upper rim* of the calix[4]arene with a metallocene. It proved however not possible to combine these two moieties. It was possible to substitute the *upper rim* of calix[4]arene with two fluorenyl moieties and it was found by X-ray crystallography that the formation of a pentachloro zirconate tetrahydrofuran complex was obtained instead of the expected calix[4]arene metallocene. By NMR and MALDI-TOF analysis it was proven that the transition metal tetrahalides are strong enough as Lewis acids to endorse the cleavage of one or more of the propoxy groups present at the *lower rim* of the calix[4]arene. The anionic polymerization of styrene was investigated as a function of addition of crown-ethers and tetrapropoxy-calix[4]arene and it was found the addition of crown-ethers strongly increased the reaction rate in the polymerization. In addition work is presented regarding the synthesis of 2,6,10-tris(*tert*-butyl)trioxatriangulene derivatised at the 12c-position and the synthesis of 7,8-dioxa[6]helicene together with structural discussions originating from the X-ray structures.

Resumé: Denne Ph.D. afhandling beskriver syntesen og de strukturelle egenskaber af en række organiske og metal-organiske molekyler. Ideen bag projektet var at kombinere de supramolekylære egenskaber af calix[4]arener med de katalytiske egenskaber af metallocener. Dette blev forsøgt ved at substituere *upper rim* af calix[4]aren med en metallocen. Det blev dog vist at det ikke var muligt at kombinere disse egenskaber. Det var muligt at substituere *upper rim* af calix[4]aren med to fluorenyl grupper og ved røntgen krystallografi blev det vist, at dannelsen af et pentachlor zirconate tetrahydrofuran kompleks fandt sted fremfor dannelsen af en calix[4]aren metallocen. Ved NMR og MALDI-TOF blev det bevist, at overgangsmetal tetrahalogenider er tilstrækkelige stærke Lewis syrer til at kløvning af en eller flere af *lower rim* propoxy grupperne på calix[4]aren fandt sted. Anionisk polymerisation af styrene blev undersøgt som funktion af tilsætningen af crown-ethere eller calix[4]aren, hvor det blev fundet at denne tilsætning kraftigt forøgede polymerisations hastigheden. Yderligere er syntesen af 2,6,10-tris(*tert*-butyl)trioxatriangulen derivatiseret i 12c-positionen og 7,8-dioxa[6]helicen præsenteret sammen med de strukturelle egenskaber for disse diskuteret.

ISBN 87-550-2627-3
ISBN 87-550-2628-1 (Internet)
ISSN 0106-2840

Print: Information Service Department, Risø, 2000

Acknowledgement

This thesis describes my work within the area of organic chemistry and supramolecular chemistry, in partial fulfillment to obtain the Danish Ph.D. degree in chemistry. The work has been carried out at Risø National Laboratory from February 1997 to February 2000.

The work was financed by Risø National Laboratory. Several people have served as my supervisors during this project and to all of those I am very grateful. First of all people I would like to thank the perfect supervisor Dr. Mikkel Jørgensen without his encouragement this project would never have been what it is. Always ready and enthusiastic with guidance and many fruitful discussions. He also deserves a special thank for helping with some of the NMR experiments presented in this thesis. Dr. Kristoffer Almdal has also served as my supervisor within the field of polymer chemistry and he also deserves a special place in this acknowledgement. Docent Jan Becher and Dr. Christine McKenzie from Department of Chemistry, University of Southern Denmark, is to be acknowledge for their help with some of the bureaucratic formalities and discussions more related to the project for which I am grateful.

Dr. Frederik C. Krebs has helped invaluable with solving the X-ray structures presented in this thesis and for this I am very grateful.

I would like to than all the wonderful people in FYS-124 for making the three years a memorable period of my life.

Finally, I thank my wonderful wife and two children for their support during this period recognizing that I owe them some of the time spend in the laboratory. Thank you.

Preface

The idea starting this project was to combine the supramolecular properties of calix[4]arenes with the catalytic properties of metallocenes. This should be done by substituting the calix[4]arene at the *upper rim* with a metallocene and therefore is the main work within the field of organic synthesis. Unfortunately it proved impossible for me to achieve the ultimate goal but as the reader will find: “If it was easy everybody would be doing it”. The thesis is divided in three chapters, the first dedicated to polymers, the second to calix[4]arenes and the third is treating two smaller project that I have spend time working with during this Ph.D. The work presented here has resulted in five publications, which all are included in *Appendix*.

The *Experimental* section describes the synthesis of 90 compounds used during this project and the indexing used in the three chapters is consistent with that found in the *Experimental* section. When a compound is indexed using a number followed by a letter this means that the compound can then not be found in the *Experimental* section. In the case of polymers only polystyrene has been prepared and they are indexed using **PS** followed by a number, fx **PS1**.

1 Catalysts for polymerization

This chapter is divided into five parts where the first part is presenting the original idea starting this Ph.D.-project. The second part presents some of the fundamental knowledge of polymers and the third part include some of the basics about Ziegler-Natta and metallocene catalysts and the special features the resulting polymers have. The fourth part is presenting the synthetic target molecules and those that were possible to synthesise and finally the fifth part is dedicated to the polymerization of styrene using crown-ethers and metallocenes as catalysts.

1.1 Introduction – The project

The initial idea giving rise to this Ph.D.-project was to combine the supramolecular capabilities of calix[4]arenes with a catalytic group like a metallocene situated at the *upper rim* of the calix[4]arene, see ***Figure 1.1***. This is reminiscent of the enzymes where a pocket holds the substrate in a specific geometry while other functional groups perform a reaction on the substrate.

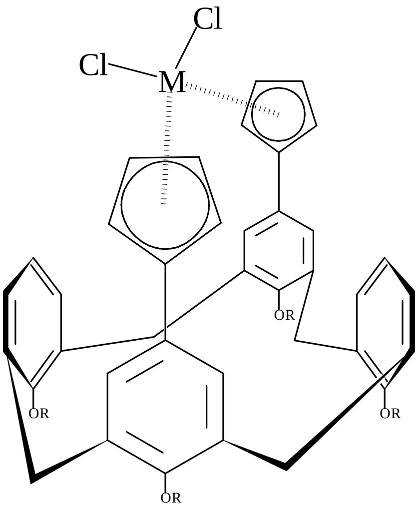


Figure 1.1. Drawing illustrating the initial idea of using calix[4]arene as template for a metallocene at the upper rim, M= Ti, Zr or Hf.

Applying this to a polymerization reaction it was envisaged that the calixarene part could serve to hold the monomer in a well-defined geometry relative to the attached metallocene catalytic site thereby controlling the tacticity of the polymeric reaction product.

While this idea was perhaps aesthetically appealing it was also rather naïve as will be apparent. The following chapter is therefore an account of the rather large number of unsuccessful attempts at reaching the desired goal: a metallocene on top of a calix[4]arene.

1.2 General polymer concepts

In our daily life we encounter polymers several times each day or even each hour often without giving it a thought. Polymers or plastics are used so many places due to several reasons such as low cost, high performance, the ability to serve in very specialized functions and long durability. One of the first polymers that was used commercially was Bakelite, made by condensation of phenol and formaldehyde, which has a relatively high thermal resistance and stiffness but unfortunately it also has a high tendency to crack if sudden stress is applied. Since then the polymer industry has expanded tremendously and the development of new polymeric materials are still finding new areas of uses where polymers often replaces other materials. Another aspect that has come to mind during the last two decades is the environmental concern about our future. Several companies have developed catalysts that are capable to crack polyethylene to lower oligomeric compounds and thereby recycling the polymeric materials.

1.2.1 Basic definitions

Polymers are macromolecules comprising of smaller repeating units or monomers where the properties of the monomeric species are projected into the properties of the polymer. Since not only the monomer have influence on the final properties but these also depend on the micro- and macro structure of the polymeric chain, a given property can be obtained by adjusting the molecular weight or the degree of branching amongst other.

All the polymers in this thesis are linear homopolymers, meaning a chain made up of identical units (except the end groups) arranged in a linear sequence. A highly commercially used linear homopolymer is polyethylene (denoted PE) having a very high molecular weight giving n high values, see ***Figure 1.2***.

$$—(CH_2CH_2)_n—$$

If M_W= 500000 g/mol
then n is around 178000.

Figure 1.2. Repeating unit in linear polyethylene (PE).

The PE synthesized at the beginning was polymerized by radical initiation under high pressure and high temperature (P > 1000 bar and T > 200 °C) and as is usually the case with free radical polymerization processes the PE produced was highly branched and not linear as shown in ***Figure 1.2***. Even though the difference in chemical structure between linear and branched PE may appear small and localized to the units forming the branch points, it have a profound effect on the properties of the PE. The linear chains can pack in a regular three-dimensional fashion, forming a crystalline phase; while the branched chains incapable of this regular packing forms an amorphous phase. Depending on the degree of branching the PE in question will have a crystallinity between the two above-mentioned extremes, e.g. crystalline domains together with some amorphous domains. The regular arrangement, and therefor the tighter packing of the chains in the crystalline domains, produces high density PE (denoted HDPE) while slightly disordered arrangements produces low density PE (denoted LDPE). Properties such as stiffness, strength (e.g. rheologically properties) and optical clarity are strongly affected by the changes in crystallinity, and since the consumers often demand high optical clarity combined with high stiffness and strength, the highly amorphous polymers are not attracting much attention from the polymeric industry. Another way of looking at branched polymers is treating them like copolymers, where the main chain ($-CH_2CHR$; where R = methyl, ethyl etc.) is made up of one monomer and the R group is made of another monomer. Then PE is described as a copolymer from ethylene and other α-olefins. A commercial available polymer confusingly called linear low-density polyethylene (LLDPE) is actually synthesized from low pressure Ziegler-Natta catalysis of ethylene and butylene. The degree of branching gives these polymer properties resembling the “normal” LDPE but the short chain branching units are incorporated by deliberate copolymerization of a second comonomer.

Assuming, for simplicity[*], that during the polymerization the vinyl monomer always add head to tail, which are normal for propylene and styrene, the polymer chain will have a microstructure that is described in terms of tacticity (Greek *taktikos* meaning order), see ***Figure 1.3***. If the substituent X placed on every second carbon atom is being other than hydrogen introduction of chirality takes place and the substituent can then by placed either on the same side of the carbon chain as its neighbor or on the opposite side.

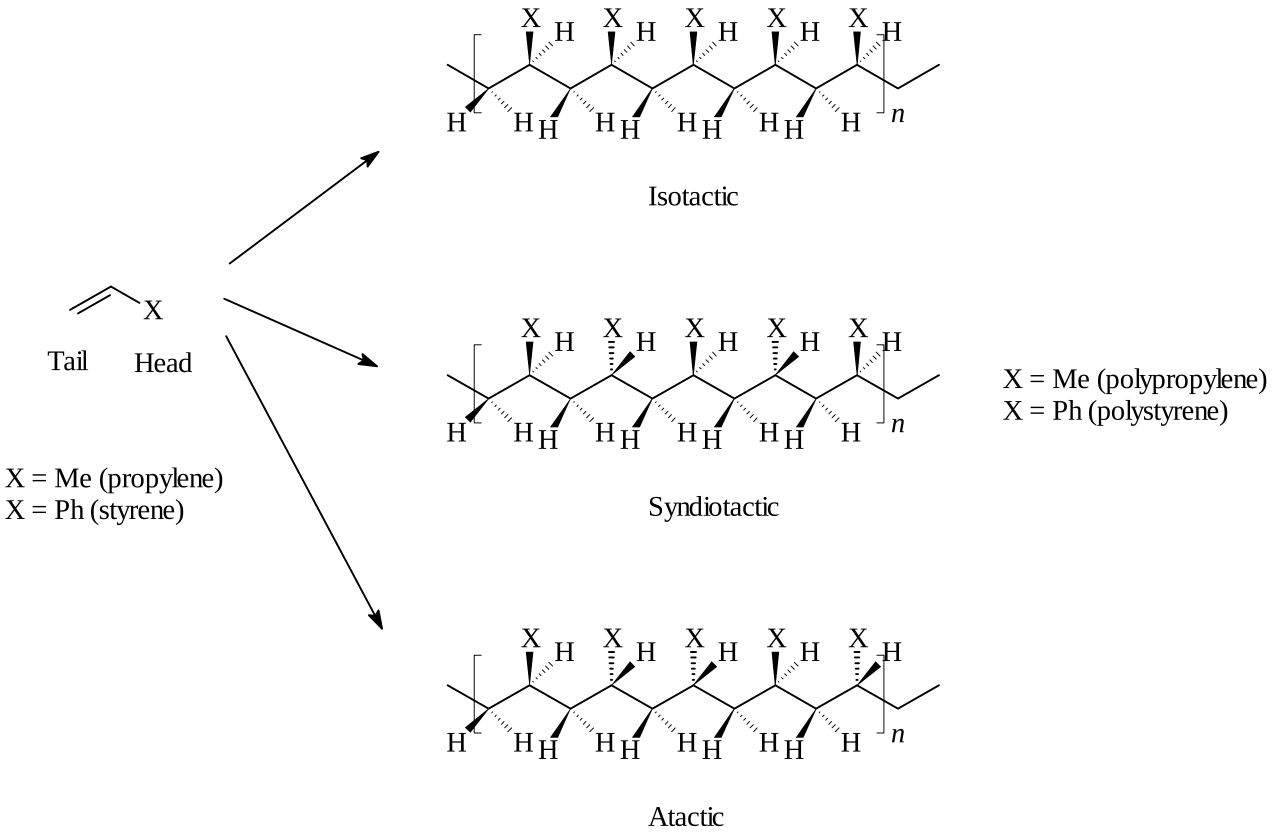


Figure 1.3. Stereoisomerism for vinyl polymerization of a prochiral monomer. The polymer chain is stretched for clarity.

If placed on the same side the X group become *meso* to the preceding X group and the polymer is called *isotactic*. On the other hand if the incorporation of the monomer happens in a manner such that each X group is opposite of each other, the polymer is called *syndiotactic*. When no preferred

---

[*] This tacticity is also present when the addition not is head to tail, but since propylene and styrene are the only two prochiral monomers used in this work there will not be any further notice on the other possibilities.

orientation of the monomer take place, the resulting polymer become *atactic* meaning that the X groups adjacent to each other are randomly placed on each side of the growing carbon chain. In real life the polymer chains are not stretched as shown above and in the case of isotactic polypropylene (denoted PP) the chains are folded into helical conformations. The, for some people often encountered, plastic beer glasses are made of atactic polystyrene (denoted PS).

The most important factor determining polymer properties is the chain length of the polymer, or the molecular weight and its distribution. The molecular weight of a polymer differs from a "normal" low-molecular weight molecule by the fact that the molecular weight of the polymer is not one specific number but a distribution of molecular weights around some mean value. The polymer has what is called a *molecular weight distribution* resulting in different molecular weight *averages*. The two most common averages used are the *number average molecular weight* (M_n) and the *weight average molecular weight* (M_w), defined by **Equation 1.1** and **Equation 1.2**. M_x is the molecular weight of a given polymer chain consisting of x monomer units having molecular weight M_0 (i.e. $M_x = x \cdot M_0$), N_x and W_x is the mole fraction ($N_x = n_x/\sum n_x$) and the weight fraction ($W_x = w_x/\sum w_x$) respectively connected with M_x.

$$M_n = \sum N_x M_x$$

Equation 1.1

$$M_w = \sum W_x M_x$$

Equation 1.2

From *size exclusion chromatography/gel permeation chromatography* (SEC/GPC) is it possible to obtain the values for M_n and M_w and the ratio between M_w and M_n gives what is called the *polydispersity*, by using ***Equation 1.3***.

$$P = \frac{M_w}{M_n}$$

Equation 1.3

The polydispersity becomes essentially a measure of the relative spread in molecular weights in a polymer. If a sample is monodisperse, M_w and M_n being equal, all polymer chains have the same length (or weight), but most commercial polyolefins have broad distributions often around 5-10.
The statistical method used in describing the origin of polydispersity for a living polymerization is a Poisson distribution, see ***Equation 1.4*** where x is chain length

$$P = 1 + \frac{x-1}{x^2} \approx 1 + x^{-1} \qquad x \text{ being large}$$

Equation 1.4

This type of distribution is also used for predicting how many cars that will arrive at a given point (or time-interval), for example predicting the peak hours at a border when vacation begins for a large number of people. One can also see that ***Equation 1.4*** is too simple a model since already for x= 100 result in a P= 1.01 which is a very narrow dispersity. When treating polymer systems this way some assumptions has been made[1], in order to reproduce some of the very narrow dispersities observed in some polymerization reactions:

- No termination or transfer during chain growth
- The initiation step is at least as rapid as the propagation step
- All the monomer molecules have equal probability of reacting (perfect mixing)

These applies for anionic addition polymerization of ethylene oxide initiated with sodium alkoxides and other polymerization systems (vinyl polymers) capable of producing narrow dispersities. In any case the distribution assumes a Poisson form. In practice when the two first conditions can be obtained the last however is often difficult to achieve.

---

[1] Flory, P. J., *J. Am. Chem. Soc.*, 1940, **62**, 1561

1.2.2 Addition-condensation polymerizations

Traditionally one can classify polymerization reactions by use of the addition-condensation system. Briefly speaking addition polymerization is reactions where the entire monomer molecule becomes part of the polymer while in condensation polymerization reactions some atoms of the monomer molecule lacks in the polymer and becomes a *condensate*, typically water or hydrochloric acid. An example of an addition and a condensation polymerization could be polyethylene and Nylon-66 (a polyamide) respectively, see ***Figure 1.4***.

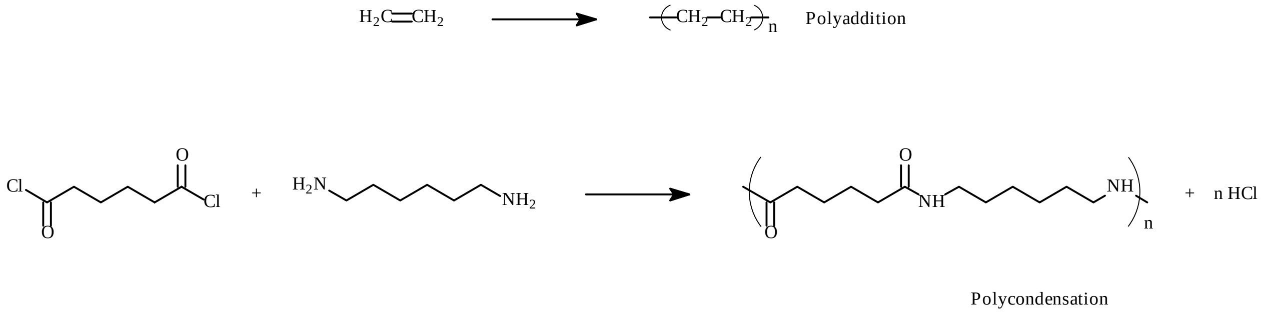


Figure 1.4. Addition-condensation polymerization, upper part is polyaddition of ethylene into polyethylene and lower part is polycondensation of adipoyl chloride and hexamethylene diamine producing Nylon 66.

When the monomers are added successively to a growing chain, initiated by some reactive species, the reaction is called chain addition polymerization. The initiator can be a radical, electrophile or nucleophile, which will then subdivide the polymerization into radical, cationic or anionic polymerization. Radical and cationic polymerization will not be mentioned any further other than to say that the initiators used include hydrogenperoxide, benzoylperoxide and *tert*-butylperoxide, or strong Lewis acids like BF_3 in the later case. The resulting polymers often have very broad polydispersities (8-10 is not uncommon) together with a high degree of branching points especially in the case of radical polymerization.

1.2.2.1 Anionic polymerization

The anionic polymerization of styrene is another good example of a chain addition polymerization, see ***Figure 1.5***, where the initiator could be *n*-BuLi but also potassium amide and sodium has been used. Normally the reaction is performed in non-polar solvents such as benzene, toluene or cyclohexane with *sec*-BuLi as initiator at a temperature about 50 °C while in this thesis only *n*-BuLi has been used. The difference between *sec*-BuLi and *n*-BuLi lies mostly in the initiation rate, the former being the fastest.

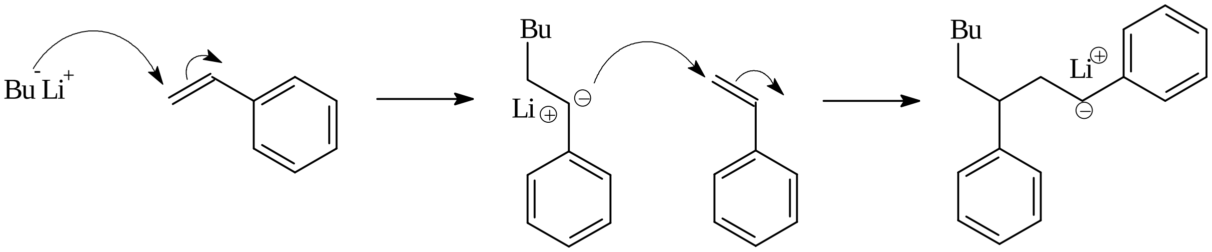


Figure 1.5. Anionic polymerization of styrene initiated by n-BuLi.

One of the most important features of anionic polymerization is that in the case of styrene (and others) there are no chain termination processes involved making the polymerization *living*. As seen in ***Figure 1.5*** the anionic polymerization of styrene (and other vinyl olefins) is living in the sense that the growing chain only reacts with monomers. This feature accounts also for the preparation of true block copolymers by sequential addition of different monomers to the living polymer. This combined with the possibility of predicting the molecular weight by simple stoichiometry (the ratio between initiator and monomer). The very narrow molecular weight distributions these polymerizations can be optimized to have, makes this type of polymerization very useful for the synthesis of tailor-made homopolymers and block copolymers.

In this section anionic polymerization of styrene will be considered and only briefly. The initiators most often used are alkyl lithium bases were the reactivity follows *sec*-BuLi > *n*-BuLi >> *tert*-BuLi and for non-polar hydrocarbon solvents the order is toluene > benzene > cyclohexane. In the case of initiators the reactivity is not following the strength in pK_B as might have been expected but is also influenced by the solvent.

The solvent influences the degree of association so the total reactivity in a given system is very complicated and still not fully understood. Addition of a polar aprotic solvent (fx THF) will increase the reactivity tremendously[*] but also reaction between solvent and the alkyl lithium initiator at the normal temperatures used (RT or above) must be considered, e.g. reaction between THF and *n*-BuLi is fast at room temperature.

The propagation reaction also depends on solvent, temperature, and the nature of the counterion introduced by the initiator, and monomer concentration. Thus making ***Figure 1.5*** a very simplified reaction scheme since association of the growing chain end with counterion or other growing chain ends is not taken into consideration.

1.2.2.2 Organometallic catalysts polymerization

Even though many consider the polymerization of vinyl olefins using organometallic catalysts, e.g. metallocenes or Ziegler-Natta catalysts, as being an anionic addition polymerization reaction this is not correct. The anionic mechanism applies to those chain addition polymerizations in which the growing chain end has a negative charge (real or formal) these being initiated by bases. But even though the chain end also contains a cation this can not be compared to the metallic cation arising from a metallocene (see ***Figure 1.6*** and ***Figure 1.18***) which after insertion of the monomer, places the positive charge on the growing chain in one of the resonance structures available.

The high reactivity of the cocatalyst necessary in the polymerization using Ziegler-Natta or metallocene catalysts, e.g. MAO (Methylaluminoxane) requires that the solvent used is aprotic and nonpolar, typically toluene or benzene is used. When the monomer used is propylene (or ethylene) it is often used in *bulk* which means that high-pressure reaction containers must be used since propylene has a rather high vapor-pressure at 50-70 °C (P = 10-30 bar[2]) which is the normal temperature-range used in the polymerization. Therefore styrene was the monomer of choice in this project.

The polymers obtained from these catalysts have narrow molecular weight distributions, often found *P*= 1.5-2.5, and very few branching points.

---

[*] THF can be used at –78 °C but then drop-wise addition of styrene is necessary

[2] Yaws, C.L.; *Chemical Engineering*, 1975, **31**, 101

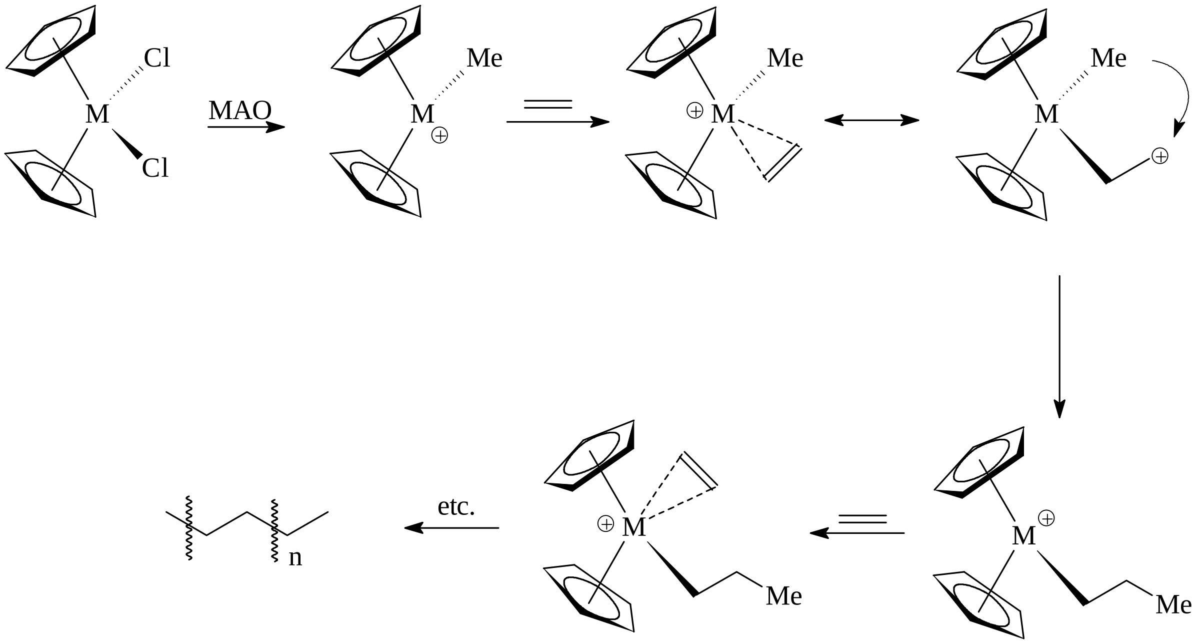


Figure 1.6. Mechanism for the polymerization of ethene using the Cp_2MCl_2/MAO system, M= Ti, Zr or Hf.

1.2.2.3 Termination processes

Unlike anionic polymerization of styrene the organometallic catalysts polymerization has several ways of terminating the chain growth[3,4,5,6]. One of the most dominant is the β-hydride elimination process amongst other pictured in ***Figure 1.7***.

Normally the β-hydride elimination (b) is a very favorable process in transition metal chemistry and has also been found to be the main reason for termination of chain propagation in metallocene and Ziegler-Natta catalyzed polymerizations. The metal atoms used in these systems are titanium, zirconium or hafnium (mostly zirconium) being high-valent early transition metals (oxidation step IV) they lack the *d* electrons necessary for donating electron density into the σ^* orbital located at

---

[3] Negishi, E-I, Kondakov, D.Y., Choueiry, D., Kasai, K., Takahashi, T.; *J. Am. Chem. Soc.*, 1996, **118**, 9577

[4] Leclerc, M.K., Brintzinger, H.H.; *J. Am. Chem. Soc.*, 1996, **118**, 9024

[5] Grubbs, R.H., Coates, G.W.; *Acc. Chem. Res.*, 1996, **29**, 85

[6] Resconi, L., Piemontesi, F., Franciscono, G., Abis, L., Fiorani, T.; *J. Am. Chem. Soc.*, 1992, **114**, 1025

the β C-H bond. The β-hydride elimination is therefore slow when using these catalysts. A good example is the *Schwartz's* reagent[7] (Cp_2ZrHCl) which readily reacts with 1-olefins to give the corresponding alkyl zirconium complex, that is very stable, and from which no β-hydride elimination takes place.

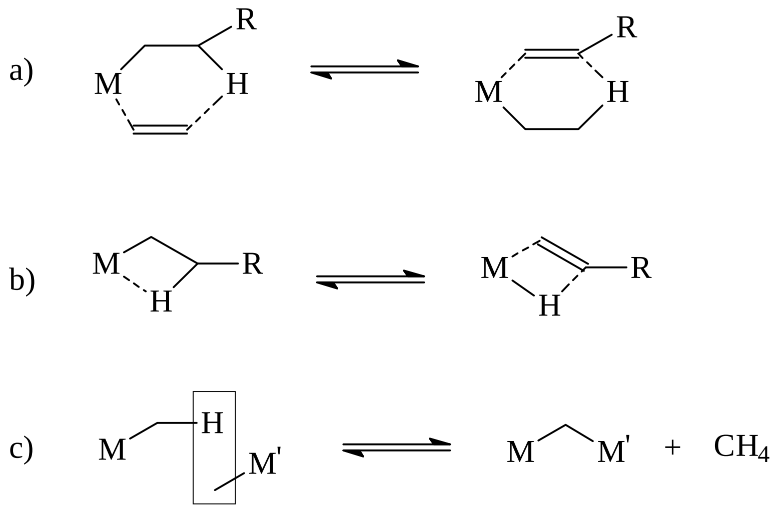


Figure 1.7. Chain termination processes, a) olefin transition, b) β-hydride elimination, c) α-hydride transition.

The two other termination processes (e.g. a) and c) in ***Figure 1.7***) are not very common and is only shown in order to indicate how branching points happens to occur. The unsaturated product from the first process (e.g. a) can react with the metal center as a normal 1-olefin, undergoing 1,2-insertion reaction, and thereby producing a branching point in the polymer chain. This happens only rarely when considering Ziegler-Natta catalysts and metallocenes however.

1.2.3 Characterization of polymers

The ways to characterize polymers are many and often one has to combine several methods in order to get substantial knowledge about a synthesized polymer. The most important method of characterization is SEC/GPC that returns information about molecular weight and distribution, but can also give information about the polymeric microstructure by analyzing the asymmetry of the distribution, see ***Figure 1.8***.

---

[7] Schwartz, J., Labinger, J.A.; *Angew. Chem. Int. Ed. Eng.*, 1976, **15**, 333

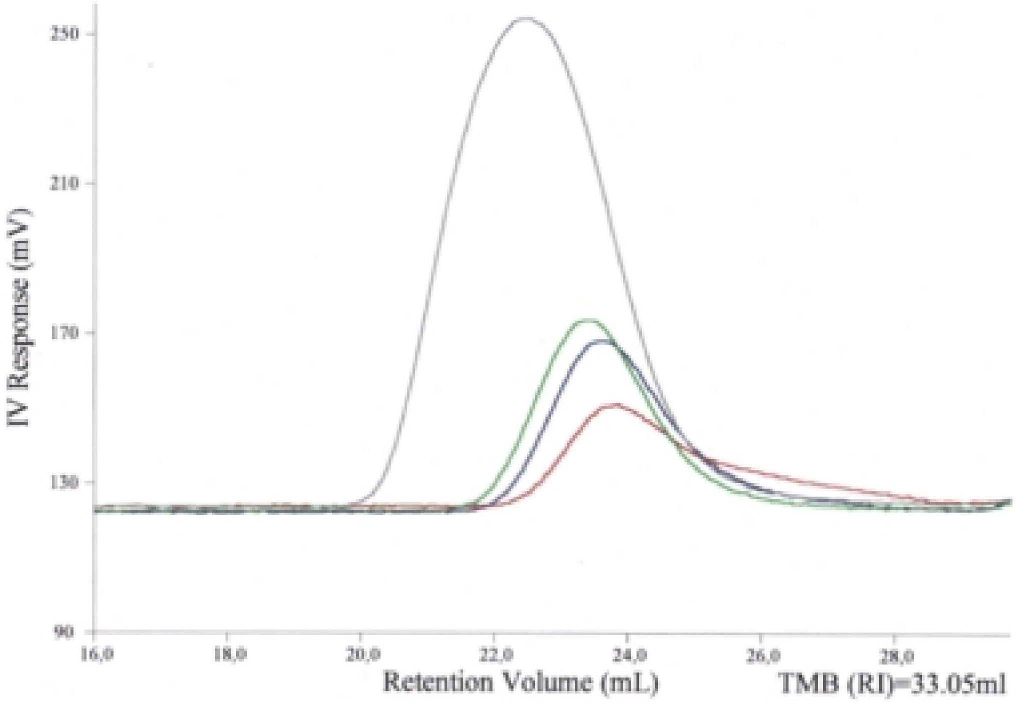
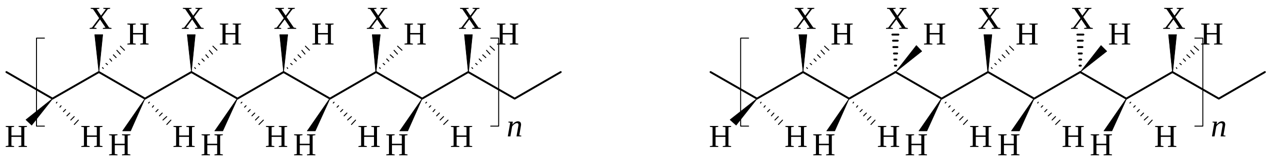


*Figure 1.8. SEC/GPC of polystyrene made by anionic and metallocene polymerization (**PS10**, M_w= 297100 g/mol (gray), **PS18**, M_w=83400 g/mol (blue), **PS19**, M_w= 42800 g/mol (red) and **PS20**, M_w= 127900 g/mol (green)).*

Matrix Assisted Laser Desorption Ionization-Time Of Flight (MALDI-TOF) is also capable of giving the molecular weight and distribution but can in some cases be rather difficult to use due to lack of adsorption of the polymer into the matrix. NMR is capable of giving structural information about the polymer but only to a limited extent due to signal broadening. Since the number of protons in a polymer chain quickly get very large the signals arising from branching and chain ends rapidly disappears in ^{1}H-NMR and in the case of ^{13}C-NMR the low sensitivity of this nucleus the signals from branching and chain ends often are absent. In the later case also the lack of relaxation mechanisms often lead to magnetic saturation of the carbon nucleus resulting in the absence of signals. Differential Scanning Calorimetry (DSC) returns the glass transition temperature and the melting point of the polymer; both can be used to elucidate the tacticity to some extent.

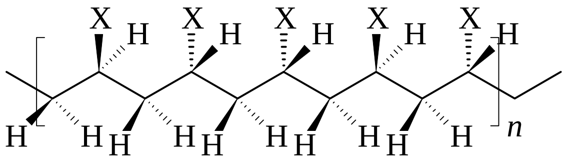
1.2.3.1 Nuclear Magnetic Resonance

As mentioned above is the elucidation of NMR spectra obtained from polymers not straightforward especially not when molecular weights become very high. Clearly the spectrum of HDPE is very simple no matter how large a molecular weight one has prepared. In the case of PP the complexity arises quickly and the same apply for polystyrene (PS). The broadening of the spectra is due to the fact that the sample consists of distributions both of molecular weights but also in structural entities. The NMR chemical shifts of protons depend on their magnetic environments which, in turn, depend on the conformations of the neighboring bonds and, thus, on the stereochemical constitution of the polymer chains. The nomenclature used describing the stereoregularity of a given polymer chain is pictured in ***Figure 1.9***.



mmmm
Isotactic

rrrr
Syndiotactic



rmrr
Atactic

Figure 1.9. The nomenclature describing the stereoregularity in a polymer chain, shown for a pentad. In the case of the atactic chain it should be taken into account that strictly speaking there is no repeating unit if truly atactic polymer chains are considered.

For a given proton in the polymer chain the magnetic environment is determined not only on the stereochemical character of the diad in which the proton is situated, but also in marked degree on the stereochemical character of the neighboring diads including second and third neighbors and even beyond. As a result, very complex ^{1}H as well as ^{13}C NMR spectra are obtained for PS (and other polymers) making it very difficult to interpret them completely[8,9,10,11]. A way to view this problem is to say that the amount of information obtained from the NMR spectra simply is too large, there are not at the present methods useful for deconvolution of the broad resonances especially in the ^{1}H NMR spectra. In the ^{13}C-NMR spectra it has been shown that the fine structure of the aromatic carbon resonances are sensitive to hexad and heptad stereosequence effects[12]. A detailed analysis of the methylene and phenyl C1 carbons of PS has been made by Sato and Tanaka[13] where they found the most important signal for determining stereoregularity is the phenyl C1 carbon signal. The approach was to prepare oligomers with the appropriate number of repeating units in order to justify the assumption that a given structural feature (fx. the C1 in a phenyl ring) was subjected to a similar chemical and magnetic environment as in the polymer. Comparison of the resonances found in the oligomers with those found in atactic PS allowed assignment. Comparing atactic, isotactic and syndiotactic PS[14] it was found that the spectrum of isotactic PS shows a single sharp peak at about 146.24 ppm (corresponding to the *mmmm* pentad), whereas in syndiotactic PS a single sharp peak at 145.13 ppm is due to a *rr* triad or *rrrr* pentad configuration, see ***Figure 1.11***. Atactic PS shows five main peaks in the range 145.12-146.17 ppm, corresponding to its various configurational sequences, see ***Figure 1.10*** and ***Table 1.1***.

Another approach is using GPC to separate PS into single oligomers and then subjecting the oligomers to multiple HPLC separations to obtain individual steric isomers[15,16,17]. This is though a very time consuming technique.

---

[8] Yoon, D.Y., Flory, P.J.; *Macromolecules*, 1977, **10**, 562

[9] Shepherd, L, Chen, T.K., Harwood, H.J.; *Polym. Bull.*, 1979, **1**, 445

[10] Segre, A.L., Ferruti, P., Toja, E., Danusso, F.;*Macromolecules*, 1969, **2**, 35

[11] Matsuzaki, K., Uryu, T., Osada, K., Kawamura, T.; *J. Polym. Sci., Part C*, 1974, **12**, 2873

[12] Chen, T.K., Gerken, T.A., Harwood, H.J.; *J. Polym. Bull.*, 1980, **2**, 37

[13] Sato, H., Tanaka, Y.; *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21**, 1667

[14] Ishihara, N., Seimiya, T., Kuramoto, M., Uoi, M.; *Macromolecules*, 1986, **19**, 2464

[15] Sato, H., Saito, K., Miyashita, K., Tanaka, Y.; *Makromol. Chem.*, 1981, **182**, 2259

[16] Tanaka, Y., Sato, H., Saito, K., Miyashita, K.; *Makromol. Chem. Rapid Commun.*, 1980, **1**, 551

[17] Sato, H., Tanaka, Y., Hatada, K.; *Makromol. Chem. Rapid Commun.*, 1982, **3**, 175

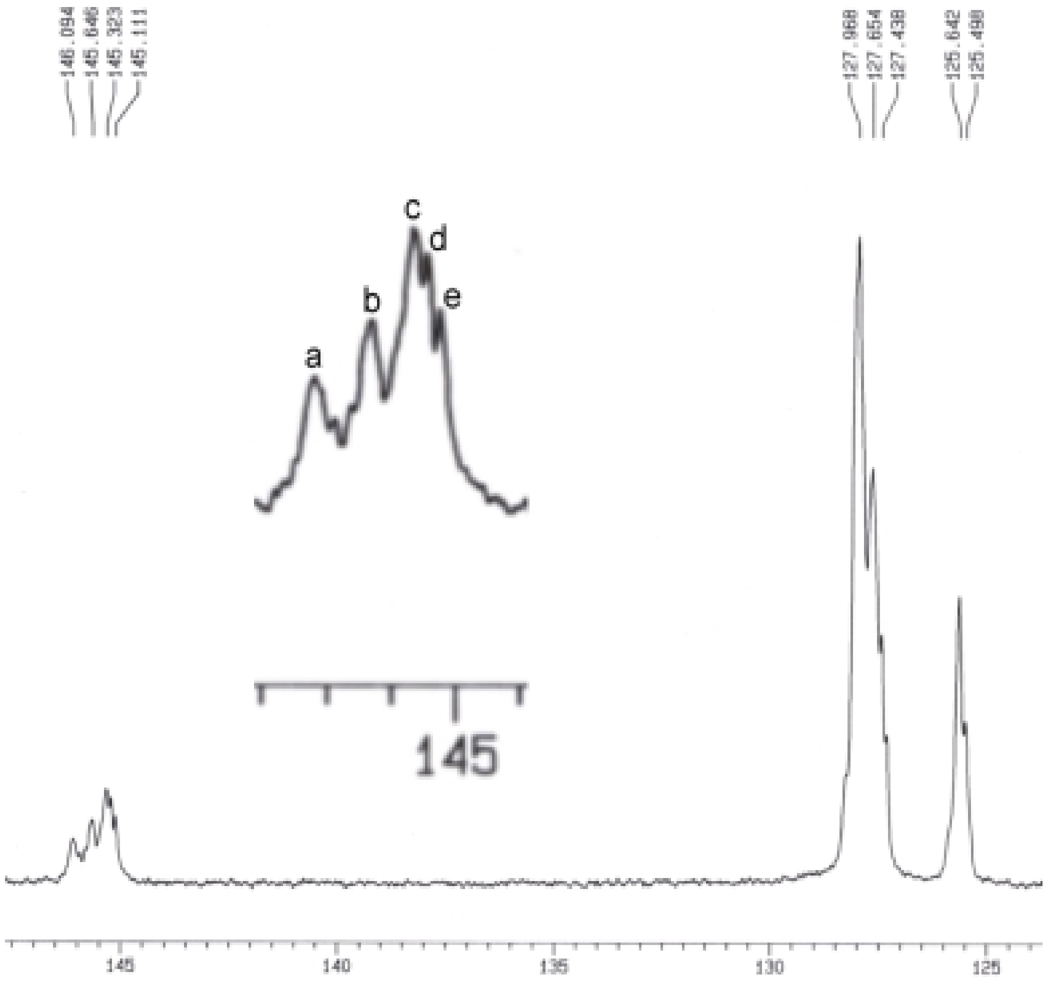


*Figure 1.10. ^{13}C-NMR spectrum of anionic polymerized atactic PS (**PS15**) in $CDCl_3$ at 300 K. Only the aromatic region shown. Insert shows the assignment of the C1 in the phenyl ring.*

Table 1.1. Assignment of C1 phenyl carbon signals measured in $CDCl_3$ at RT. The signal numbering refers to insert in Figure 1.10.

Signal	Chemical shift (ppm)	Assignment[14]
a	146.2-145.9	*mmmm* *mmmr*
b	145.9-145.5	*mmrr* *mmrm*
c	145.5-145.3	*rmmr* *rmrm* *rrmr*
d	145.2	*rrrm*
e	145.1-144.8	*rrrr* *mrrm*

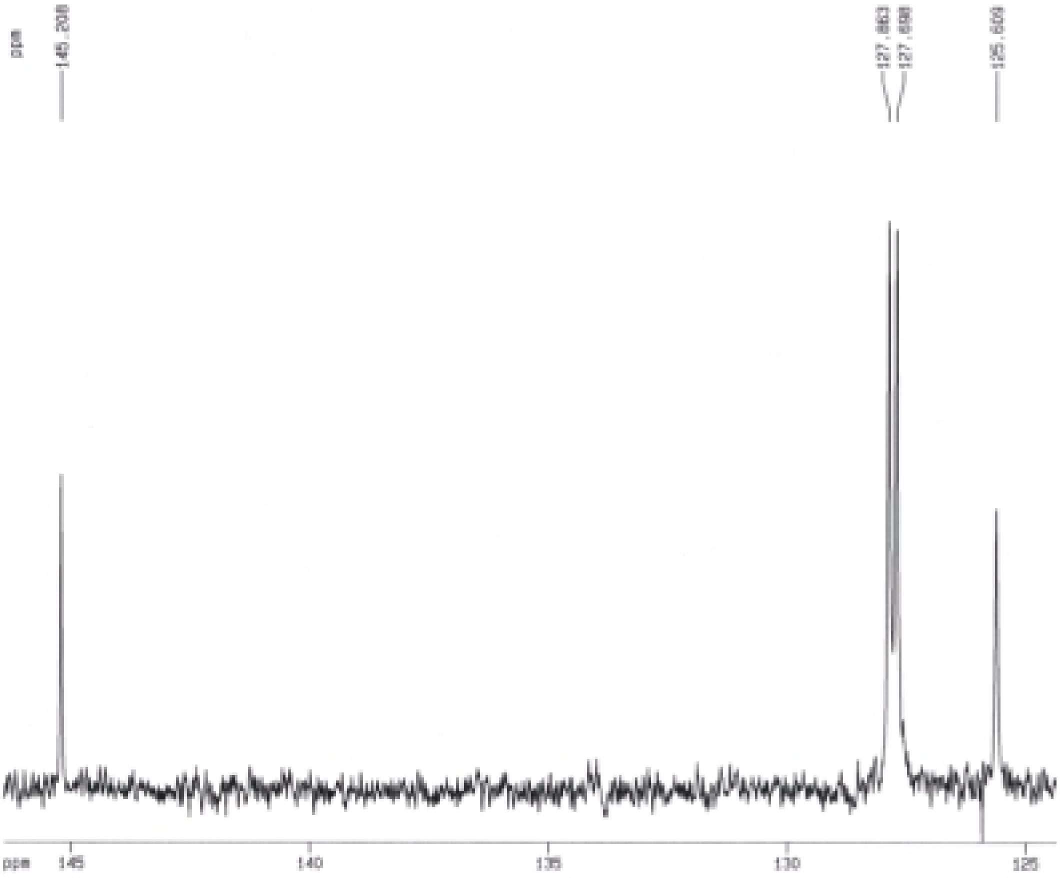


*Figure 1.11. ^{13}C-NMR spectrum of metallocene catalyzed syndiotactic PS (**PS20**) in $CDCl_3$ at 300K. Only aromatic region shown.*

Similarly has the tacticity of oligostyrenes been investigated using on-line HPLC/^{1}H-NMR[18] where a PS 530 (PS with average molecular weight of 530 g/mol) were separated into the pure oligomers (e.g. dimer and up to heptamers) followed by characterization by NMR.

As indicated by ***Figure 1.12*** and ***Figure 1.13*** the proton spectra in the former case lacks information useable for interpretation of the stereoregularity (other than to say this polymer is atactic). While in the later spectrum assigning spin-spin coupling constants is actually possible in the aromatic region (found to be 3.1 Hz) as well as in the aliphatic region (found to be 6.6 Hz).

---

[18] Pasch, H., Hiller, W., Haner, R.; *Polymer*, 1998, **39 (8-9)**, 1515

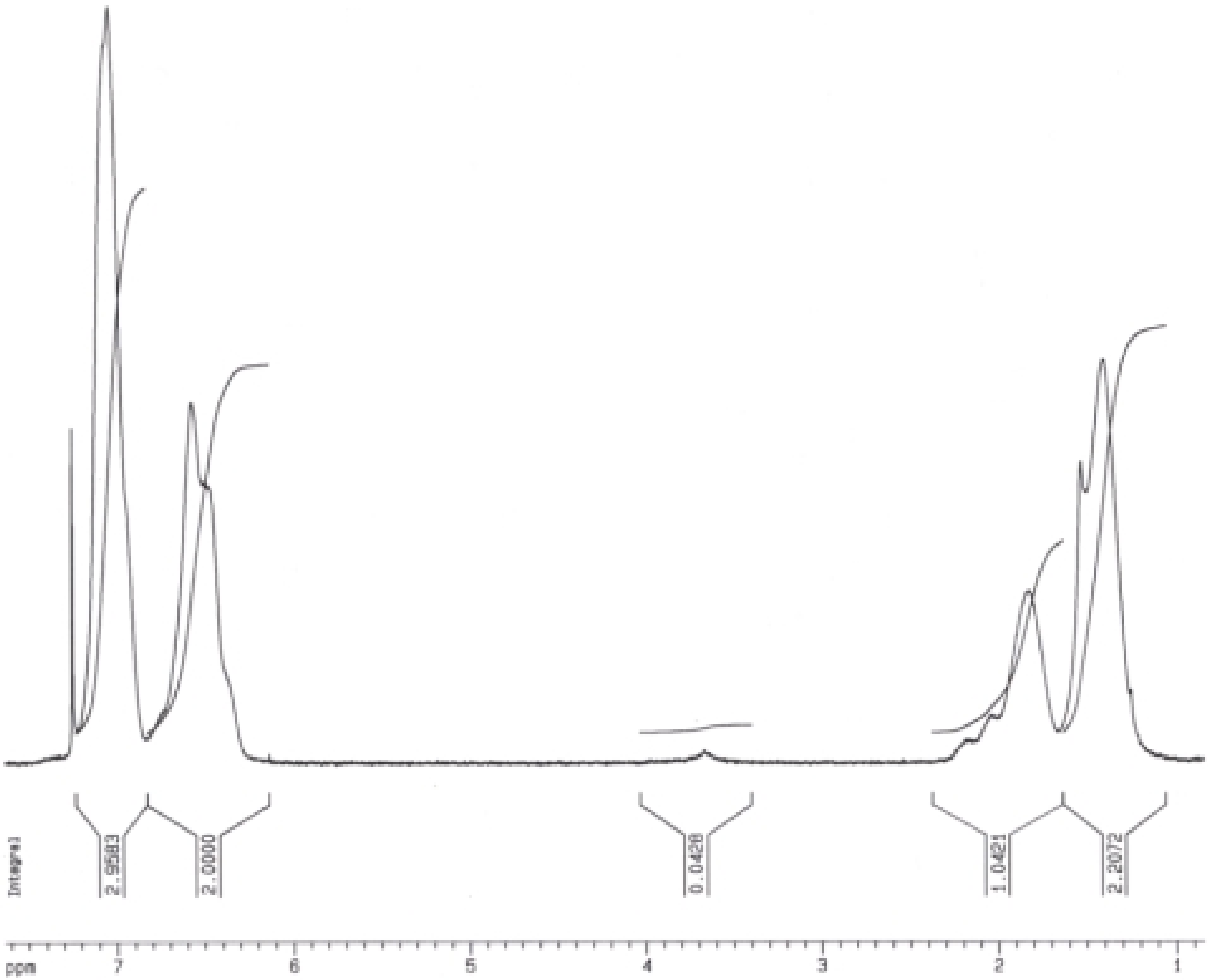


*Figure 1.12. ^{1}H-NMR spectrum of anionic polymerized atactic PS (**PS15**) in $CDCl_3$ at 300 K.*

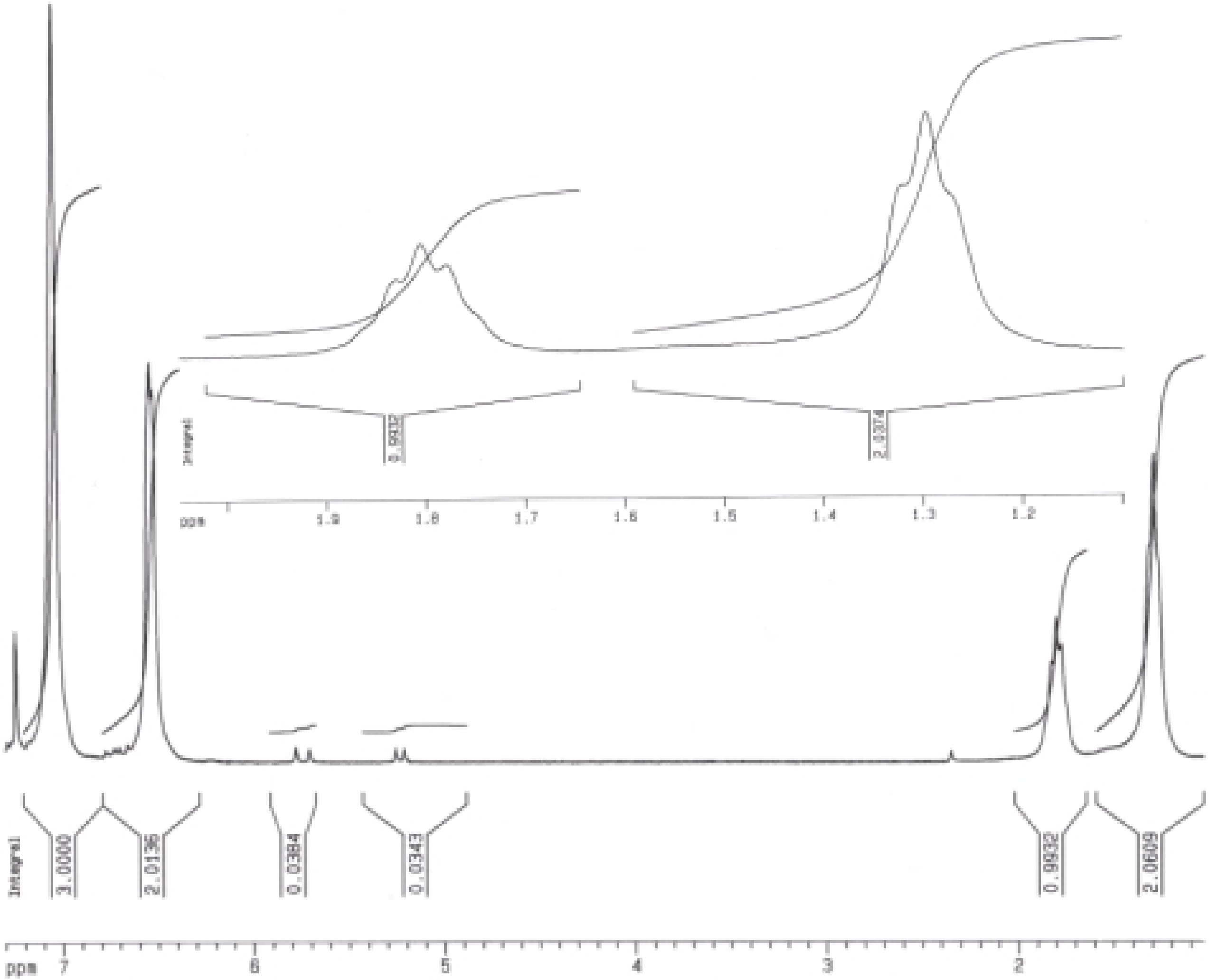


Figure 1.13. ^{1}*H-NMR spectrum of metallocene catalyzed syndiotactic PS (**PS20**) in* $CDCl_3$ *at 300K. Insert is a magnification of the aliphatic region.*

1.2.3.2 Differential Scanning Calorimetry

The information attained from DSC on polymers is the glass transition temperature (T_g) and the melting point (T_m). The glass transition temperature is the temperature at which the amorphous parts of the polymer change from a glassy state to a viscous or rubbery, or said in another way it is the temperature at which a second order phase transition takes place. Since the mobility of the individually polymer chains have a direct influence on the glass transition temperature, the value of T_g have information about the tacticity of the polymer. To some extent is the molecular weight of the polymer also reflected in T_g and the following equation can be used to predict the glass-transition temperature empirically[19], see ***Equation 1.5***.

$$T_g = 100°C - \frac{10^5}{M_w}$$

Equation 1.5

As can be seen from the above equation molecular weights above 20000 g/mol contribute only little to this property. The value of T_g determines which applications a given polymer can be used in while the T_m determine the temperature range useable in processing of the polymer. Atactic PS and isotactic PS have T_g around 95.1 °C and 94.1 °C respectively[20] and the melting point of syndiotactic PS is around 275 °C. The glass transition temperature of syndiotactic PS is difficult to determine since the polymer has a very strong tendency to crystallize. The melting point of isotactic PS is around 224 °C.

---

[19] Reding, F.P., Faucher, J.A., Whitman, R.D.; *J. Polym. Sci.*, 1962, **57**, 483

[20] Naumann, M., Duran, R.; *Polym. Prep.*, 1991, **32**, 96

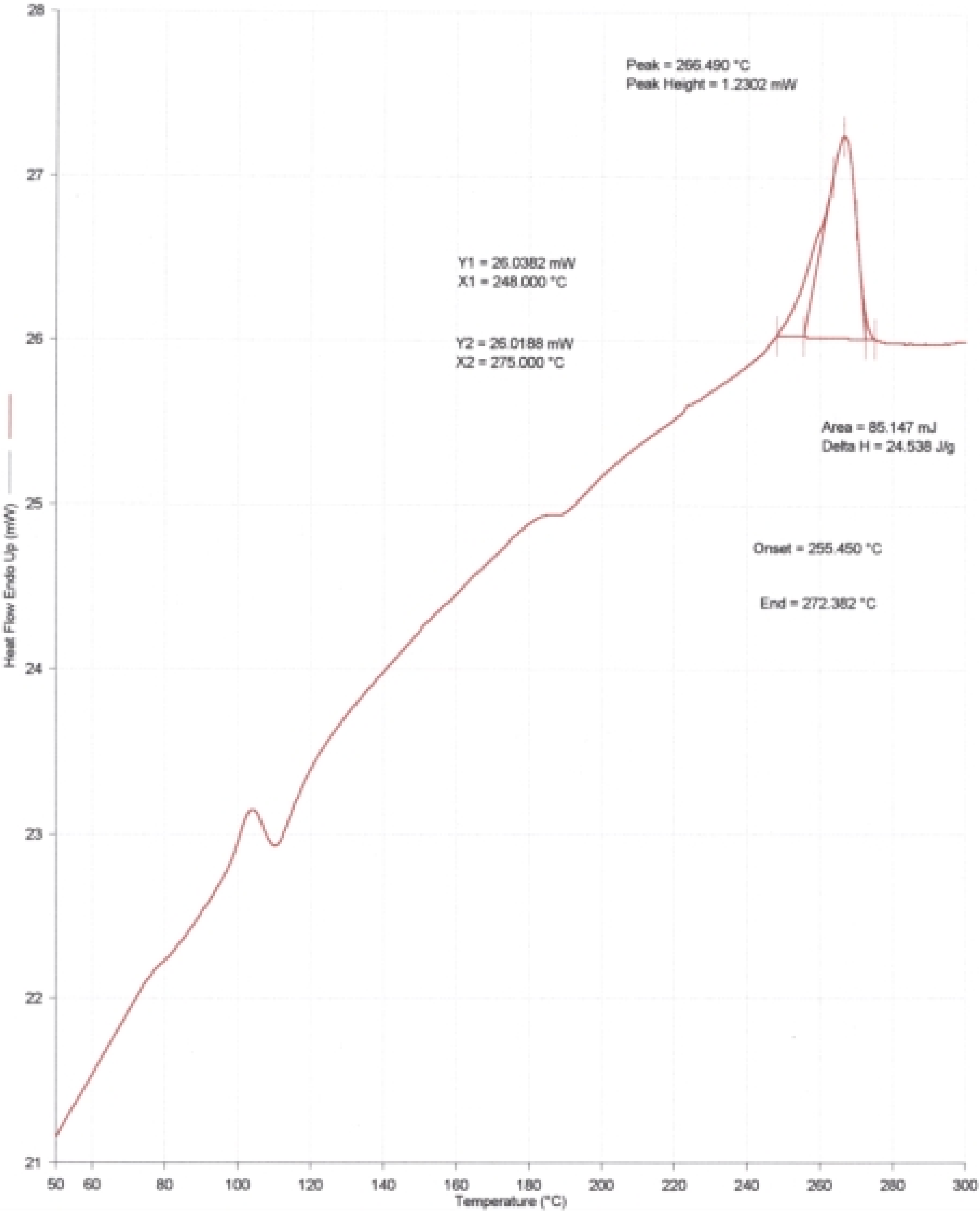


*Figure 1.14. DSC on syndiotactic PS (**PS20**) is showing the melting at 266.5 °C.*

1.3 Introduction to Ziegler-Natta and metallocene catalysts

The area of Ziegler-Natta and metallocene catalysts is very large[21,22,23,24,25,26,27] and at some times difficult to access. Being a multi billion dollars industry many companies have made research within this field. There are a very extensive collection of articles and unfortunately also a large portion of patents. One must also have in mind that several large industrially companies have a large knowledge from their own research that are not and properly never will be accessibly for other than themselves. The most famously patent within this area of research is properly the German patent No. 973626 with the inventors Karl Ziegler, Heinz Breil, Erhard Holzkamp and Heinz Martin from November 18, 1953 with the title "Verfahren zur Herstellung von hochmolekularen Polyëthylenen". This chapter in the thesis is not meant to be a comprehensive description of the very large area of research but only a brief survey introducing the concepts and some of the hot shots within this area.

1.3.1 Traditional Ziegler-Natta catalysts

Since Karl Ziegler in 1953 found that transition metal halides combined with aluminum alkyls had a profound effect on the reaction of building long-chain aluminum alkyls the development of catalysts intended for polymerization of olefins has expanded almost exponentially. While nickel salts resulted in dimerization of ethene producing butene, Ziegler found that $TiCl_4$ catalyzed the polymerization of ethene into relatively high melting linear polyethylene (LPE). This reaction did not require high pressure nor high temperature in contradiction to the conventionally methods which were free radical polymerization of ethene at that time. The potential of this synthetic method

---

[21] Brintzinger, H.H., Fischer, D., Mülhaupt, R., Rieger, B., Waymouth, R.M.; *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1143-70

[22] Kaminsky, W., Arndt, M.; *Adv. Polymer Science*, 1996, **127**, 143-187

[23] Breslow, D.S.; *Prog. Polym. Sci.*, 1993, **18**, 114-95

[24] Huang, J., Rempel, G.L.; *Prog. Polym. Sci.*, 1995, **20**, 459-526

[25] Hoveyda, A.H., Morken, J.P.; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1262-84

[26] Gupta, V.K., Satish, S., Bhardwaj, I.S.; *Rev. Macromol. Chem. Phys.*, 1994, **C34**, 439-514

[27] Sinn, H., Kaminsky, W.; *Adv. Organomet. Chem.*, 1980, **18**, 99-149

was expanded substantially in 1954 when Gulio Natta prepared and characterized isotactic polypropylene containing the same absolute configuration of the stereogenic carbon atom in the monomeric repeat units in long sections of the main chain. In 1963 Ziegler and Natta both were awarded the Nobel Prize in chemistry for these discoveries. The $TiCl_4/AlEt_3$ mixtures that Ziegler used were found to produce polymeric $TiCl_3$, which is a solid with a layered structure, with titanium having octahedral coordination. This is a heterogeneous catalyst as most of the Ziegler-Natta catalysts are. The surface morphology is thought to determine the stereoregularity of polypropylene since it produces a steric limitation on the approach of the monomer prior to the insertion in the metal-alkyl bonding, see ***Figure 1.15***. It is well accepted now that the active species is a metal-alkyl compound with one unsaturated coordination site[28] (marked with a square) *cis* to the alkyl ligand, normally referred to as the Cossee-Arlman mechanism.

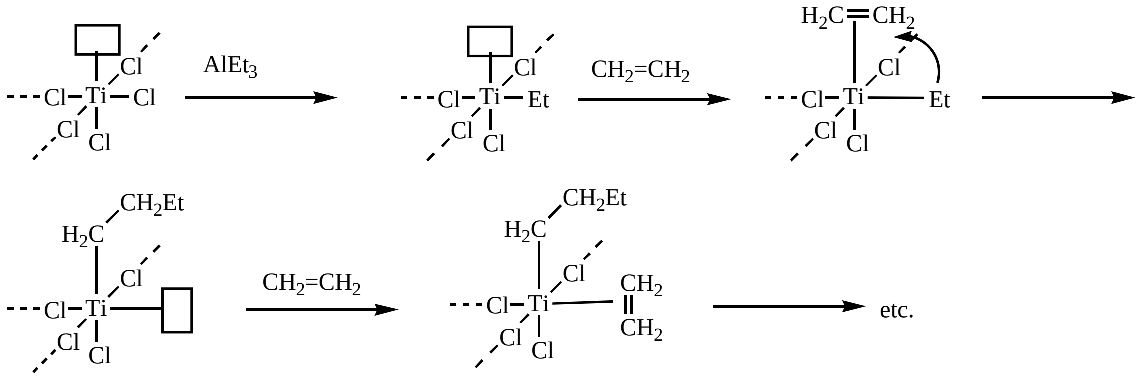


Figure 1.15. The Cossee-Arlman mechanism for polymerization of ethylene with a Ziegler-Natta catalyst here $TiCl_4$ activated with $AlEt_3$.

Even though these catalysts at that time was intensively investigated and used commercially in the expanding global production of polymers the yield of polymer with respect to the transition metal was poor and so was the control of tacticity. One had to remove the catalyst residues, which caused corrosion of the processing equipment and color formation in the polymer, as well as low stereo-irregular amorphous and low molecular weight wax-like by-products by means of solvent extraction. Modern catalysts allow high yield polymer production combined with high stereoregularity and low “leave-in” amount of catalyst. This has been achieved by immobilizing the

---

[28] Rodriguez, L.A.M., Gabant, J.A.; *J. Polym. Sci., Part C*, 1963, **4**, 125

transition metal compound on silica, alumina or magnesium surfaces[29]. Productivity as high as 1000 kg polypropylene pr. gram transition metal with a stereoregularity up to 99 % and a molecular weight exceeding 500000 g/mol has been achieved and amazingly still getting better. In order to get even better stereochemical control combined with other possibilities to control the polymeric properties the search for homogeneous catalysts began.

1.3.2 Metallocenes

Normally the concept Ziegler-Natta catalyst are used for the heterogeneously catalysts as described above while the homogeneously catalysts are called metallocenes. Unfortunately some precise definitions of the two concepts are lacking in the literature and one will find in some cases that the use and meaning of these words are mixed. Strictly speaking is a metallocene a sandwich compound where the transition metal atom is centered between normally two co-planar cyclopentadienyl ligands, see ***Figure 1.16***. But when the polymeric chemists use the word “metallocene” it usually describes the bent metallocene dihalide sandwich complexes and so will be the case in this text.

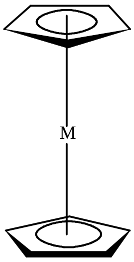


Figure 1.16. Definition of a metallocene.

One very important difference between the traditional Ziegler-Natta catalysts and the metallocenes is that the later being single site catalysts resulting in well-defined active sites present in specific amounts. Thus improving the reproducibility of the polymerization.

---

[29] Barbe, P.C., Cecchin, G., Noristi, L.; *Adv. Polym. Sci.*, 1987, **81**, 1

The first metallocene used for studying the polyinsertion reaction mechanism of ethene was bis(η^5-cyclopentadienyl)titanium dichloride, normally denoted Cp_2TiCl_2, as early as 1957 by Natta in Milano[30] and Breslow at Hercules[31]. When activated with aluminum alkyls this metallocene could polymerize ethene but not propene. It was not until 1973 when Reichert and Meyer[32] found that if traces of water, normally known as a severe catalyst poison, were present in the reaction-medium this would improve the catalytic properties and in 1976 Sinn and Kaminsky[33] polymerized propene by catalysis of a metallocene.

This improvement was attributed to the formation of an aluminoxane from partially hydrolyzed aluminum alkyls. Sinn and Kaminsky introduced a new class of aluminum alkyl activators in 1976 made from controlled hydrolysis of trimethylaluminum with the formula $Me_2AlO\text{-}(MeAlO)_n\text{-}OAlMe_2$ with n being between 5 and 20. This activator is named MAO (methylaluminoxane) and is commercially available as a solution in toluene. A fact is that the uses of MAO in commercially productions of polymers have resulted in a great number of disputes between competitive companies where one part is claiming that the other part has violated their patent. This is due to the rather complex mixture of products resulting from the partially hydrolysis of trimethylaluminum, consisting of linear, branched and cyclic MAO still containing some amount of non-reacted trimethylaluminum. The MAO has three main purposes:

- Alkylation of the transition metal atom thereby activating the catalyst
- Favor the formation of cationic metallocenes[34] by acting as Lewis acid complexing the counterion (e.g. Cl^-) producing a unsaturated coordination site at the transitions metal atom
- Removing small scale impurities from the monomer and also from the solvent

As mentioned above Sinn and Kaminsky were the first to polymerize propene using Cp_2MCl_2, where M= Ti, Zr or Hf, activated by MAO. These catalysts produced ideally atactic polypropylene being the first time perfectly atactic polypropylene was obtained in a catalytic process[35]. Previously

---

[30] Natta, G-, Pino, P., Mazzanti, G., Giannini, U.; *J. Am. Chem. Soc.*, 1957, **79**, 2975

[31] Breslow, D.S., Newburg, N.R.; *J. Am. Chem. Soc.* 1957, **79**, 5072

[32] Reichert, K.H., Meyer, K.R.; *Makromol. Chem.*, 1973, **169**, 163

[33] Kaminsky, W., Kopf, J., Sinn, H., Vollmer, H-J.; *Angew. Chem.*, 1976, **88**, 688

[34] Green, M.L.H, Sassmanshausen, J.; *Chem. Comm.*, 1999, 115

[35] Sinn, H., Kaminsky, W.; *Adv. Organomet. Chem.*, 1980, **18**, 99

this kind of polypropylene had been prepared from isotactic polypropylene epimerized with palladium at elevated temperature. In order to influence the equilibrium favoring the formation of the unsaturated 14 valence electron transition metal species $(Cp_2M\text{-}R\text{-olefin})^+$ one has to use MAO in large excess, normally requiring a Al/metallocene molar ratio above 200 mol/mol, preferably in the range of 1000 to 7000 mol/mol. Actually a large number of different complexes are formed when the metallocene and MAO are mixed together, where the presence of some intermediates are depending of the ratio between the metallocene and MAO. The mechanism for metallocene catalyzed polymerization are the same as for Ziegler-Natta catalysts, see ***Figure 1.6*** and ***Figure 1.15***.

There are other ways of activating the catalyst than using MAO[36,37] and these are either protonating a metallocene dialkyl complex or abstraction of R^- from the same complex, see ***Figure 1.17***.

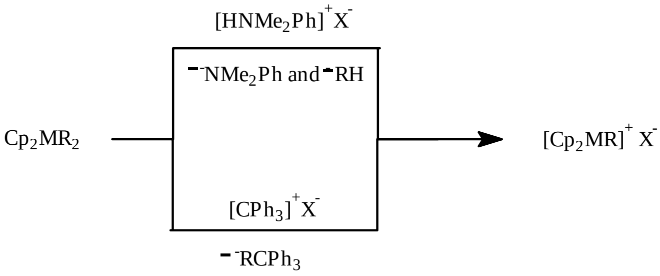


Figure 1.17. Other ways of activation of a metallocene catalyst.

The activation step add another adjustable property tuning the catalyst and that is X^- which depending on the strength of coordination to the cationic species (e.g. Cp_2MR^+ above) are cable to enhance or reduce the reactivity of the catalyst. If X^- is a non-coordinating anion (fx $B(C_6F_5)_4^-$) the catalyst is activated into a very reactive cationic species.

The nature of the transition metal atom also have a influence on the catalytic properties and normally the reactivity follows the order M= Ti << Hf < Zr.

As mentioned above the original metallocene catalyst Cp_2MCl_2/MAO system did only produce atactic polypropylene that from a commercially point of view was unattractive. A large amount of man-hours was spent on preparing a catalyst that could produce isotactic polypropylene. One could argue that no stereochemical control would be expected from that kind of catalyst since no chirality

---

[36] Horton, A.D., de With, J.; *Chem. Commun.*, 1996, 1375

[37] Chien, J.C.W., Tsai, W.M., Rausch, M.D.; *J. Am. Chem. Soc.*, 1991, **113**, 8570

or prochirality are present. But work of Ewen[38] showed that Cp_2TiPh_2/MAO at room temperature was non-stereoselective but below –30 °C the resulting polypropylene was an isotactic stereoblock type. Explanations were based on the assumption that the chirality of the last monomeric unit was responsible for stereochemical control, see ***Figure 1.18***. In 1985 Brintzinger[39] synthesized the first stereospecific catalyst, racemic *ansa* ethylene (4,5,6,7-tetrahydro-1-indenyl)$_2$MCl_2 with M= Ti, Zr, Hf (**1A**) (*ansa* = handle), that produces isotactic polypropylene with an activity of 80 kgPP/mmol metal, having a M_w of 15000 g/mol and a melting point at 125 °C.

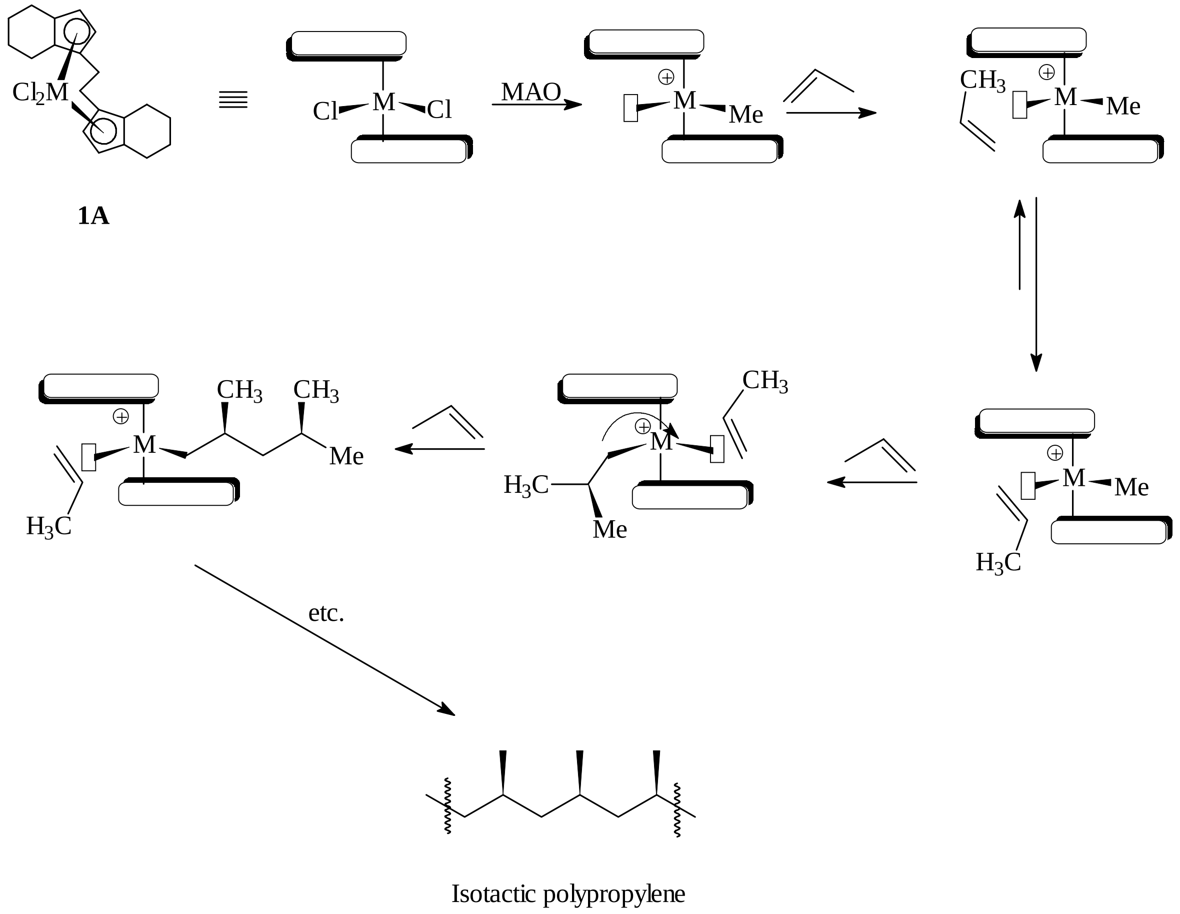


*Figure 1.18. Mechanism for the production of isotactic polypropylene with the catalyst **1A** activated by MAO.*

It can be seen from ***Figure 1.18*** that for the C_2-symmetrically racemic *ansa* metallocene, the altered position of the polymer chain after insertion does not influence stereochemical control because both

---

[38] Ewen, J.A.; *J. Am. Chem. Soc.*, 1984, **106**, 6355

[39] Wild, F.R.W.P., Zsolnai, L., Huttner, G., Brintzinger, H.H.; *J. Organomet. Chem.*, 1982, **232**, 233

positions are identical. If however a C_s-symmetrically metallocene, such as CMe_2 (1-cyclopentadienyl) (9-fluorenyl)$ZrCl_2$ (**1D**[40] in ***Figure 1.19***), is used the resulting polypropylene is syndiotactic.

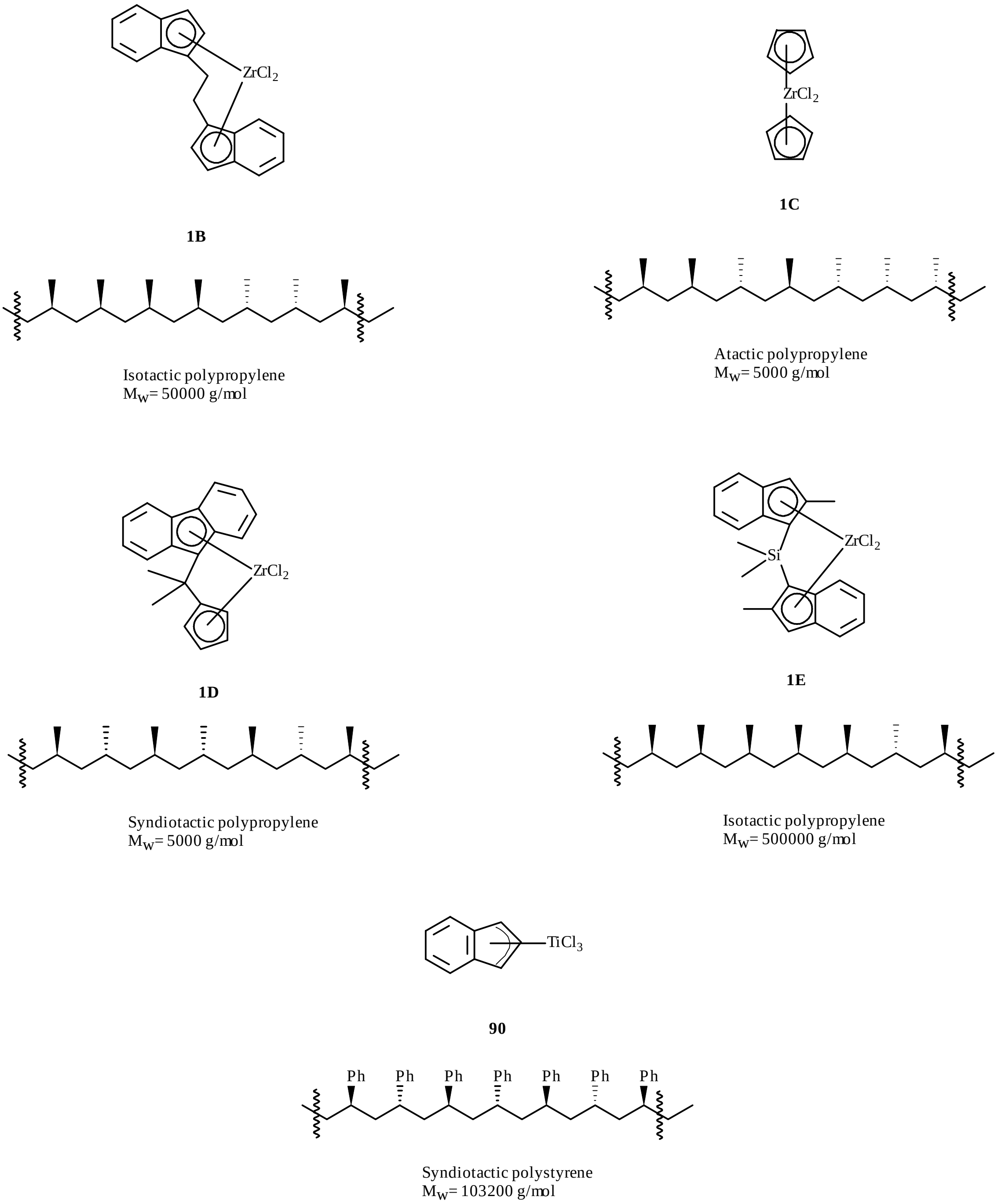


Figure 1.19. The effect substitution has on the molecular weight and tacticity of the polymer for some selected metallocenes. In the case of ***90*** *the polymerization is discussed later.*

---

[40] Razavi, A., Atwood, J.L.; *J. Organomet. Chem.*, 1993, **459**, 117

This arises because the position of the growing polymer chain determines chirality of the metal center. After each insertion step the absolute configuration of the transition metal center alternate, producing syndiotactic polypropylene with alternating absolute configurations of the stereogenic carbon atom in the monomeric repeat units.

Other substitution patterns of the cyclopentadienyl ligands has been investigated thoroughly in order to improve chain propagation with respect to chain termination, in particular chain transfer via β-hydride elimination or chain transfer with the monomer, thereby raising the molecular weight. In ***Figure 1.19*** are presented some of the metallocenes in order to show the effect of substitution on molecular weight.

On an industrial scale the production of highly syndiotactic polystyrene is performed using $CpTiCl_3$/MAO or $Ti(OPh)_4$/MAO resulting in polystyrene with melting points about 265 °C. The higher melting polyolefins are of interest in engineering resin applications where high heat distortion temperature combined with strength, stiffness, and toughness is required. It has recently been found that trichloro(η^5-indenyl)titanium (**90**) is a significantly better catalyst than $CpTiCl_3$ and the former can be enhanced even more by substitution with a phenyl group in the 1-position[41].

1.3.3 Synthetic strategies

In the synthesis of the above mentioned catalysts there are normally more or less only one strategy that are used and that is nucleophilic substitution reaction on one of the transition metal tetrahalides, the metal atom being Ti, Zr or Hf. The nucleophile used is often the lithium or (rarely) magnesium compound obtained from simple deprotonisation, see ***Figure 1.20***. The cyclopentadiene is generated by thermal cracking of the Diels-Alder dimer as a low-boiling liquid. One of the two protons can readily be removed by reaction with a strong base such as alkali metals or alkali metal hydrides giving salts of the cyclopentadienyl anion. Alkali metal Cp-compounds are essentially ionic and air-sensitive.

---

[41] Foster, P., Chien, J.C.W., Rausch, M.D.; *Organometallics*, 1996, **15**, 2404

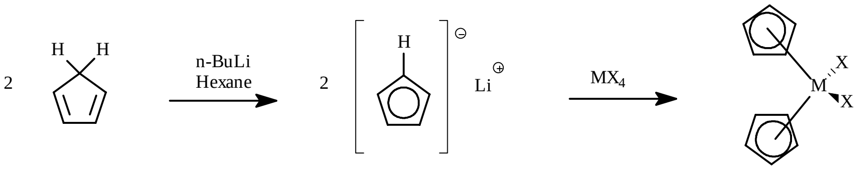


Figure 1.20. The normal strategy for the substitution on transition metal tetrahalides. M= Ti, Zr or Hf and X= Cl or Br.

The Cp ligand increases the stability of the complex significantly being a 6π electron system and is contributing with those in the η^5-bonding between the transition metal atom and the ligand. If Cp_2TiCl_2 is reacted with another two equivalents of CpLi the compound formed is $(\eta^5\text{-Cp})_2Ti(\sigma\text{-Cp})_2$ as black-violet crystals. This increase in stability is clearly shown when comparing e.g. Cp_2TiCl_2 with $TiCl_4$ the latter being a very strong Lewis acid hydrolyzing in air while the Cp_2TiCl_2 can be washed with 6 M HCl without decomposition. Another example of the significance that the Cp-ligands have on stability is that the tetra-alkyl titanium compounds are very unstable (the most stable is $TiMe_4$ but still this compound must be kept below –60 °C) while the Cp_2TiR_2 are even more stable than the Cp_2TiCl_2.

The introduction of substituents into the Cp-ring is facile and provides a convenient way to modify the electronic and steric properties of both the Cp-ring but also of the transition metal center. Introducing five methyl groups, making the Cp* (1,2,3,4,5-pentamethylcyclopentadienyl), results in increased steric hindrance but also increased electronic density on the transition metal center. This effect is due to the inductive electronic effect while silicon-substituents will have the well-known β-cation stabilizing effect on the activated transition metal center and thereby as shown above increasing the catalytic properties of the metallocene. Other derivatives of the Cp-ligand are indenyl and fluorenyl ligands. While the Cp and fluorenyl ligands mostly bind in a η^5 manner the indenyl ligand has the opportunity to bind in a η^3 manner thereby decreasing the electronic energy by a gain in aromaticity, see ***Figure 1.21***.

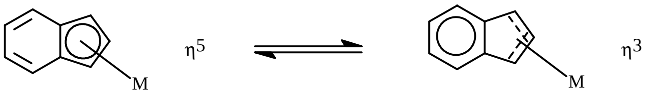
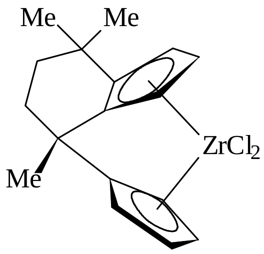


Figure 1.21. The $\eta^5 \rightarrow \eta^3$ *rearrangement for indenyl ligand systems.*

Such rearrangements can have important consequences for the reactivity of metal complexes and their catalytic properties.

The geometry of metallocenes is commonly tetrahedral with an angle between the two Cp ligands around 130° and an angle between the two non-Cp ligands around 95°. By substitution these angles can be varied and an angle as low as 115° has been achieved in **1F**[42], see ***Figure 1.22***. When the angle between the Cp ligands is decreased the angle between the non-Cp ligands is increased and thereby opening the gab within which the polymer-chain is growing.



1F

Figure 1.22. Metallocene with an angle of 115° between the two Cp ligands.

A way to prepare mono-Cp complexes, the so-called *half-sandwich* complexes, is to treat a trimethylsilyl derivative with MX_4, see ***Figure 1.23***. While the reaction runs smoothly when M= Ti the reaction normally require heating for M= Zr or Hf.

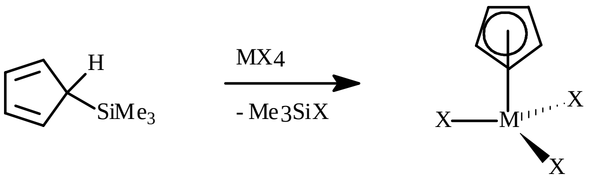


Figure 1.23. Synthesis of mono-Cp complexes.

---

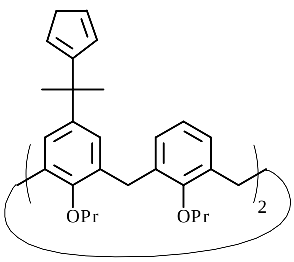
[42] Küber, F., *Proceedings of Metallocenes Europe 97'*; 1997

The advantage of this reaction is that no other reagents are present and the solvent used is CH_2Cl_2 or toluene when heating is necessary. The by-product, e.g. Me_3SiX, is easily removed together with the solvent by evaporation normally.

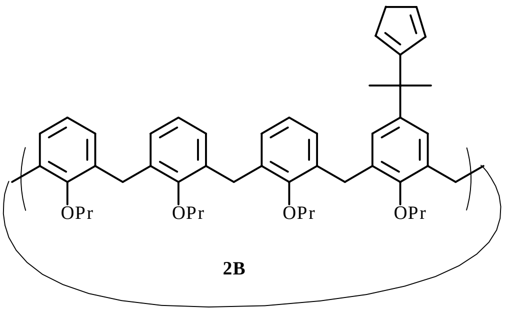
1.4 Synthetic target and what could be made

As described in the first part of this chapter the original idea was to combine the supramolecular properties of calix[4]arenes with the catalytic properties of metallocenes by using the *upper rim* of the calix[4]arene as template. For this purpose a rather large number of calix[4]arenes have been prepared in order to achieve the ever changing target molecules, see ***Figure 1.24***, where the molecules indicated by a number followed by a letter (fx. **2A**) has not been synthesised while those only indicated by a number (fx. **15**) can be found in the *Experimental* section. A discussion concerning the synthesis will be given in the next chapter. The catalysts that were synthesised have been used to gain experience in the field of using metallocenes as catalyst to polymerize olefins. Especially **90** have been used to polymerize styrene producing *syndiotactic* polystyrene, see the next part.

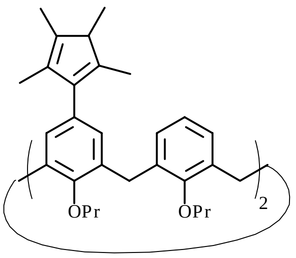
Since the calix[4]arenes proved to be a improper template for the metallocenes the usability as crown ethers was used in another part of the project were anionic polymerization of styrene was investigated. The calix[4]arenes shown in ***Figure 1.25*** was synthesised and used in the polymerization of styrene, see next part.



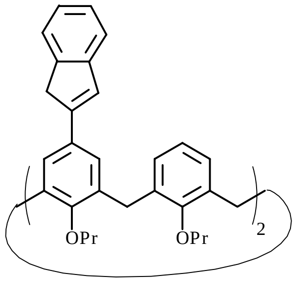
2A



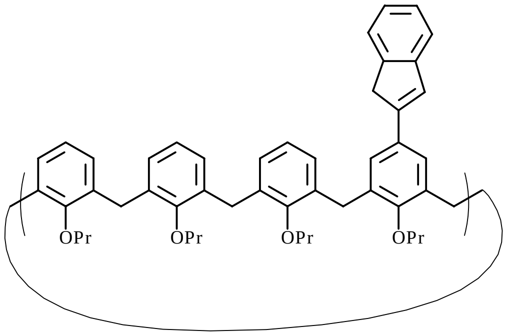
2B



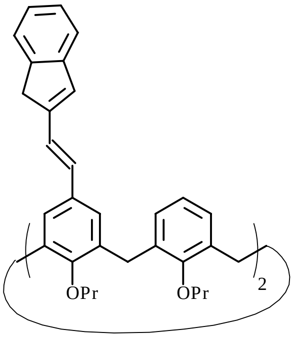
2E



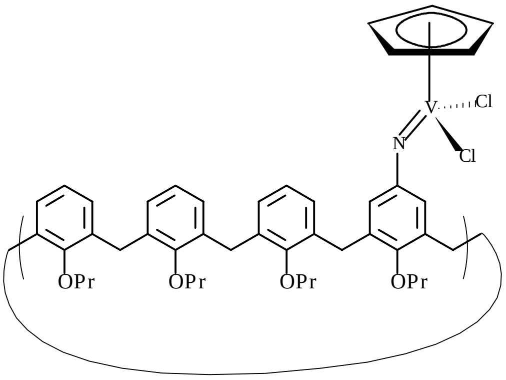
2F



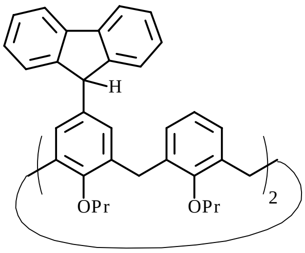
2G



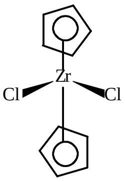
2I



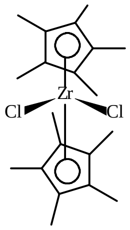
2O



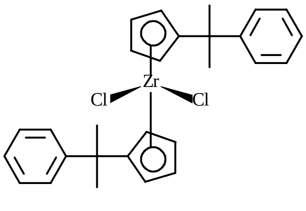
15



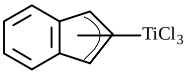
73



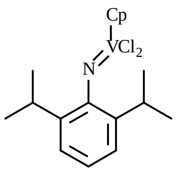
74



75



90



76

Figure 1.24. The target molecules attempted synthesised during the metallocene project.

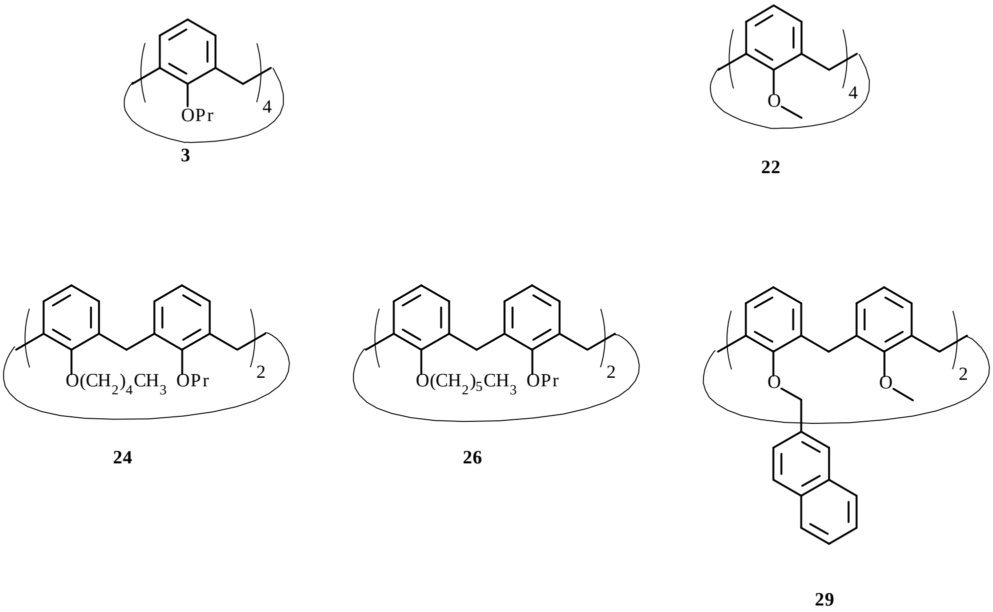


Figure 1.25. Calix[4]arenes used in the anionic polymerization of styrene.

1.5 Polystyrenes

During this thesis study the polymerization of styrene was investigated as a model reaction to gain experience in this field. Anionic polymerization was used to prepare *atactic* polystyrene while catalysis with home-made (though known) indenyl trichloro titanium (**90**) produced *syndiotactic* polystyrene and the polymers was characterized with SEC/GPC, DSC and ^{1}H and ^{13}C NMR. The anionic living polymerization of styrene catalyzed by *n*-BuLi was also investigated using ^{7}Li NMR. These model polymerizations where compared to reactions where simple calix[4]arenes or crown-ethers was used as catalysts in the hope of controlling the tacticity of the product.

1.5.1 Anionic polymerization of styrene

Anionic polymerization of styrene catalyzed by alkyl lithium was described in the beginning of this chapter. The reaction was carried out as described in the *Experimental* section, part two, producing the polystyrenes **PS1-PS4**, see ***Table 1.1***.

Table 1.2. The collected data used in the anionic polymerization of styrene. The ratio between initiator and styrene is in all experiments 1/10, which in theory should result in a polystyrene with a molecular weight about 1040 g/mol, corresponding to a chain length of 10 monomeric units.

Polymer Nr.	**PS1**	**PS2**	**PS3**	**PS4**
Initiator	Bu^tLi	*n*-BuLi	*n*-BuLi	*n*-BuLi
[Initiator]/M	0.032	0.132	0.132	0.132
Solvent	Cyclohexane	Cyclohexane	Toluene	Toluene
Reaction Time / min	30	30	10	10
Reaction Temperature / °C	40-50	40-50	Ambient	40-50
Yield / %	78	46	25	66
Glass-transition temp. / °C	82.9	74.0	81.4	81.6
Peak molecular weight / g/mol	4450	2660	3500	4220
Polydispersity M_w/M_n	1.26	1.07	1.10	1.14

All four polystyrenes was found to be *atactic* as expected by NMR analysis and the low glass-transition temperatures can be explained in terms of the low molecular weight observed, as explained previously.

Since the polymerization had performed so well it was attempted using ^{7}Li-NMR in order to elucidate if it was possible to monitor the difference between the different lithium species present during the polymerization. To this purpose a NMR tube was first charged with *n*-BuLi/C_6H_{12} in C_6D_{12}, see ***Figure 1.26*** left part, where two lithium species are present. This could be the tetramer and hexamer, e.g. $(n\text{-BuLi})_4$ and $(n\text{-BuLi})_6$ species, where normally in hydrocarbon solvents mainly the hexamer is present[43]. When addition of THF was performed the ^{7}Li-NMR spectrum changed as expected into a spectrum of the dimer, e.g. (n-BuLi)$_2$, see ***Figure 1.26*** middle part.

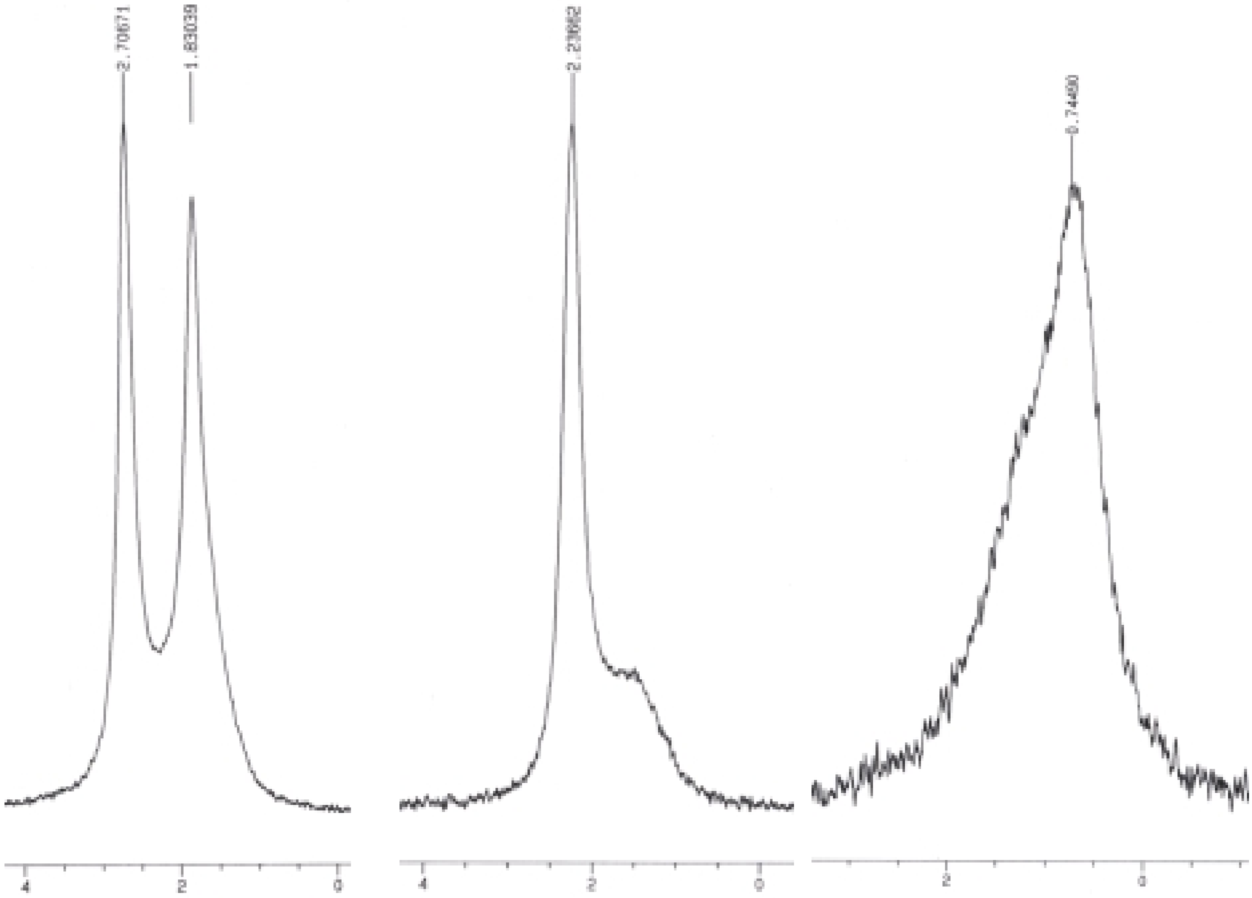


Figure 1.26. ^{7}*Li-NMR of n-BuLi/*C_6H_{12} *in* C_6D_{12} *at 300 K. Left; before adding THF, middle; after adding THF and right; after adding styrene (7 equivalents).*

When addition of styrene (7 equivalents) took place the signal changed again, see ***Figure 1.26*** right part, which must be interpreted as being the lithium polystyrene/styrene complex since ^{1}H-NMR showed that the polymer still was growing. The resulting polystyrene was by GPC found to have a molecular weight of 11600 g/mol having a polydispersity of 1.34.

---

[43] Fraenkel, G., Beckenbaugh, W.E., Yang, P.P.; *J. Am. Chem. Soc.*, 1976, **98**, 6878

1.5.2 Polystyrenes from metallocenes

The metallocene type catalyst trichloro(η^5 indenyl)titanium (**90**) and N-(2,6-diisopropylbenzene) iminium-cyclopentadienyl-vanadium dichloride (**76**) was prepared as shown in ***Figure 1.27***, and used for the preparation of *syndiotactic* (**PS18-PS20**) and *atactic* polystyrenes (**PS21**), see *Experimental* section part two for details.

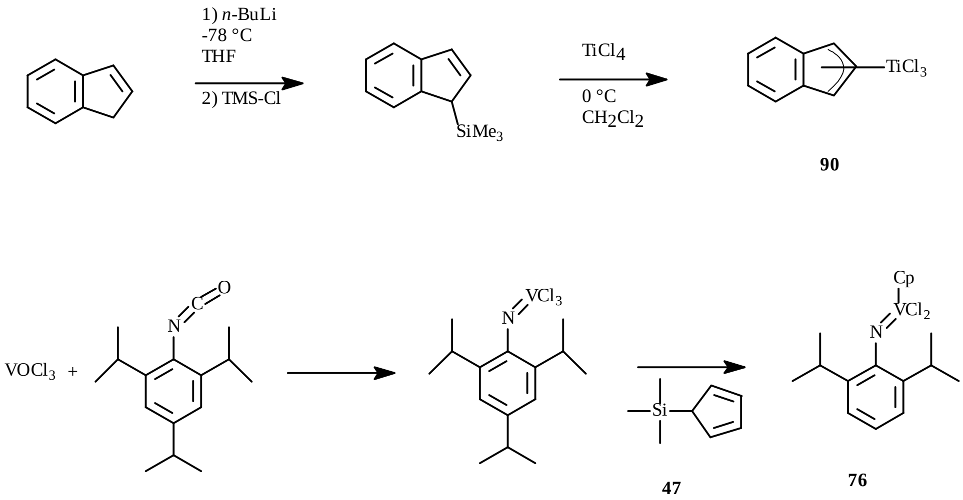


*Figure 1.27. The synthesis of trichloro(η^5 indenyl)titanium (**90**) and N-(2,6-diisopropylbenzene) iminium-cyclopentadienyl-vanadium dichloride (**76**).*

*Table 1.3. Results from the GPC and DSC analysis performed on polystyrene using **90** (**PS18**, **PS19**, **PS20**) and **76** (**PS21**) as catalysts in the polymerization. In the first three polymers the NMR indicated that the polymers were syndiotactic and for the last polymer it was found to be atactic.*

Polymer Nr.	**Melting point or glass-transition temp. / °C**	**Peak molecular weight / g/mol**	**Polydispersity M_w/M_n**
PS18	263/T_m	81500	3.52
PS19	260/T_m	69200	3.69
PS20	266/T_m	103200	1.82
PS21	93.3/T_g	11000	1.87

The polystyrenes (**PS18**-**PS20**) obtained from the catalyst **90** had a very high degree of *syndiotacticity*, see ***Figure 1.11*** and ***Figure 1.13***, analyzed by NMR. In the ^{1}H-NMR spectrum of the polymers obtained from this catalyst the coupling constants was measurable and in the ^{13}C-NMR spectrum only one resonance was observed for the C1 phenyl carbon.

The results from the DSC analysis is rather straight-forward to analyze since the melting point of the *syndiotactic* polystyrenes, e.g. **PS18**, **PS19** and **PS20** follows the molecular weight. Compared to other polystyrenes where the exact amount of *syndiotactic* polystyrene has been found by extraction with 2-butanone (removing *atactic* and *isotactic* polystyrene) these polystyrenes contain somewhere in the range of 90-95 % *syndiotactic* polystyrene[44]. The polydispersities are higher than would be expected but might be caused by a different ratio between the catalyst and the cocatalyst, e.g. MAO. In all the four cases above the ratio was about 3000 (Al/M, M= Ti or V) which is around midways in the normal interval of 1000-7000.

These experiments was only conducted in order to prepare polystyrene using those catalysts and to find out if the polymerization was possible in “normal” laboratory glass-ware and using standard grade reagents.

1.5.3 Calix[4]arenes and Crown-ether catalysis

The use of crown ethers in the living anionic polymerization of styrene was found to be non-existent. In the literature the effects of adding TMEDA, which towards alkyllithium reagents has the same ability as crown ethers to breakdown the oligomeric aggregates of these, was described[45]. By chelating the cation of the alkyllithium reagent to TMEDA the aggregate is dissolved and the anion becomes much more reactive which then normally results in an increased rate of reaction. Since the great Nobel Prize winning work of Pedersen[46], Jean Marie Lehn and Cram[47] crown ethers has been known to have the same effect and since the *lower rim* of

---

[44] Foster, P., Chien, J.C.W., Rausch, M.D.; *Organometallics*, 1996, **15**, 2404

[45] Bywater, S., Black, P., Worsfold, D.J., Schué, F.; *Macromolecules*, 1985, **18**, 335

[46] Pedersen, C.J.; *J. Am. Chem. Soc.*, 1967, **89**, 2495 and 7017

[47] Cram, D.J., Cram, J.M.; *Science*, 1974, **183**, 803

calix[4]arenes resembles the structure of crown ethers[48] it was thought to be an exciting investigation.

The idea of using calix[4]arenes as chelating agent arose from the findings discussed in the next chapter, but other examples can be found in the literature were calix[4]arenes crown ethers has been used to extract cesium ions[49,50] selectively in the presence of sodium ions or lead; cadmium and copper ions[51]. Recently the use of a calix[4]arene-neodymium complex was found to catalyze polymerization of styrene using di-*n*-butylmagnesium as a cocatalyst and HMPA (HexaMethylPhosphorAmide) as an additive[52].

For this study the *lower rim* derivatised calix[4]arenes (**3**, **22**, **24**, **26** and **29**) shown in ***Figure 1.28*** were prepared. The asymmetric substituted derivatives, e.g. **24**, **26** and **29**, was prepared with the idea that this could have a chance of influencing the tacticity of the resulting polystyrene.

The polymerization was first tried using *n*-BuLi in cyclohexane and **3** in equivalent amount (**PS5**). Upon mixing the calix[4]arene **3** and *n*-BuLi the reaction mixture turned orange in color with some development of heat. However when the addition of 10 equivalent freshly distilled styrene took place the well-known red solution resulted. The solution was then stirred at 40-50 °C for 30 min. during which period of time the color turned even more deep red.

Since the starting orange color and heat might be an indication that another reaction than simple complexation was taken place, a NMR tube was prepared containing **3** in deutero benzene (C_6D_6) and one equivalent of *n*-BuLi in cyclohexane (C_6H_{12}) was added.

---

[48] Danil de Namor, A.F., Salazar, L.E.P., Tanco, M.A.L., Kowalska, D., Salas, J.V., Schulz, R.A.; *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 3111

[49] Lamare, V., Dozol, J-F., Fuangswasdi, S., Arnaud-Neu, F., Thuéry, P., Nierlich, M., Asfari, Z., Vicens, J.; *J. Chem. Soc., Perkin Trans. 2,* 1999, 271

[50] Seung, J.K., Pang, J.H., Yu, I.Y., Lee. W.K., Suh, I.H., Kim, J.K., Cho, M.H., Kim, E.T., Ra, D.Y.; *J. Chem. Soc., Perkin Trans. 2,* 1999, 837

[51] van der Veen, N.J., Egberink, R.J.M., Engbersen, J.F.J., van Veggel, F.J.C.M., Reinhoudt, D.N.; *Chem. Commun.,* 1999, 681

[52] Zheng, Y-S., Shen, Z-Q., *European Polymer Journal,* 1999, **35**, 1037

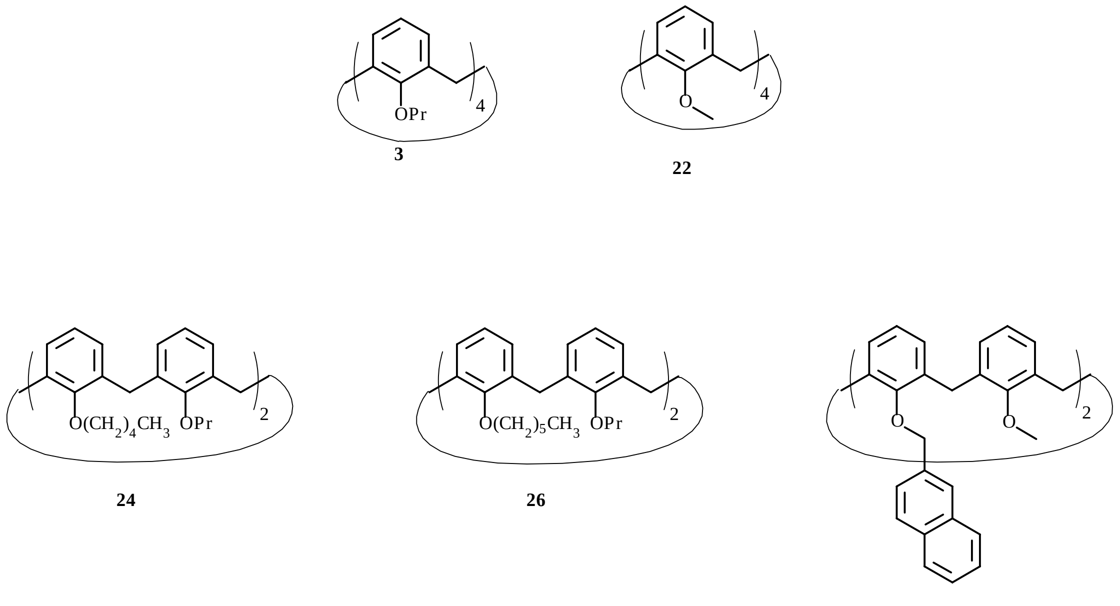


Figure 1.28. Calix[4]arenes synthesised in order to investigate the possible influence their addition had on the anionic polymerization of styrene.

The resulting solution was analyzed by ^{1}H-NMR as a function of time, see ***Figure 1.29***. After 20 min of reaction time the spectrum has changed dramatically and in a rather unexpected way. In order for **3** and other compounds to be useful in this type of reactions, e.g. anionic polymerization, it is necessary that no reaction between the initiator and “crown ether” takes place other than the desired complexation. Otherwise reproducibility of the polymerization becomes very difficult since the amount of initiator available for reaction with the monomer is uncontrollable which again disrupt the normally linear correlation between the ratio of initiator/monomer and the final molecular weight of the polymer.

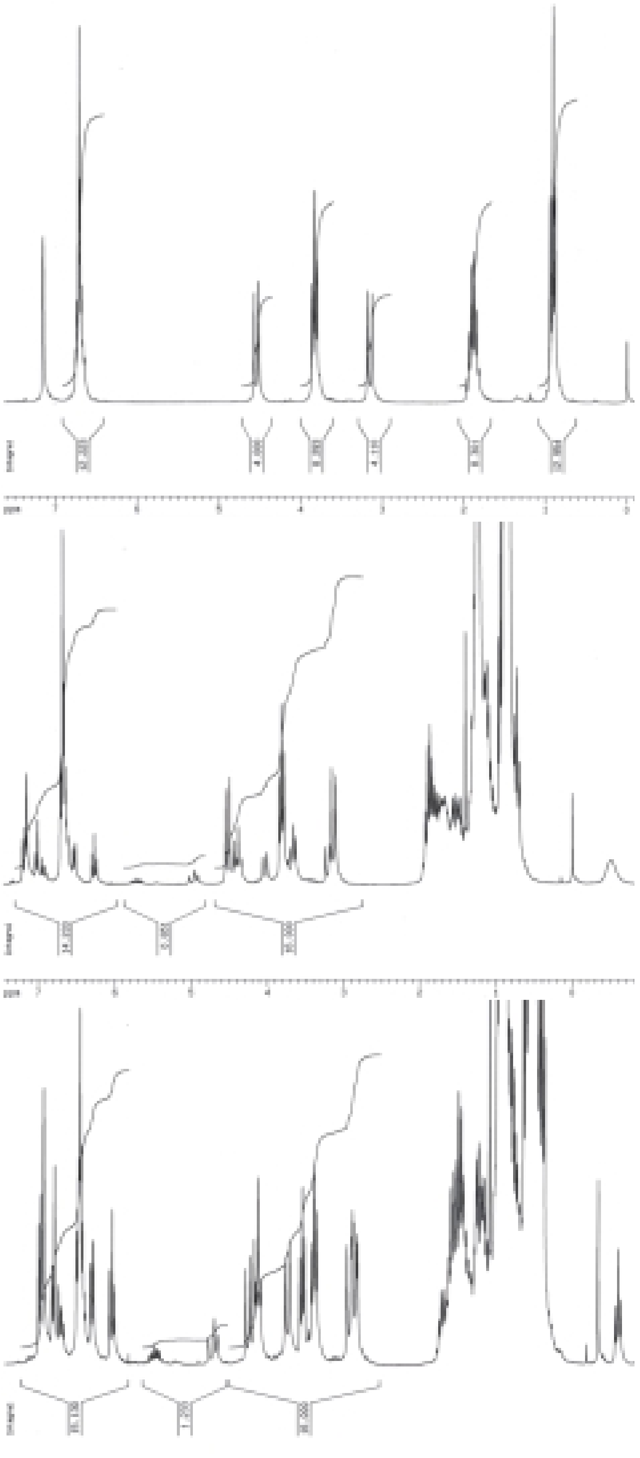


*Figure 1.29. ^{1}H-NMR spectrum of **3** (56.4 mg) in C_6D_6 (1 ml) at 300 K, upper spectrum, while the spectrum in middle was performed immediately after addition of one equivalent of 1.40 M n-BuLi (0.7 ml) in cyclohexane, and the lower spectrum was performed after a reaction time of 20 min.*

Since the lower spectrum in ***Figure 1.29*** indicates that actual reaction between initiator and **3** has taken place, the reaction mixture was quenched by addition of MeOH, followed by ^{1}H-NMR analysis hoping that the spectrum of **3** was observed, see ***Figure 1.30***.

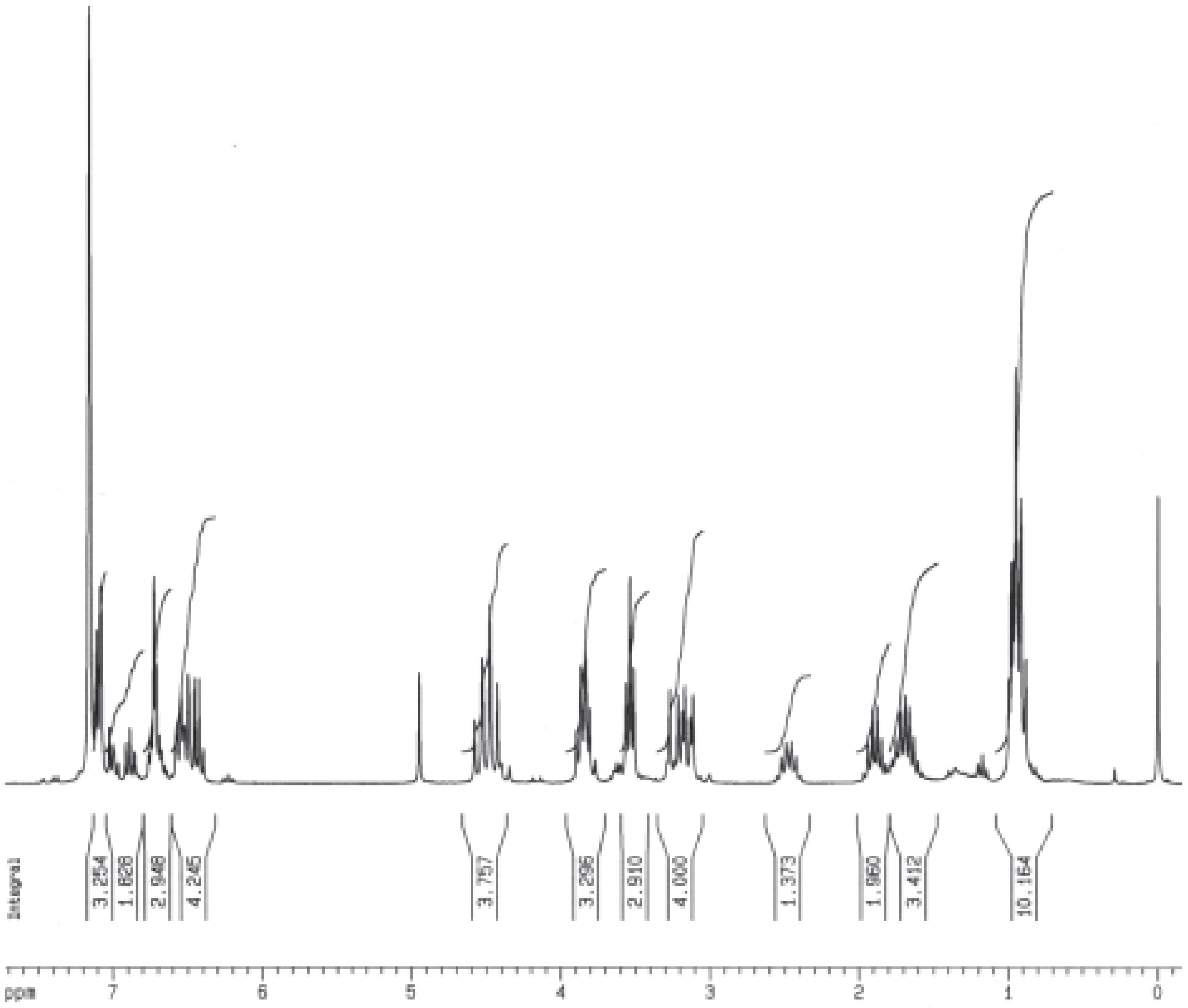


Figure 1.30. ^{1}H-NMR spectrum of the products obtained after quenching the sample from

***Figure 1.29** with MeOH.*

As seen from ***Figure 1.30*** compound **3** was not the only product recovered from the reaction, some of the propoxy groups had been cleaved and the *cone* conformation original imposed in compound **3** was also altered into *partial cone* and *1,3-alternate*. MALDI-TOF verified this observation, see ***Figure 1.31***, where the main peaks can be related to tripropoxy-monohydroxy-calix[4]arene and dipropoxy-dihydroxy-calix[4]arene and only a minor peak relates to compound **3**. This observation was of course not very cheerful since the polymerization reaction has to be run at the same time scale, e.g. 20-30 min, otherwise very low amounts of polymer is obtained, and the calix[4]arenes usability as crown ethers in this type of reaction had to be neglected.

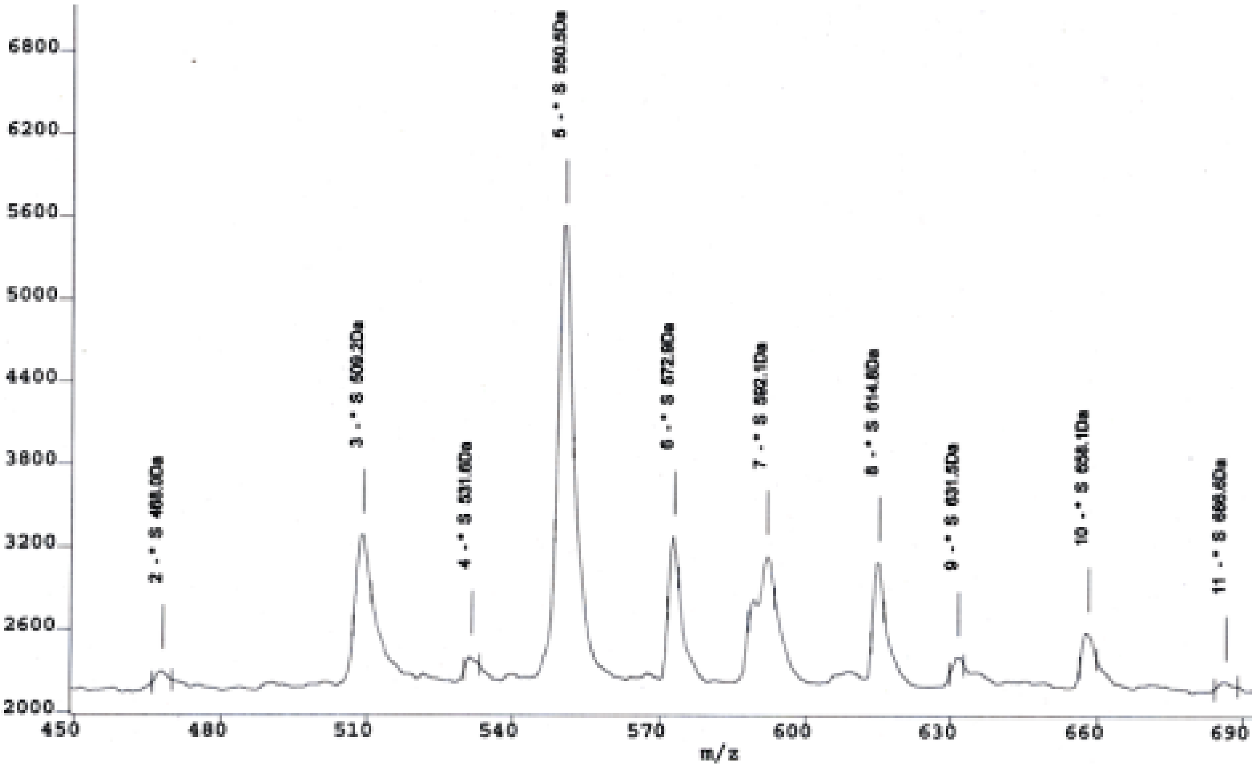


Figure 1.31 MALDI-TOF spectrum of the products obtained after quenching the sample from

***Figure 1.29** with MeOH. Mass peak 550.5 corresponds to tripropoxy-monohydroxy-calix[4]arene (together with 572.9 and 590.1 resulting from binding of sodium and potassium ions respectively) and mass peak 592, together with 614.8 and 631.5, is from **3**. Mass peak 509 corresponds to dipropoxy-dihydroxy-calix[4]arene together with 531.4.*

More encouraging was the use of regular crown ethers, like 18-Crown-6 or 12-Crown-4, where a experiment similar to the above mentioned using the former instead of a calix[4]arene was performed. After one hour of reaction the quenching with MeOH and analysis by ^{1}H-NMR and GC-MS was performed. Even though other products than 18-Crown-6 were obtained those were only present as minor by-products. When using 18-Crown-6 the polymerization was almost quantitatively after only 5-10 min both at room temperature (**PS10** and **PS12**) but also when the polymerization was performed at low temperature, e.g. –78 °C (**PS11**), see ***Table 1.4***.

Table 1.4. The collected data used in the anionic polymerization of styrene. The ratio between initiator and styrene is in all experiments 1/10, which in theory should result in a polystyrene with a molecular weight about 1040 g/mol, corresponding to a chain length of 10 monomeric units.

Polymer Nr.	**Crown ether**	**Initiator**	**Solvent**	**Reaction Time / min**	**Reaction Temperature / °C**	**Yield / %**
PS1	None	Bu^{t}Li	Cyclohexane	30	40-50	78
PS2	None	*n*-BuLi	Cyclohexane	30	40-50	46
PS3	None	*n*-BuLi	Toluene	10	Ambient	25
PS4	None	*n*-BuLi	Toluene	10	40-50	66
PS5	**3**	*n*-BuLi	Cyclohexane	30	40-50	30
PS6	**3**	*n*-BuLi	Cyclohexane	30	-78	None
PS7	12-Crown-4	*n*-BuLi	Toluene	10	-78	53
PS8	12-Crown-4	*n*-BuLi	Toluene	10	Ambient	93
PS9[*]	12-Crown-4	*n*-BuLi	Toluene	10	Ambient	86
PS10	18-Crown-6	*n*-BuLi	Cyclohexane	5	Ambient	90
PS11	18-Crown-6	*n*-BuLi	Toluene	10	-78	91
PS12[*]	18-Crown-6	*n*-BuLi	Toluene	10	Ambient	92
PS13	Benzo-12-Crown-4	*n*-BuLi	Toluene	Overnight	Ambient	None
PS14	Dicyclohexano-18-Crown-6	*n*-BuLi	Toluene	10	-78	90
PS15	Dicyclohexano-18-Crown-6	*n*-BuLi	Toluene	10	Ambient	59
PS16	Benzo-18-Crown-6	*n*-BuLi	Toluene	10	Ambient	None
PS17	4’-Methylbenzo-18-Crown-6	*n*-BuLi	Toluene	Overnight	Ambient	None

From ***Table 1.4*** it is clear that the addition of 18-Crown-6, dicyclohexano-18-Crown-6 and 12-Crown-4 increases the reaction rate but when the crown ether is substituted with an aromatic moiety the polymerization fails. This properly due to reaction between the crown ether and initiator, similarly to the case when calix[4]arene **3** is added, and this reaction takes place very quickly since the leaving group is these cases now is a phenoxy rather than a propyl group.

The prepared polystyrenes was then subjected to analysis by GPC, DSC and NMR in order to determine the tacticity of the collected polymer, see ***Table 1.5***. The NMR analysis was restricted to ^{1}H-NMR since ^{13}C-NMR on polymers is rather time-consuming often in the range of 10 hours for each spectrum if proper analysis should be possible. Therefore the statement that the polymers were

---

[*] In this experiment the living character of the polymerization was seen by first consuming one equivalent styrene followed by the addition of another equivalent styrene. The reaction time indicated is the reaction time before and after the second addition.

found all to be atactic should be viewed accordingly carefully and further analysis might be advisable but outside the range of this project. This aspect has though not been investigated further due to lack of time.

Table 1.5. Results from the GPC and DSC analysis performed on polystyrene using anionic polymerization. In all cases the NMR showed that the polymers were atactic.

Polymer Nr.	Glass-transition temp. / °C	Peak molecular weight / g/mol	Polydispersity M_w/M_n
PS1	82.9	4450	1.26
PS2	74.0	2660	1.07
PS3	81.4	3500	1.10
PS4	81.6	4220	1.14
PS5	65.3	2120	1.26
PS7	108.2	207300	2.35
PS8	105.8	150900	3.57
PS9*	105.3	144000	4.04
PS10	106.0	185000	2.88
PS11	90.9	12000	1.48
PS12*	105.9	199300	3.53
PS14	107.4	307300	3.05
PS15	105.2	155800	2.71

The DSC analysis is also rather ambiguous since low glass-transition temperatures is observed in the cases **PS1** to **PS5**, e.g. those without crown ether or with compound **3** added, and rather high glass-transition temperatures is observed in the rest, with the exception of **PS11**. The low glass-transition temperatures can be explained in terms of the low molecular weight observed for the first five polymers, as explained above in the case of **PS1-PS4** and according to ***Equation 1.5***, but for the rest the high glass-transition temperatures is rather difficult explained. The molecular weight of the polymers having the high glass-transition temperatures is in all cases above 140000 and the normal rule of thump is that when comparing polymers having molecular weight above 20000 the glass-transition temperature is constant with regard to molecular weight. The glass-transition temperature is also a function of heating rate but in all the above measurements the heating rate was 10 °C/min which is sufficiently slow in order to ensure that the observed glass-transition temperature is very close to the so-called zero glass-transition temperature, e.g. the theoretical observed when heating rate is 0 °C/min. Another possibility could be that the DSC was improper calibrated which is likely since the glass-transition temperatures are more or less the same when speaking about the high molecular weight samples.

When comparing the two tables, e.g. ***Table 1.4*** and ***Table 1.5***, the following conclusions can be made. If addition of crown ethers is used the molecular weight of the polystyrene becomes much higher within the same reaction time and with an increased polydispersity compared to the experiments without crown ethers. This indicates that only a small part of the initiator reacts with the styrene but at the same time the addition of crown ethers also increases the reactivity since the increased chain-length was produced in the same reaction time. There seems no large difference in using the different crown ethers **PS8**, **PS10** and **PS15**; though in the latter two cases the molecular weight increases a little together with a slightly decrease in polydispersity. But when comparing the **PS7** and **PS14** the increased molecular weight is also followed by an increase in polydispersity, disregarding **PS11**.

All the above experiments were run in ordinary laboratory glass-ware that was flame dried prior to use, the solvents and monomer were dried and distilled by standard methods, the concentration of the initiator was determined by titration but rigorously controlled conditions were not present. It must therefor be emphasized that these observations should be retried in highly controlled manners, e.g. purification and distillation of solvents and monomer using vacuum line technique, distillation of the initiator and recrystallisation of the crown ethers, in order to make sure that the above conclusions are valid. But these preliminary results indicate that someone should take the effort and time since they are rather interesting.

---

[*] In this experiment the living character of the polymerization was seen by first consuming one equivalent styrene followed by the addition of another equivalent styrene. The reaction time indicated is the reaction time before and after the second addition.

2 Calixarenes

As long ago as 1872 Johann Friedrich Wilhelm Adolph von Baeyer began the investigation on the reaction between phenol and formaldehyde in presence of strong acids[1]. The products were characterized as cement-like substances at that time, but now at the beginning of a new millenium we call them polymers. Adolph von Baeyer and others had recognized that this hard, cement-like material should have a potential as an item of commerce. On February 18, 1907 Leo Baekeland filed for a patent to make the material called Bakelite[2] made from phenol and formaldehyde in presence of a small and controlled amount of base. The structure of Bakelite at that time was totally unknown, and still today some details are not clearly understood. It was clear though that phenol reactive at the ortho and para positions formed a highly cross-linked network where each phenolic residue is attached to three other phenolic residues, see ***Figure 2.1***.

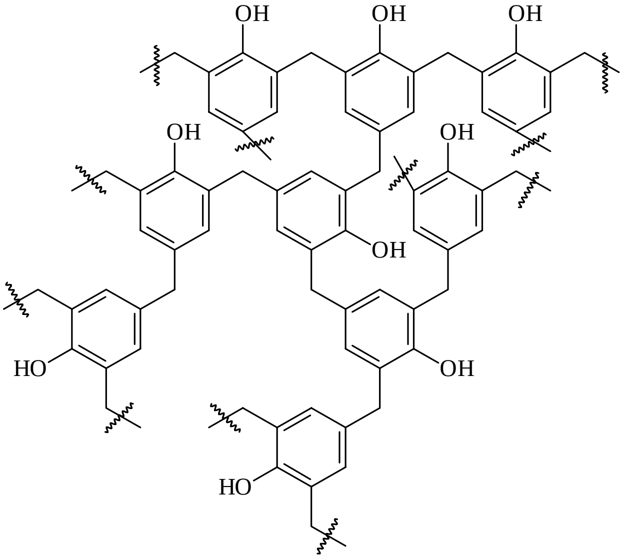


Figure 2.1. Section of the Bakelite structure.

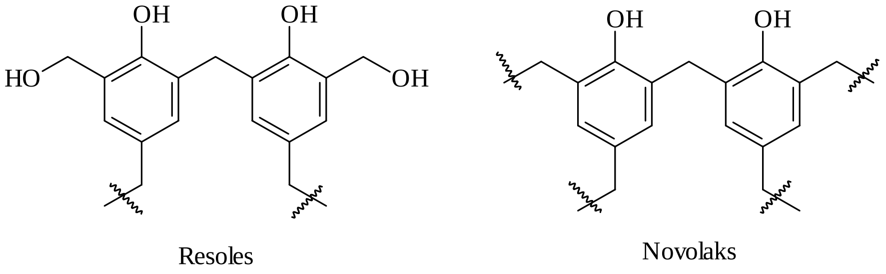
---

[1] Baeyer, A.; *Ber.*, 1872, **5**, 25

[2] Baekeland, L.H.; *U.S. Patent 942699*, October 1908

2.1 Introduction to calix[4]arenes

A way to reduce the number of reactive positions was to block the para-position by using para-*t*-butylphenol, which was the idea of Alois Zinke and Erich Ziegler thereby also reducing the highly cross-linked structure to a linear polymer. They wanted to study the so-called *curing* process, where resoles can be converted into novolak structures, see ***Figure 2.2***.



Resoles

Novolaks

Figure 2.2. Partial structures of resoles and novolaks.

In 1941 they published the results from heating the "precursor" or resin[*] in linseed oil[3] but no structure was written for the product isolated, having elemental analysis indicating $C_{11}H_{14}O$ and the absence of ether linkages. It was not until 1944 that Zinke[4] introduced the idea of a cyclic tetrameric structure based on the cryoscopic molecular weight combined with the above found elemental analysis, see ***Figure 2.3***.

1

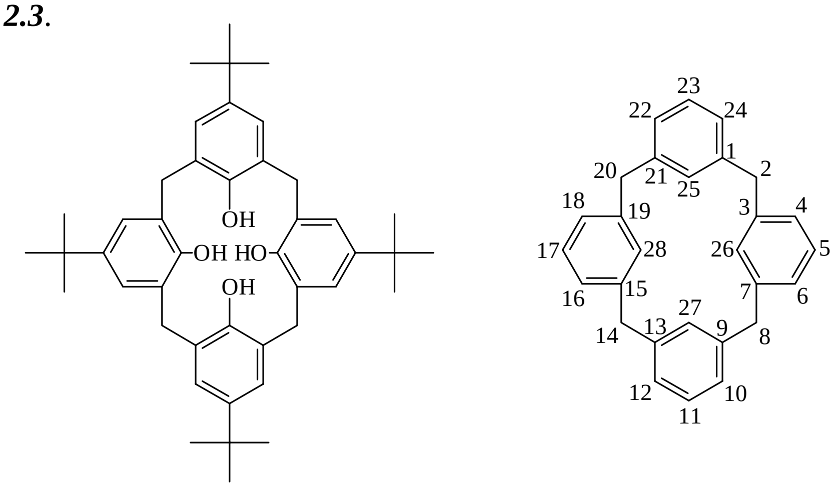


*Figure 2.3. Left is shown the cyclic tetrameric structure of 5,11,17,23-tetra(tert-butyl)-25,26,27,28-tetrahydroxycalix[4]arene (**1**). Right is shown the numbering of the cyclic structure.*

---

[*] the initial product obtained from reacting *p-tert*-butylphenol and formaldehyde in the presence of base or acid

[3] Zinke, A., Ziegler, E.; *Ber.*, 1941, **74**, 1729

The systematic name reported by Chemical Abstracts is pentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,26,27,28-tetrol-5,11,17,23-tetrakis(1,1-dimethylethyl) but luckily Gutsche had a more friendly nomenclature for the compound (**1**) and proposed 5,11,17,23-tetra(*tert*-butyl)-25,26,27,28-tetrahydroxycalix[4]arene[5], see ***Figure 2.3***. Having this structure the calixarenes belong to the class of $[1_n]$metacyclophanes. The name calix meaning beaker is a good description of one of the four conformations the calix[4]arenes are capable of adopting (depending on the substitution pattern), see ***Figure 2.4*** where the *cone* conformation is shown. The four aryl groups form a cavity resembling a beaker or basket. The suffix arene refers to the aromatic units and the number in the brackets ([n]) specifies the number of aromatic units defining the calixarene in speak. Depending on the preparative details, calixarenes can be made with different values of n, but when n= 4, 6, 8 the calixarene can be prepared in good yields relatively easy while other values of n is difficult to prepare and often only in very low yields.

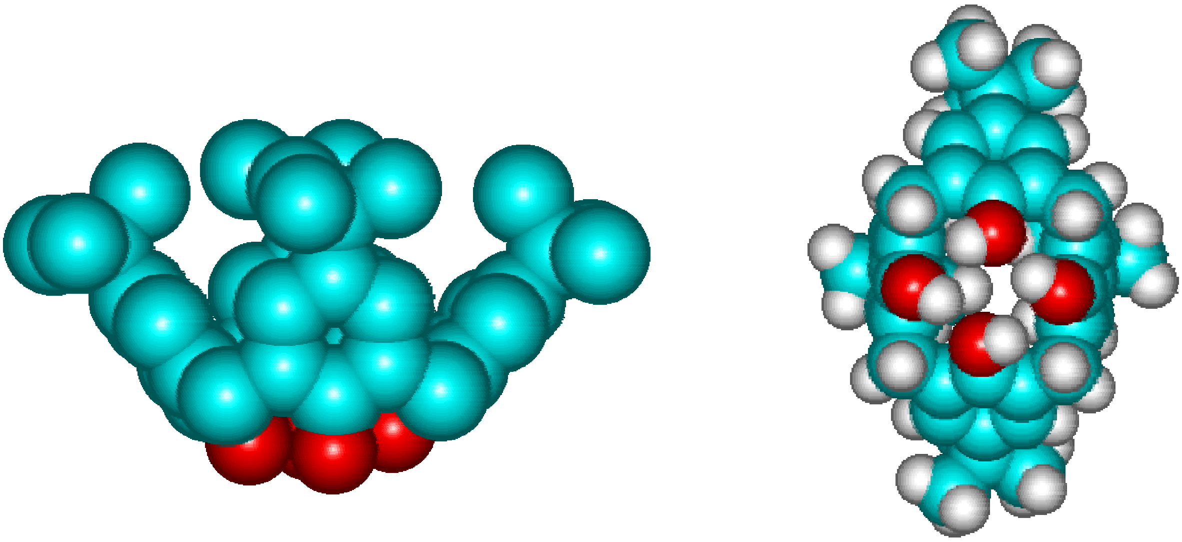


Figure 2.4. Left is shown a space filling molecular model of ***(1)*** *without hydrogen, right is* ***(1)*** *pictured from the lower rim side.*

---

[4] Zinke, A., Ziegler, E.; *Ber.*, 1944, **77**, 264

[5] Gutsche, C.D., Muthukrishnan, R.; *J. Org. Chem.*, 1978, **43**, 4905

In these types of molecular structures two distinct regions are present, the *lower rim* where the phenolic oxygens are situated and the *upper rim* defined by the para positions of the aromatic nuclei. As seen in ***Figure 2.4*** (right part), the phenolic oxygens are “closing” the basket due to intramolecular hydrogen bonds thereby making the *cone* conformation the preferred when discussing 25,26,27,28-tetrahydroxy-calix[4]arenes. This conformation has been confirmed by X-ray[6] and ^{1}H-NMR studies[7]. When ^{1}H-NMR studies are performed in polar solvents such as pyridine-d$_5$ the hydrogen bonding in the calixarene is disrupted and so is the pseudo C_{4v} symmetry[8],[9]. Another way of disrupting the intramolecular hydrogen bonding is by functionalization of the hydroxy groups; the tetramethoxy and tetraethoxy derivatives of calix[4]arene are no longer fixed in the *cone* conformation. These substituents are small enough to pass through the intraannulus allowing one or two aromatic units to rotate around the axis that passes through the *meta* carbon atoms bonded to the bridging methylene groups. The conformations, available though this type of rotation, are *cone*, *partial cone*, *1,3-alternate* and *1,2-alternate* pictured in ***Figure 2.5***.

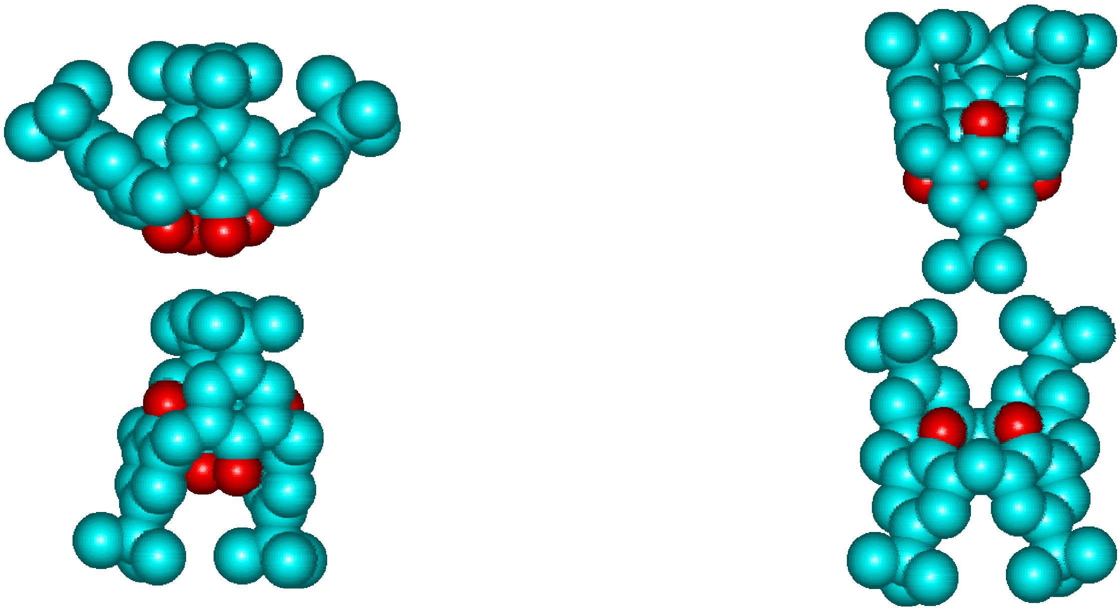


Figure 2.5. Representations of the cone (upper left), partial cone (upper right), 1,3-alternate (lower left) and 1,2-alternate (lower right) conformations showed without the alkoxy groups.

---

[6] Andreetti, G.D., Ungaro, R., Pochini, A.; *J. Chem. Soc., Chem. Commun.*, 1979, 1005

[7] Kämmerer, H., Happel, G., Caesar, F.; *Makromol. Chem.*, 1972, **162**, 179

[8] Gutsche, C.D., Bauer, L.; *Tetrahedron Letters*, 1981, **22**, 4763

[9] Gutsche, C.D., Bauer, L.; *J. Am. Chem. Soc.*, 1985, **107**, 6052

When the alkyl group is propyl or larger the rotational barrier is large enough to ensure stability to above 200 °C and depending on the method used it is possible to isolate the four different conformers as thermodynamically stable compounds[10,11,12]. The *cone* conformation shown above still possesses some degree of flexibility, especially at room temperature, and it has been shown that the C_{4v} symmetry that normally is observed by ^{1}H-NMR actually is a convolution of two C_{2v} symmetrical *pinched cone* conformers, see ***Figure 2.6***.

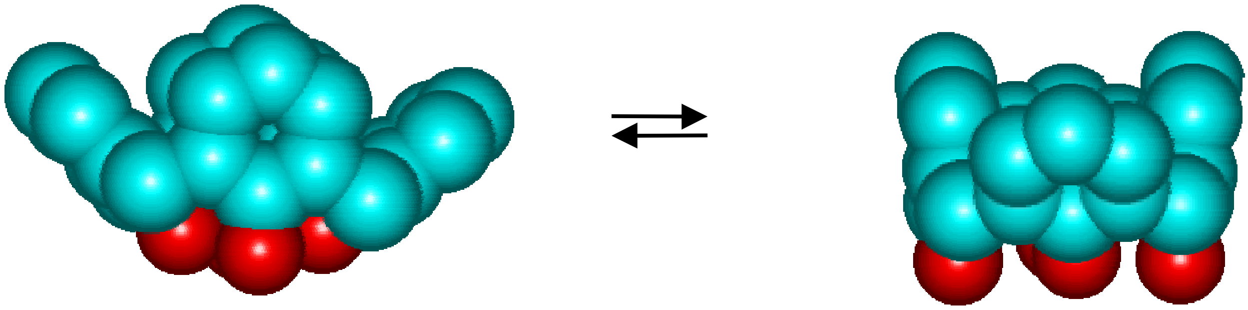


Figure 2.6. The rapid interconversion between the two C_{2v} symmetrical pinched cone conformers. Again shown without alkoxy substituents.

The coalescence temperature for this type of exchange is normally well below room temperature with a $\Delta G^\ddagger$ around 10-15 kcal/mol[13,14].

A very powerful tool to distinguish between the four conformations is NMR spectroscopy since the resonances of the methylene bridges are very different for each conformer, see ***Figure 2.7*** and ***Table 2.1***. The actual resonance frequency is to some extent rather dependent on the solvent in use and the given range is for a nonpolar solvent as $CHCl_3$. The geminal coupling constant of the methylene-bridge is normally in the range of 13-14 Hz depending on how the calix[4]arene is substituted. Similarly is the ^{13}C-NMR also a powerful tool where the methylene carbon atoms normally are found around 30-32 ppm depending on substitution and conformation. As expected for

---

[10] Iwamoto, K.; Araki, K.; Shinkai, S.; *J. Chem. Soc. Perkin Trans. 1*, 1981, 1611

[11] Gutsche, C.D., Balram, D., Jeffrey, A.L., Kwang, H.N., Lorenz, J.B.; *Tetrahedron*, 1983, **39**, 409

[12] Iwamoto, K., Shinkai, S.; *J. Org. Chem.*, 1992, **57**, 7066

[13] Ikeda, A., Tsuzuki, H., Shinkai, S.; *J. Chem. Soc. Perkin Trans. 2*, 1994, 2073

[14] Arduini, A., Fabbi, M., Mantovani, M., Mirone, L., Pochini, A., Secchi, A., Ungaro, R.; *J. Org. Chem.*, 1995, **60**, 1454

the *cone* conformers only one signal is observed but if the calix[4]arene is substituted in a way destroying the symmetry then the NMR spectra quickly gets more complicated.

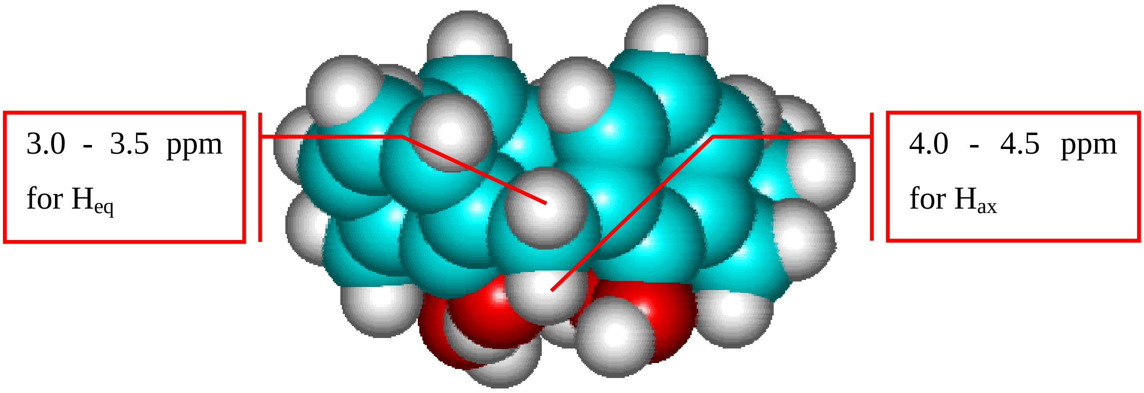


Figure 2.7. ^{1}H-NMR signals for the two methylene hydrogen atoms. The assignment was done using NOE-experiments on calix[4]arene derivatives[15]*.*

Table 2.1. ^{1}H-NMR patterns for the methylene protons of calix[4]arenes in various conformations.

Conformation	**^{1}H-NMR pattern**
Cone	One pair of doublets
Partial cone	Two pairs of doublets (1:1) or one pair of doublets and one singlet (1:1)
1,3-Alternate	One singlet
1,2-Alternate	One singlet and two doublets (1:1)

2.1.1 Synthesis

The original procedure by Zinke[3,4] lacked reproducibility since the yields as well as the actual products formed were varying to a large extent. Cornforth[16] and later Gutsche[17] found that

---

[15] Arduini, A., Pochini, A., Reverberi, S., Ungaro, R.; *Tetrahedron*, 1986, **42**, 2089

[16] Cornforth, J.W., D'Arcy Hart, P., Nicholls, G.A., Rees, R.J.W., Stock, J.A.; *Br. J. Pharmacol.*, 1955, **10**, 73

[17] Gutsche, C.D., Iqbal, M., Stewart, D.; *J. Org.Chem.*, 1986, **51**, 742

following the procedure by Zinke the base-induced condensation of p-substituted phenols and formaldehyde produced mixtures, which sometimes contained and sometimes did not contained the cyclic tetramer. The problem arise due to a neutralization of what is referred to as the “precursor” to removing some, but not all, of the base which is initially added to effect the condensation. The “precursor” is a thick viscous mass and therefor this neutralization becomes very difficult to reproduce from one experiment to another. For some unknown reason the product from the curing process is dependent on the amount of base present. Investigations by Gutsche showed that the yield of tetramer reaches a maximum at 0.03-0.04 equivalents of base and falls rapidly on both sides of the maximum. If the amount of base present was increased the product isolated was instead the cyclic hexamer (e.g. calix[6]arene) which was discovered by accidence when a ten-fold amount of base was used. Also the nature of base, or rather the cation, has a significant effect on the outcome. Using LiOH as base the yields are very low, NaOH tends to give maximum yields of the cyclic octamer (which then is cracked to the cyclic tetramer, see later in this section), while KOH, RbOH and CsOH produces the cyclic hexamer in highest yields.

The procedure for preparing the tetra(*tert*-butyl)-tetrahydroxy-calix[4]arene (**1**)[18] is given in the *Experimental* section in detail; a mixture of p-*tert*-butylphenol, 37 % formaldehyde and NaOH (0.045 eqv. to the phenol) is heated for 2 hours at 110-120 °C to produce the “precursor”. The “precursor” is then refluxed in diphenyl ether for another 2 hours, cooled and added ethyl acetate to precipitate (**1**) in 62 % yield. If the “precursor” instead is refluxed in xylene (mixture) the product collected will be the octa(*tert*-butyl)-octahydroxy-calix[8]arene[19] in 60-65 % yield. If the base in use is KOH (0.34 eqv.), followed by reflux in xylene the product will be the hexa(*tert*-butyl)-hexahydroxy-calix[6]arene[20] in 80-85 % yield. As indicated above is the synthesis of the cyclic octamer and tetramer very similarly except for the choice of solvent and thereby temperature causing Gutsche[21] to suggest that the cyclic octamer is the kinetic product while the cyclic tetramer is the thermodynamic product. It was proven by heating octa(*tert*-butyl)-octahydroxy-calix[8]arene in diphenyl ether and identifying the product as tetra(*tert*-butyl)-tetrahydroxy-calix[4]arene (**1**).

The mechanism for formation of the calixarenes is an incompletely solved problem still. The initial step in the sequence of reactions are reasonably well understood, starting with an *ortho*-

---

[18] Gutsche, C.D., Iqbal, M.; *Org. Synth., Coll. Vol.*, 1993, **8**, 75

[19] Munch, S.H., Gutsche, C.D.; *Org. Synth., Coll. Vol.*, 1993, **8**, 80

[20] Gutsche, C.D., Dhawan, B., Leonis, M., Stewart, D.; *Org. Synth., Coll. Vol.*, 1993, **8**, 77

[21] Gutsche, C.D.; *Acc. Chem. Res.*, 1983, **16**, 161

hydroxymethylation of p-*tert*-butylphenol followed by an arylation thought to proceed via an intermediate *ortho*-quinonemethide, see ***Figure 2.8***, which then reacts with another phenolate anion producing a diphenylmethane derivative and so fourth.

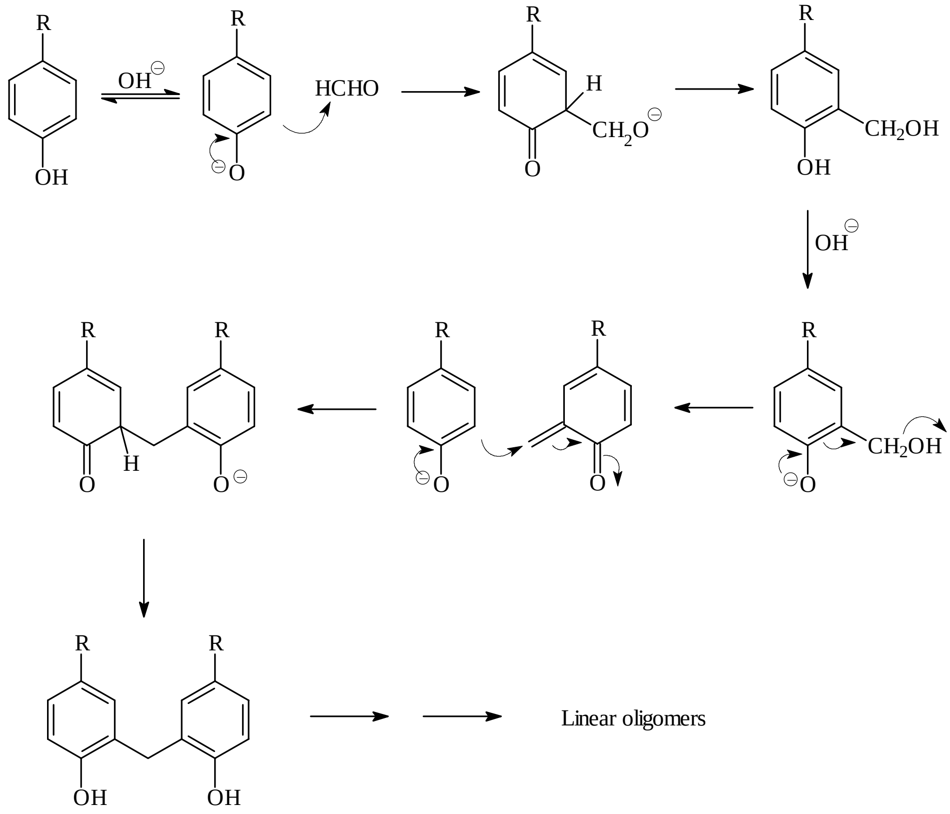


Figure 2.8. Proposed mechanism for the formation of linear oligomers.

The presence of more than 36 noncyclic components are present in the “precursor” by HPLC analysis but none cyclic components was found[22]. How the cyclic oligomers are produced from this mixture remains to be clarified and will not be treated in more detail than to say that the proposed mechanisms are rather disputable[23,24,25,26] having the actually reaction conditions in mind. The concentration of reactants is unfavorable for the cyclization to take place which normally require high dilution.

---

[22] Gutsche, C.D.; *Monographs in Supramolecular Chemistry*, 1989, **1**

[23] Dhawan, B., Chen, S.-I., Gutsche, C.D.; *Makromol. Chem.*, 1987, **188**, 921

[24] Paulus, E., Böhmer, V.; *Makromol. Chem.*, 1984, **185**, 1921

[25] Dhawan, B., Gutsche, C.D.; *J. Org. Chem.*, 1983, **48**, 1536

2.1.1.1 Upper rim functionalization

At present the chemistry of calixarenes has been developed extensively making several different functionalizations possible. In order to introduce a given functional group removing the alkyl group, usually *tert*-butyl, is necessary and is done by a retro Friedel-Craft alkylation reaction; transalkylation in the presence of a Lewis acid and an acceptor solvent such as phenol[27]. The de-alkylation can be used on both tetrahydroxy-calix[4]arenes and tetraalkoxy-calix[4]arenes. The reaction can also in some instances be used for selective removal of alkyl groups if the *lower rim* has been partially esterified[28], e.g. to produce dibenzoyl-dihydroxycalixarene, since the alkyl groups *para* to a phenol are released more readily than those *para* to an esterified OH group, see ***Figure 2.9***.

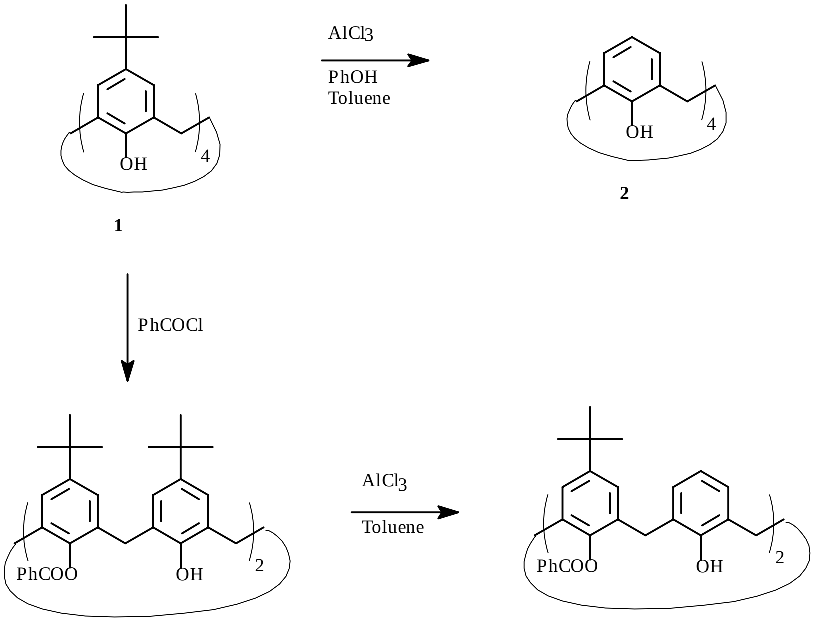


Figure 2.9. De-alkylation of calix[4]arenes.

Electrophilic substitution has been used to functionalize the *p*-H calixarene by which introduction of sulfonic acids, nitro and halogens derivatives have been accomplished. Experience has shown that calix[4]arene ethers behave better in electrophilic substitution compared to the *p*-H

---

[26] Gutsche, C.D., Gutsche, A.E., Karaulov, A.I.; *J. Incl. Phenom.*, 1985, **3**, 447

[27] Tashiro, M., Fukata, G., Mataka, S., Oe, K.; *Org. Prep. Proced. Int.*, 1975, **7**, 231

[28] Gutsche, C.D., See, K.A.; *J. Org. Chem.*, 1992, **57**, 4527

tetrahydroxy calix[4]arene (**2**), making the starting material the *p*-H tetraalkoxy calix[4]arene the preferred choice. The nitro groups has recently been introduced by *ipso*-nitration on the tetra(*tert*-butyl)-tetraalkoxy-calix[4]arene by using nitric acid in acetic acid[29] resulting in the corresponding tetranitro-calix[4]arenes (R_1-R_4 = NO_2, Y_1-Y_4 = H or alkyl, see ***Figure 2.10***) in good yields. If the starting *p*-H calixarene is partially substituted at the *lower rim*, the substitution takes place at the more reactive phenol rings (R_1, R_3 = NO_2, Y_1, Y_3 = H, Y_2, Y_4 = ArCO), see ***Figure 2.10***. The nitro groups can then by reduced to amino groups by reaction with Raney nickel/hydrazine in good yields (60-70 %).

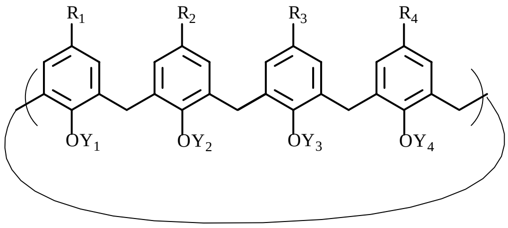


Figure 2.10. Electrophilic substitution of calix[4]arenes. Variation of Y_1-Y_4 and R_1-R_4 is explained in text above and beneath.

Functionalization with halogens has been restricted to bromine[30,31] and iodine[32] using N-BromoSuccinimide (NBS) and silver trifluoroacetate/I_2 respectively. Both reactions proceed to the tetra-halogenated calix[4]arene (R_1-R_4 = Br or I, Y_1-Y_4 = alkyl) in around 90 % yields.

Selective Gross formylation[33,34] and nitration[35] has been achieved from the *p*-H calix[4]arene (R_1-R_4 = CHO or NO_2; R_1-R_3 = CHO or NO_2, R_4 = H; R_1,R_3 = CHO or NO_2, R_2, R_4 = H; R_1 = CHO or NO_2, R_2-R_4 = H; Y_1-Y_4 = $CH_2CH_2OCH_2CH_3$).

Larsen and Jørgensen[31] have developed another very useful regioselective functionalization starting from the readily available tetrabromo-tetrapropoxy-calix[4]arene (**4**). This method allow selectively

---

[29] Jakobi, R.A., Böhmer, V., Grüttner, C., Kraft, D., Vogt, W.; *New J. Chem.*, 1996, **20**, 493

[30] Gutsche, C.D., Pagoria, P.F.; *J. Org. Chem.*, 1985, **50**, 5795

[31] Larsen, M., Jørgensen, M.; *J. Org. Chem.*, 1996, **61**, 6651

[32] Arduini, A.; Pochini, A.; Sicuri, A.R., Secchi, A., Ungaro, R.; *Gazz. Chim. Ital.*, 1994, **124**, 129

[33] Arduini, A., Fanni, S., Manfredi, G., Pochini, A., Ungaro, R., Sicuri, A.R., Ugozzoli, F.; *J. Org. Chem.*, 1995, **60**, 1448

[34] Arduini, A., Manfredi, G., Pochini, A., Sicuri, A.R., Ungaro, R.; *J. Chem. Soc., Chem. Commun.*, 1991, 936

[35] Van Loon, J.D., Heida, J.F., Verboom, W., Reinhoudt, D.N.; *Recl. Trav. Chim. Pays-Bas*, 1992, **111**, 353

bromine-lithium exchange at the *upper rim* and thereby accessing a large diversity of functionality's otherwise not or only hardly obtainable, see ***Table 2.2***.

*Table 2.2. Selective bromine-lithium exchange at the upper rim of 5,11,17,23-tetrabromo-25,26,27,28-tetrapropoxy-calix[4]arene (**4**) and of 5,17-dibromo-25,26,27,28-tetrapropoxy-calix[4]arene (**5**). The letters is referring to Figure 2.10, Y_1-Y_4 = propyl. In each row is the product, obtained after reaction with a given electrophile, indicated by italic script. The number in bold is referring to the numbering used in the Experimental section.*

	R_1	R_2	R_3	R_4
1 eqv.	**Li**	Br	Br	Br
n-BuLi/THF/-78 °C	*COOH*			
> 2 eqv.	**Li**	Br	**Li**	Br
n-BuLi/THF/-78 °C	*H (**5**)*		*H (**5**)*	
	COOH		*COOH*	
	OH		*OH*	
	CHO		*CHO*	
8 eqv.	**Li**	**Li**	**Li**	**Li**
t-BuLi/THF/-78 °C	*D*	*D*	*D*	*D*
	COOH	*COOH*	*COOH*	*COOH*
	SCH_3	SCH_3	SCH_3	SCH_3
2 eqv.	**Li**	H	**Li**	H
n-BuLi/THF/-78 °C	*COOH (**19**)*		*COOH (**19**)*	
	*CHO (**8**)*		*CHO (**8**)*	
	$B(OH)_2$ *(**17**)*		$B(OH)_2$ *(**17**)*	

The above mentioned regioselective bromo-lithium exchange reaction accesses the functionalization necessary in biaryl coupling reactions. The three most used types of reactions available for biaryl couplings are Suzuki[36], Negishi[37] and Stille[38] coupling reactions, see ***Figure***

---

[36] Miyaura, N., Suzuki, A.; *Chem. Rev.*, 1995, **95**, 2457

[37] Negishi, E.; *J. Org. Chem.*, 1977, **42**, 1821

2.11. In the case of calixarenes all three has been used to prepare *deep* or *large cavity* calixarenes[39,40,41,42,43].

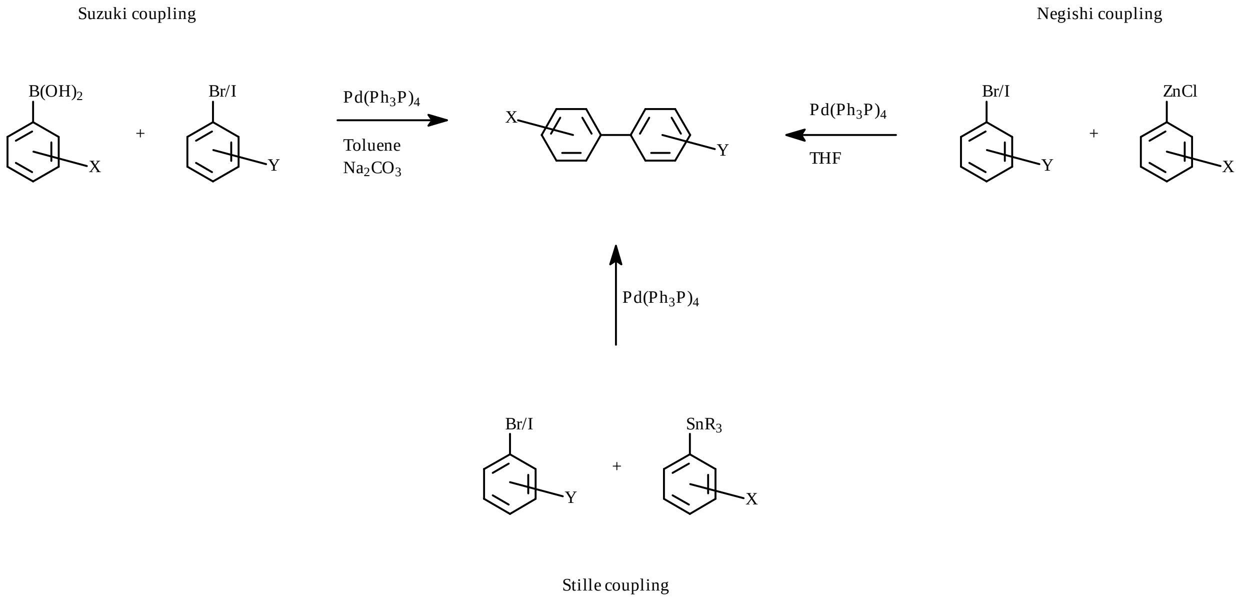


Figure 2.11. Suzuki, Negishi and Stille biaryl coupling reactions.

2.1.1.2 Lower rim functionalization

The functionalization of the *lower rim* is in this thesis restricted to the preparation of ether linkages on calix[4]arenes. This can by done either partial or exhaustive both using the Williamson reaction. The etherification can generally be effected on all of the hydroxy groups if sufficiently reactive reagents are used. Methyl, ethyl, propyl, allyl and benzyl ethers have been prepared by this reaction in good yields[44]. If the group introduced is bulkier than ethyl the product will be a calix[4]arene locked in one of the four possible conformations, see ***Figure 2.5***. The

---

[38] Stille, J.K.; *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 508

[39] Arduini, A. Pochini, A., Rizzi, A., Sicuri, A.R., Ungaro, R.; *Tetrahedron Letters*, 1990, **31**, 4653

[40] Haino, T., Harano, T., Matsumura, K., Fukazawa, Y.; *Tetrahedron Letters*, 1995, **36**, 5793

[41] Wang, M.S., Nicoud, J-F.; *Tetrahedron Letters*, 1993, **34**, 8237

[42] Juneja, R.K., Robinson, K.D., Johnson, C.P., Atwood, J.; *J. Am. Chem. Soc.*, 1993, **115**, 3818

[43] Larsen, M., Jørgensen, M.; *J. Org. Chem.*, 1997, **62**, 4171

[44] Gutsche, C.D., Dhawan, B., Levine, J.A., No, K.H., Bauer, L.J.; *Tetrahedron*, 1983, **39**, 409

stereochemical outcome of the reaction is highly dependent on the nature of the base, counterion, solvent and temperature[45]. The method used for obtaining the *cone* conformation is treatment of the tetrahydroxy-calix[4]arene (**2**) with excess of NaH in DMF or DMF/THF at room temperature followed by addition of the proper halogenide also in excess. If the *1,3-alternate* conformation is wanted the base is change to Cs_2CO_3 and the solvent is DMF at 80 °C or refluxing acetonitrile[46]. The two other conformations are very difficult to prepare demanding extensive column chromatography and are often only found as by-products in reaction mixtures of the *cone* or *1,3-alternate* conformations. It has been suggested that the faster the alkylation reaction is the more of the *cone* conformer is formed[47].

The trialkylated calix[4]arene can by synthesized in good yields if BaO/$Ba(OH)_2$ is used as base in DMF at 70 °C and excess of alkylhalide[48]

In the case of disubstituted calix[4]arenes the substitution pattern can by either 25,27-disubstituted (called *1,3-disubstituted* or *distal*) or 25,26-disubstituted (called *1,2-disubstituted*). The later though more difficult to isolate in large quantities. The most usable method for preparing the *1,2-disubstituted* calix[4]arene is selectively cleavage of two adjacent methoxy groups in 25,26,27,28-tetramethoxy-calix[4]arene (**22**) with $TiBr_4$ in $CHCl_3$[49]. The *1,3-disubstituted* calix[4]arenes is normally synthesized from tetrahydroxy-calix[4]arene by using one equivalent K_2CO_3 as base and two equivalents of the alkylating agent in refluxing acetonitrile or acetone. The later solvent is preferable since the amount of by-products is lower than when using acetonitrile. The product is prepared in the *cone* conformation in good to high yields.

A monosubstituted (e.g. 25-substituted) calix[4]arene can be synthesized by three ways, see also ***Figure 2.12***:

---

[45] Groenen, L.C., Ruël, B.H., Casnati, A., Timmerman,P., Verboom, W., Harkema, S., Pochini, A., Ungaro, R., Reinhoudt, D.N.; *Tetrahedron Letters*, 1991, **32**, 2675

[46] Verboom, W., Datta, S., Asfari, Z., Harkema, S., Reinhoudt, D.N.; *J. Org. Chem.*, 1992, **57**, 5394

[47] Gutsche, C.D., Reddy, P.A.; *J. Org. Chem.*, 1991, **56**, 4783

[48] Iwamoto, K., Araki, K., Shinkai, S.; *Tetrahedron*, 1991, **47**, 4325

[49] Arduini, A., Casnati, A., Dodi, L., Pochini, A., Ungaro, R.; *J. Chem. Soc., Chem. Commun.*, 1990, 1597

- indirectly by selective removal of one of the two groups from a 25,27-disubstitued calix[4]arene or selective removal of three groups from a 25,26,27,28-tetrasubstitued calix[4]arene by using either one or three equivalents of trimethylsilyliodide (Me_3SiI) respectively[50]
- directly by alkylation of the tetrahydroxy-calix[4]arene with excess of alkylating agent in presence of 1.2 equivalents of CsF in DMF[51]
- directly by alkylation of the tetrahydroxy-calix [4]arene with alkylbromide in acetonitrile using $NaHCO_3$ as base.

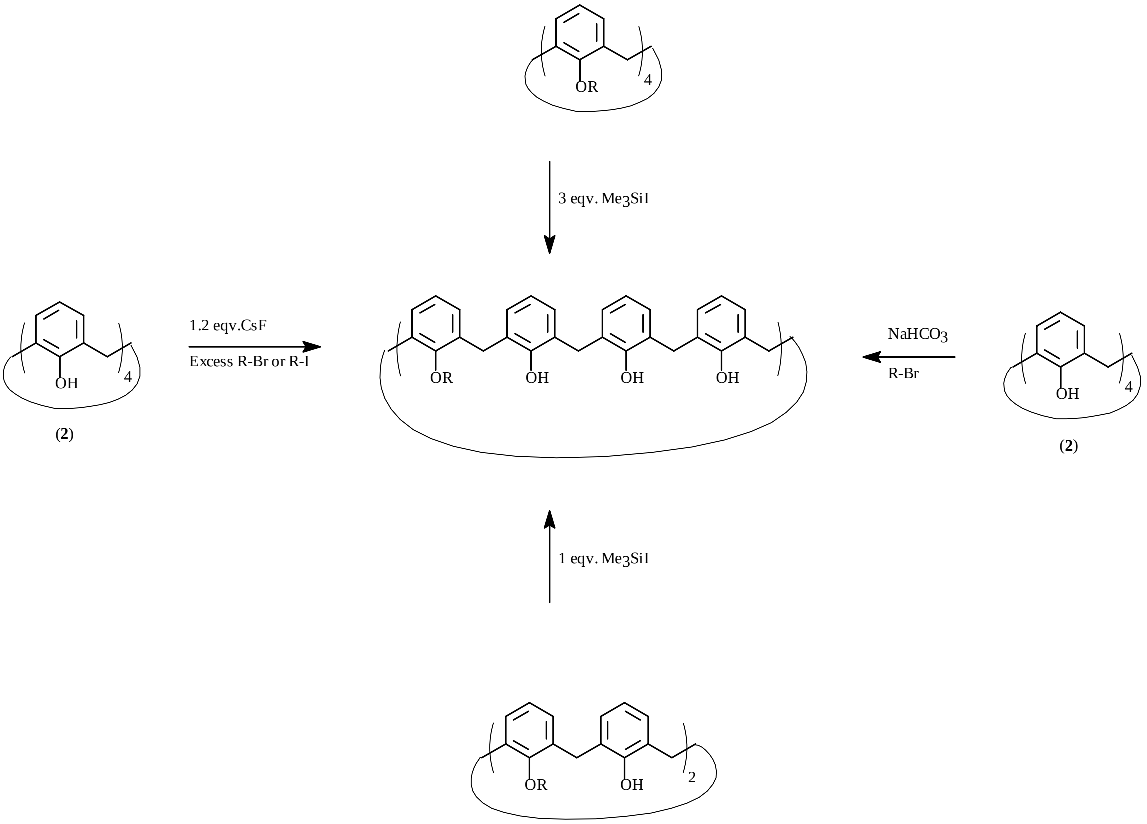


Figure 2.12. The mono-functionalization of calix[4]arene.

The reason for using these very weak bases in the alkylation is the small difference between pK_{a1} and pK_{a2}, see ***Figure 2.13***.

---

[50] Böhmer, V., Vogt, W., Harris, S.J., Leonard, R.G., Collins, E.M., Deasy, M., McKervey, M.A., Owens, M.; *J. Chem. Soc., Chem. Commun.*, 1987, 896

[51] Groenen, L.C., Ruel, B.H.M., Casnati, A., Verboom, W., Pochini, A., Ungaro, R., Reinhoudt, D.N.; *Tetrahedron*, 1991, **47**, 8379

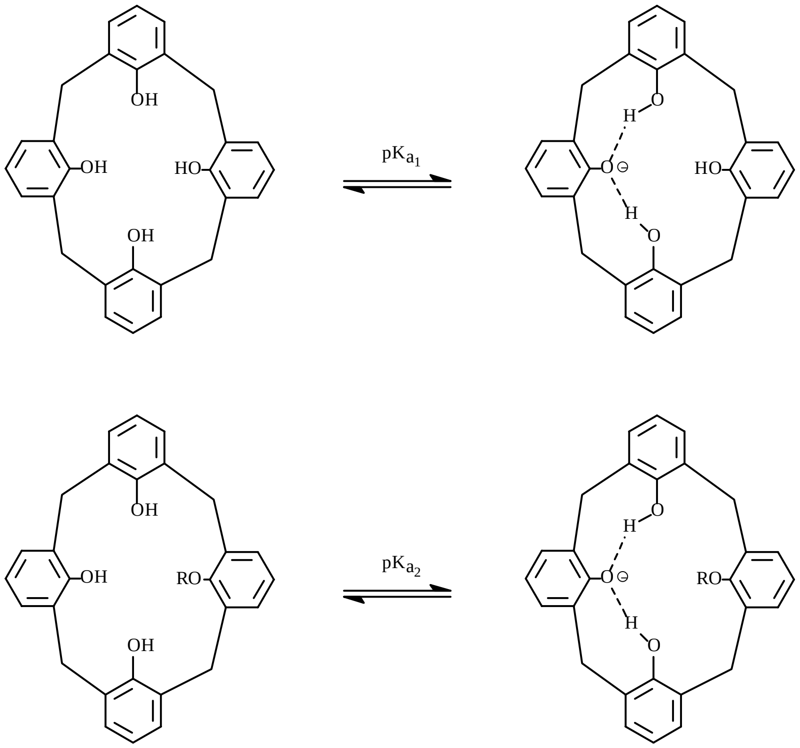


Figure 2.13. The two dissociation processes and the difference between pK$_{a1}$ and pK$_{a2}$ responsible for the selective functionalization at the lower rim of calix[4]arene.

As seen above both of the anions are strongly stabilized by hydrogen bonding demanding a very delicate choice of bases used in the deprotonisation. If can also be seen that any alkylation beyond the second (e.g. *distal*) requires the use of stronger bases since no significant stabilization from hydrogen bonding can occur.

2.2 Synthesis

In this section some of the different synthetic strategies examined during the project will be outlined and the results presented. The order in which the different strategies are presented represents more or less also the time-line of my Ph.D-study.

2.2.1 Cyclopentadiene derivatives of calix[4]arenes

The first target molecule chosen was the precursor **2A**, see ***Figure 2.14***, based on the availability of the starting materials. The precursor should after deprotonisation and reaction with a transition metal tetrahalide result in the corresponding metallocene.

The dimethyl fulvene (**45**) is easily prepared in about 80 % yield by reaction of acetone and cyclopentadiene using pyrrolidine as base followed by acid work-up and distillation. The synthesis of **46** was successful either when using the Grignard reagent (e.g. PhMgBr) or when phenyllithium was used, followed by addition of a catalytic amount of CuI[52,53,54]. Though it was found that using phenyllithium increased the amount of by-products, probably because reflux overnight was necessary.

With these results in mind the synthesis of **2A** was attempted starting with bromo-lithium exchange on 5,17-dibromo-25,26,27,28-tetrapropoxy-calix[4]arene (**5**) using 4 equivalents of *tert*-BuLi followed by addition of excess dimethyl fulvene (**45**) and catalytic amount of CuI. The collected product was found to be 25,26,27,28-tetrapropoxy-calix[4]arene (**3**) both by NMR and MALDI-TOF. The same product was isolated when the reaction was tried using the di-zinc chloride calix[4]arene, e.g. addition of anhydrous $ZnCl_2$ after the bromo-lithium exchange[55]. It was then tried to use the 5-bromo-25,26,27,28-tetrapropoxy-calix[4]arene (**33**) instead which is simpler because only one reactive site is present but again the product collected was **3** regardless of reaction conditions. By GC-MS on the reaction mixture it was found that dimethyl fulvene obviously has a

---

[52] Corey, E.J., Posner, G.H.; *J. Am. Chem. Soc.*, 1967, **89**, 3911

[53] Posner, G.H.; *Org. Reac.*, 1972, **19**, 1-113

[54] Bertz, S.H., Dabbagh, G., Villacorta, G.M.; *J. Am. Chem. Soc.*, 1982, **104**, 5824

[55] Larsen, M.; Jørgensen, M.; *J. Org. Chem.*, 1997, **62**, 4171

strong tendency to dimerize in a Diels-Alder reaction forming **2C**; this type of reaction is not seen when synthesizing compound **46** since the addition reaction proceed rather quickly compared to the Diels-Alder reaction.

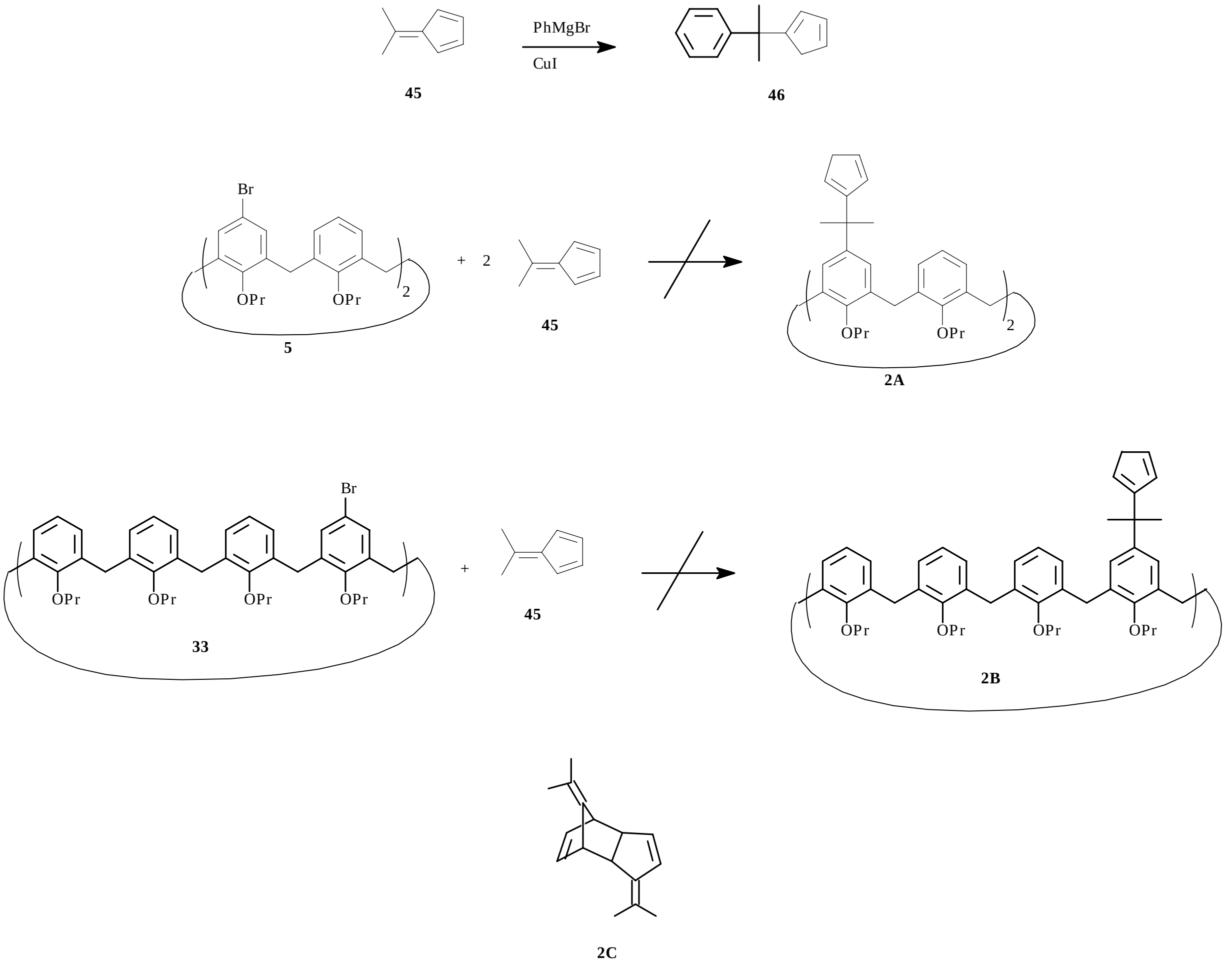


*Figure 2.14. The synthesis of **46** and the attempted synthesis of **2A**, **2B**. Product **2C** arising from a Diels-Alder type dimerization of **45** and was determined by GC-MS.*

In order to avoid the possibility of the Diels-Alder reaction, attempts were made to use the 2,3,4,5-tetramethylcyclopent-2-enone (**50**) instead, see ***Figure 2.15***. This compound was found to react with PhMgBr producing compound **2D** though not isolated but only analyzed by GC-MS. Unfortunately the reaction with the 5,17-dilithio-tetrapropoxy-calix[4]arene was not possible regardless of temperature. The only product isolated was again the dehalogenated calix[4]arene (**3**). This result can be rationalized as an unfortunate combination of a stericly demanding nucleophilic attack on the ketone (**50**), competing with the proton abstraction from the same. In order to reduce the later reaction the di-zinc chloride calix[4]arene was tried also, but the result was still unsuccessful.

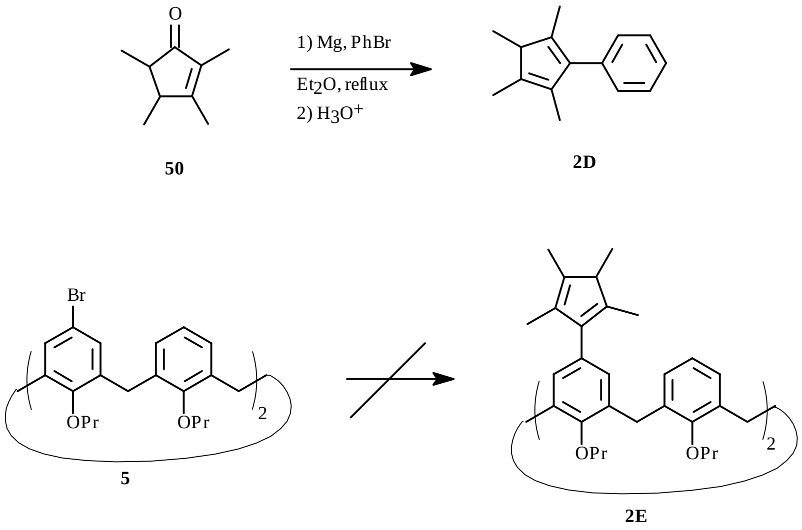


*Figure 2.15. Strategy for using the more steric demanding substituent 2,3,4,5-tetramethylcyclopent-2-enone (**50**).*

2.2.2 Indenyl calix[4]arenes

Due to the lack of success with the preparation of cyclopentadienyl substituted calix[4]arenes it was decided to focus on indenyl derivatives instead. Indene and bis-indene metallocenes are also interesting polymerization catalysts as discussed in chapter one. This part was initiated by the successful synthesis of a model compound: 2-(4-methoxybenzene)-1H-indene (**54**) in 37 % yield from reaction of PhMgBr and 2-indanone (**52**) followed by heating in sulfuric acid, see ***Figure 2.16***.Compound **52** have been used to prepare a zirconocene (and a hafnocene) dichloride that can catalyze the polymerization of propylene with alternating domains with different tacticity.

An obvious first synthetic target was to substitute 5,17-dibromo tetrapropoxy-calix[4]arene (**5**) with indene groups to produce **2F**. Deprotonation of the indene groups followed by addition of $ZrCl_4$ should then give the desired calixarene catalyst.

2.2.2.1 Reaction with indan-1-one and epoxy-indene

The 5,17-dilithio tetrapropoxy-calix[4]arene was prepared and reacted with **52** at –78 °C in order to slow the possible acid-base reaction. But the instant appearance of a deep red colored solution, indicative of the indanone anion, clearly showed that addition reaction had not taken place and only tetrapropoxy-calix[4]arene (**3**) was collected (in 76 % yield) and identified by NMR and MALDI-TOF. It was then tried to use the Grignard reagents since those are known to exceed the lithium reagents in rate of nucleophilic addition reactions. The transmetallation was done using freshly prepared $MgBr_2$*THF at –78 °C but again the result was only (**3**) and the same result was obtained when using the zinc reagent also. Cerium reagents has proved valuable in nucleophilic addition reactions were the electrophile is prone to deprotonisation[56,57,58]. This has been illustrated by addition of trimethylsilylmethyllithium to 2-indanone, where using the lithium reagent only 6 % yield was obtained of the addition product but with the cerium reagent 83 % yield was collected[59]. Even when the transmetallation of dilithiocalix[4]arene was done using anhydrous $CeCl_3$ the product was still identified as **3**.

The history was repeated when 5-bromo-tetrapropoxy-calix[4]arene (**33**) was used instead of **5**, after the reaction, **3** was identified by NMR, and in some cases collected in 80 % yield. The mother-liquid was found to contain small amounts of **3** and unidentifiable compounds, which probably were formed by aldol-condensation reaction.

---

[56] Imamoto, T., Kusumoto, T., Tawarayama, Y., Sugiura, Y., Mita, T., Hatanaka, Y., Yokoyama, M.; *J. Org. Chem.*, 1984, **49**, 3904

[57] Imamoto, T.; *Pure & Appl. Chem.*, 1990, **62**, 747

[58] Imamoto, T., Takiyama, N., Nakamura, K., Hatajima, T., Kamiya, Y.; *J. Am. Chem. Soc.*, 1989, **111**, 4392

[59] Johnson, C.R., Tait, B.D.; *J. Org. Chem.*, 1987, **52**, 281

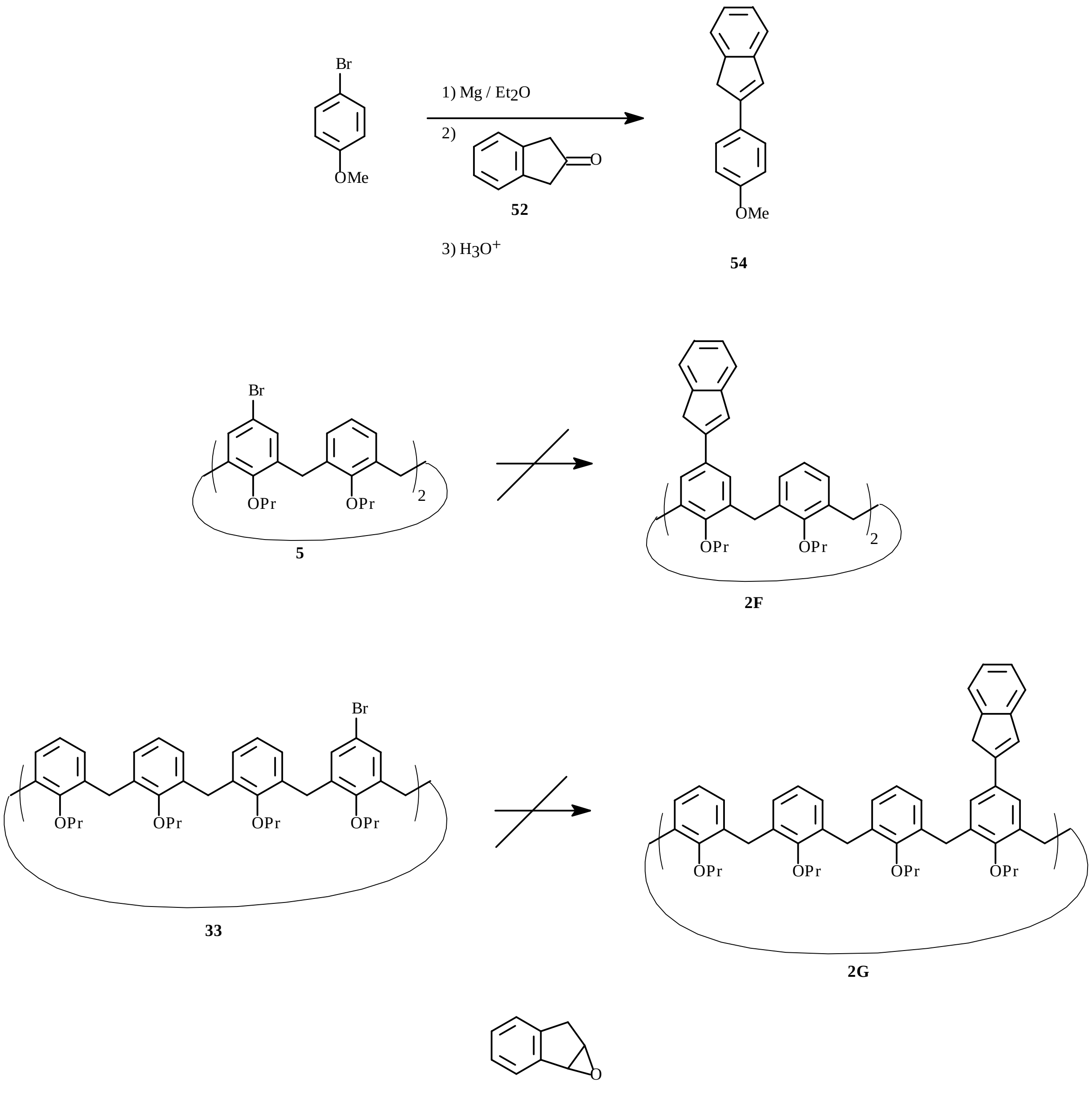


*Figure 2.16. Strategy for the synthesis of **54** and the attempted synthesis of **2F** and **2G** using **52** and **60**.*

To circumvent the difficulties observed with the indanone (and also with tetramethylcyclopentenone) another strategy was needed. The epoxide of indene (**60**) was prepared in the hope that it might react as an electrophile with a metallated calix[4]arene. The preliminary model reaction with PhMgBr was successful as monitored by GC-MS proceeding to full conversion to the expected phenyl-indanol in two hours at ambient temperature in THF. When applied to one of the two calixarenes above, e.g. **5** or **33**, the addition was absent no matter how long time or which solvent there was used. The stability of **60** however, is not suitable for conditions like reflux in THF during several hours and apparently is the reactivity of the metallo-calixarene as nucleophile not high enough.

2.2.2.2 Heck, Suzuki and Neghishi couplings

Since products **2F** and **2G** in theory should be accessible by biaryl coupling reactions, e.g. Heck, Suzuki and Negishi, this approach was tested. The Heck reaction between iodobenzene and indene proceeded readily and the product 2-phenyl-1H-indene (**53**) was collected in 43 % yield using $(PPh_3)_2PdCl_2$ as catalyst in DMF and Et_3N after reflux overnight, see ***Figure 2.17***.

The calix[4]arenes **12**, **17**, **37, 43**, **51**, **63** and **65** were synthesised to act as substrates in the Heck and Suzuki coupling reactions. The Negishi reaction was not performed since the results above indicated that no success could be expected when using basic reagents as the zinc-aryl necessary in this type of biaryl couplings. In the Heck and Suzuki reaction the catalyst $(PPh_3)_2PdCl_2$ was used due to its higher stability towards light, moisture and oxygen compared to the "traditional" catalyst, e.g. $(PPh_3)_4Pd$. In the Heck reactions DMF and Et_3N was used as solvent and base respectively, while in the Suzuki reactions toluene and aqueous 2 M Na_2CO_3 were used. The reaction mixture was refluxed 18 hours (or overnight), that is the standard procedure, in both types of reactions. However in any case the starting material was collected even in the case were a very promising new catalyst system ($Pd_2(dba)_3$ and a aminophosphine, 1,1'-biphenyl-1-dimethylamino-1'-di(cyclohexyl)phosphine) which is reported to make 4-chlorotoluene react with phenylboronic acid at room temperature in 94 % yield[60].

---

[60] Old, D.W., Wolfe, J.P., Buchwald, S.L.; *J. Am. Chem. Soc.*, 1998, **120**, 9722

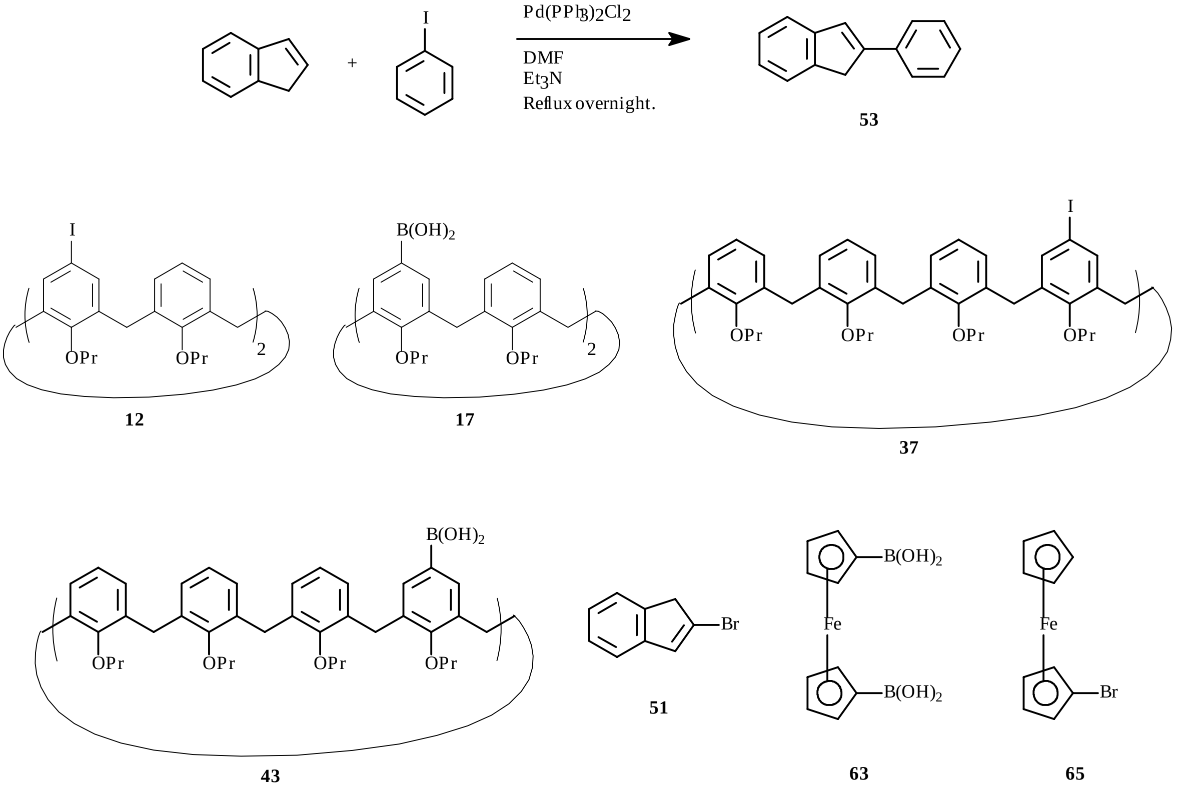


Figure 2.17. Compounds used in the biaryl coupling reactions.

2.2.2.3 Horner-Wadsworth-Emmons reactions

The HWE (Horner-Wadsworth-Emmons) reaction was then investigated and 5,17-diformyl-tetraproxy-calix[4]arene (**8**), 5-formyl-tetrapropoxy-calix[4]arene (**34**), 2-formyl-1H-indene (**56**)[61], 5,17-di(diethylphoshonatmethylester)-tetrapropoxy-calix[4]arene (**13**) and (1H-indene-2-yl)-methyl-phosphonic acid diethyl ester (**59**) were prepared, see ***Figure 2.18***. The synthesis of **56** was first tried using Vilsmeier conditions starting from indene, e.g. DMF/$POCl_3$ at 0 °C in 1,2-dichloroethane followed by heating since GC-MS showed no formation of the product. After two hours of reflux the product, e.g. **56**, was formed in approximately the same amount as the starting material, so reflux was therefor continued overnight assuming that this would complete the reaction. The following day the reaction mixture had turned into tar and GC-MS showed a forest of signals.

---

[61] Arnold, Z.; *Coll. Czechoslov. Chem. Commun.*, 1965, **30**, 2783

The heating obviously had been too extensive and it was found that changing the solvent to $CHCl_3$ and leaving the reaction at RT for 4 days produced the aldehyde **56** in good yield. The reduction of **56** to the alcohol **57** was first attempted using $NaBH_4$ in EtOH but no formation of **57** could be found but when applying the Meerwein-Pondorff-Verley reduction, e.g. heating $Al(OPr^i)_3$ in dry Pr^iOH together with the aldehyde and removing the produced acetone by distillation, the alcohol was collected in almost quantitatively yields.

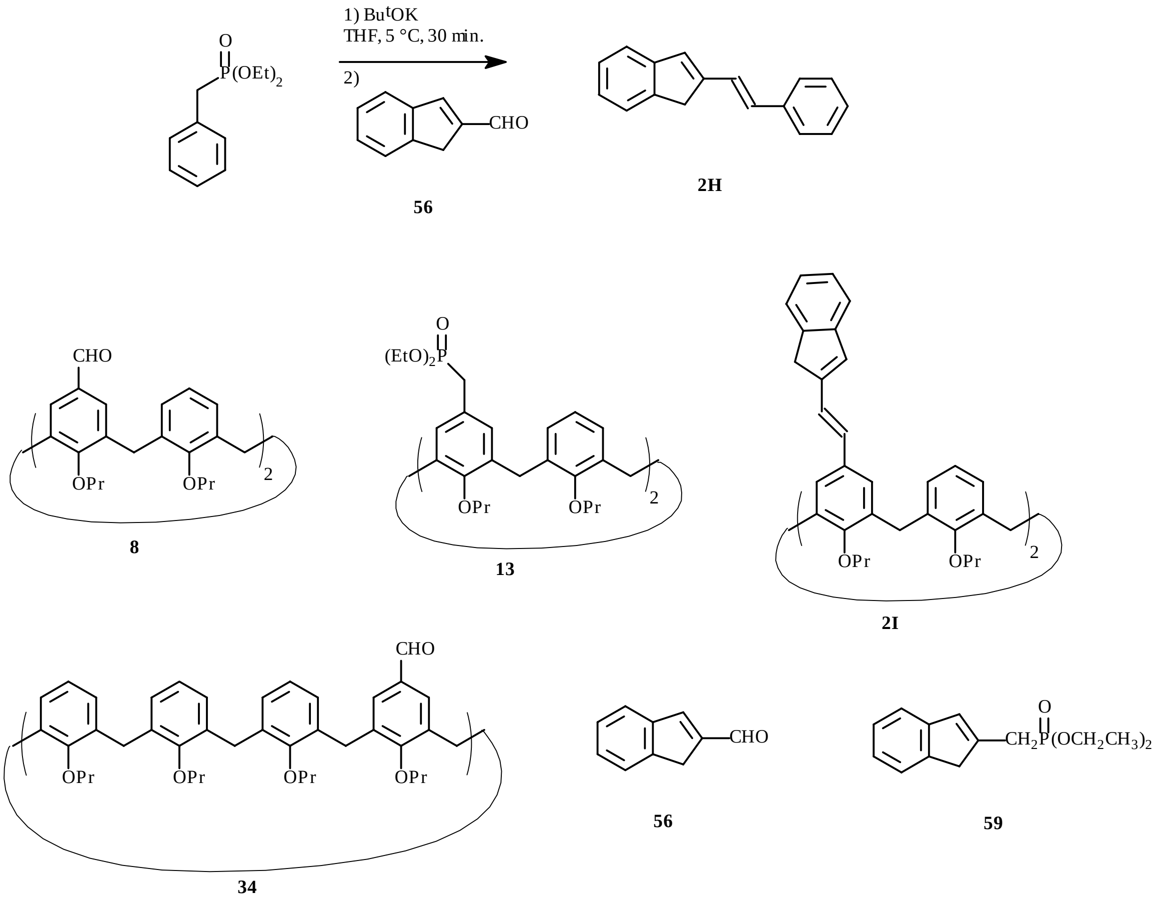


*Figure 2.18. Synthetic strategy the synthesis of **2H** and the attempted synthesis of **2I**, using compounds **8**, **13**, **34**, **56** and **59**.*

Compound **2H** was found by GC-MS analysis to be formed exclusively by the reaction between the benzyl diethylphosphonat ester and **56**. In order to reduce the possibility of deprotonisation of **56** it was chosen first to deprotonise **13** using Bu^tOK in THF followed by slow addition of **56**. The starting materials were recovered quantitatively and confirmed by MALDI-TOF and GC-MS. The functionality was then exchanged, e.g. reaction between **8** and **59**, but this did not make any difference since **59** when reacting with Bu^{t}OK was found to by deprotonised at the indene-CH_2 group and not at the α-position to the phosphonat ester[*].

2.2.3 Vanadium catalysts

Due to the disappointments discussed above the attention was focused on another group of catalysts capable of polymerizing styrene into polystyrene[62] namely half-sandwich imido vanadium complexes of the type $CpV(NAr)Cl_2$ (**2J**), see ***Figure 2.19***. The aryl group should then be a calix[4]arene, see *Figure 1.24*. The imido ligand stabilizes transition metal complexes in high oxidation state because of their ability to participate in extensive ligand-to-metal π donation[63]. Further is the combination of a cyclopentadienyl ligand and an imido ligand on a Group 5 metal considered to have similar molecular orbitals, in both energy and shape, as the Group 4 metallocene fragments (Cp_2M)[64], the so-called isolobal relationship[65]. The compound **76** was prepared from the 2,6-diisopropylaniline isocyanate, which is commercially available, in 50 % yield and is isolated as a brown powder that seems rather stable in air. Appearing to be a useful strategy the compounds **40**, **66** and **67** were synthesised. First it was necessarily to find a way to synthesise a calix[4]arene isocyanate of which none has been published in the literature. The conventional methods are phosgenation of an aromatic amine using phosgene or triphosgene[66], pyrolysis of acid azides, dehydration of hydroxamic acids (Lossen rearrangement), or rearrangement of N-haloamides by reaction with base (Hoffmann rearrangement). Other synthetic routes[67] has been developed in recent years, reaction of aromatic hydroxamic acid with thionyl chloride forming a substituted 1,3,2,4-dioxathiazole S-oxide which thermal rearrange to give the isocyanate and sulfur dioxide[68].

---

[*] Found by quenching with D_2O and analyzed by NMR

[62] Buijink, J-K.F., Meetsma, A., Teuben, J.H., Kooijman, H., Spek, A.L.; *J. Organomet. Chem.*, 1995, **497**, 161

[63] Nugent, W.A., Mayer, J.M.; *Metal-Ligand Multiple Bonds*, Wiley Interscience, New York, 1998

[64] Williams, D.N., Mitchell J.P., Poole, A.D., Siemeling, U., Clegg, W., Hockless, D.C.R., O'Neill, P.A., Gibson, V.C.; *J. Chem. Soc., Dalton Trans.*, 1992, 739

[65] Hoffman, R.; *Angew. Chem., Int. Edn. Engl.*, 1982, **21**, 711

[66] Kurita, K., Iwakura, Y.; *Organic Synthesis*, **59**, 195

[67] Tafesh, A.M., Weiguny, J.; *Chem. Rev.*, 1996, **96**, 2035

[68] Burk, E.H., Carlos, D.D.; *J. Heterocycl. Chem.*, 1970, **7**, 177

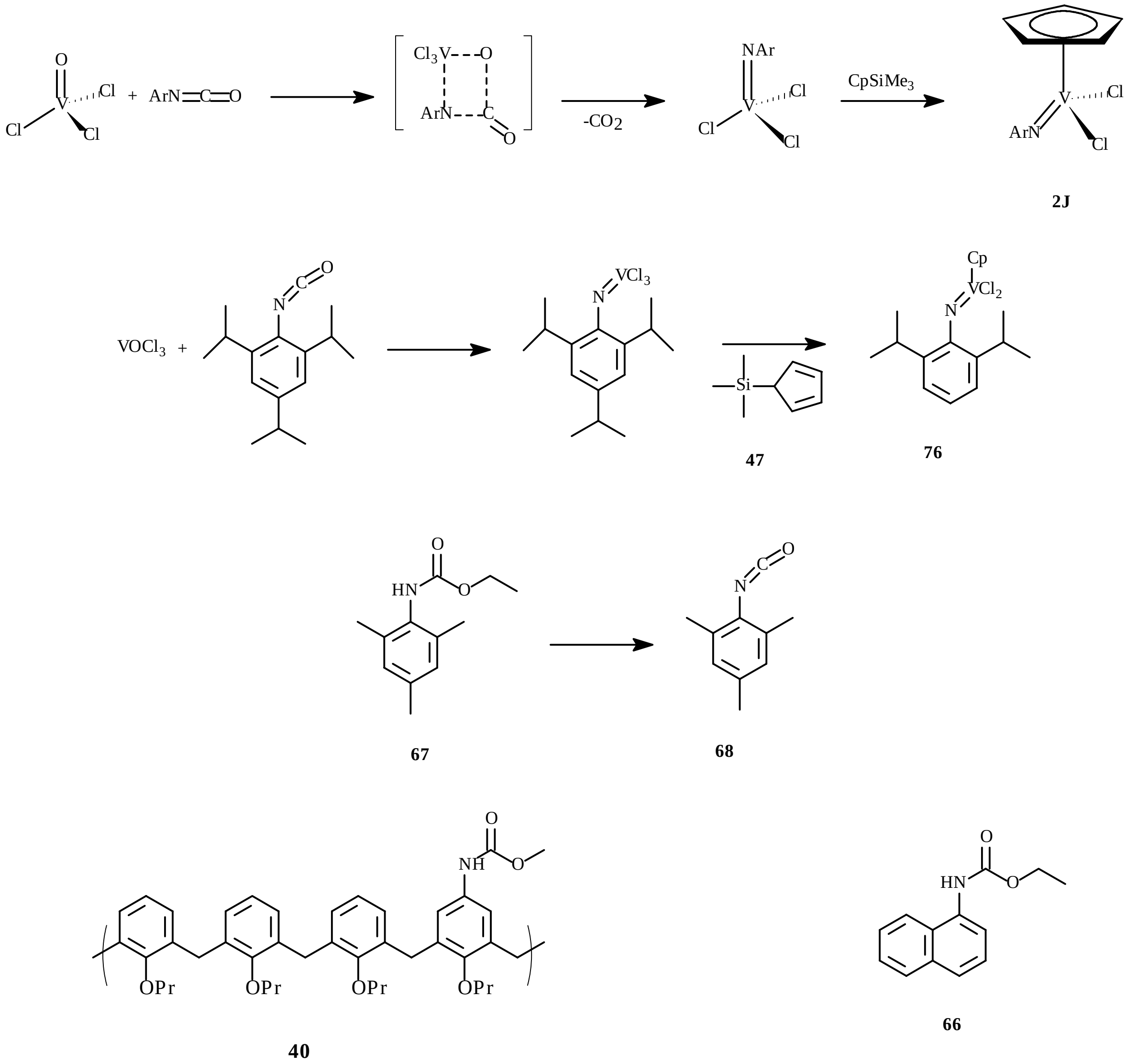


*Figure 2.19. Synthetic strategy the synthesis of compounds of the type **2J**, using compounds **40**, **47**, **66** and **67/68**.*

Another reaction is the elimination of alcohol from a urethane by reaction of boron trichloride[69] or chlorocatecholborane[70] in the presence of triethylamine; the reaction mechanism is presented in ***Figure 2.20***. The latter reaction was found to produce the isocyanate wanted in quantitative yields without any side-reactions.

---

[69] Butler, D.C.D., Alper, H.; *Chem. Commun.*, 1998, 2575

[70] Valli, V.L.K., Alper, H.; *J. Org. Chem.*, 1995, **60**, 257

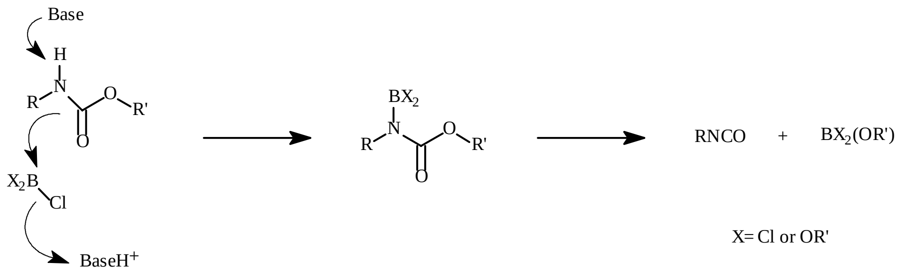


Figure 2.20. Mechanism for the synthesis of isocyanate by reaction between a carbamate ester and boron trichloride or chlorocatecholborane.

When this method was applied to **40** the corresponding mono-isocyanate was isolated (using the same procedure as for **68**, see Experimental section) and identified by NMR (^{1}H-NMR showed the removal of NH and ester group and ^{13}C-NMR showed the N$\underline{C}$O at 157 ppm and the removal of the ester group) but when adding $VOCl_3$ to the isocyanate it was clear that decomposition of the calix[4]arene had taken place. The reaction mixture instantaneously turned black and neither NMR nor MALDI-TOF confirmed that a calix[4]arene was still present. The $VOCl_3$ being a very strong Lewis acid and properly the reaction observed are a cleavage of the tetrapropoxy groups. This type of reaction is discussed in more detail in the next section where the same type of reaction was proved to be the case in the fluorenyl calix[4]arenes.

2.3 Fluorenyl calix[4]arenes

Disappointed about the lack of success from the attempts discussed above the strategy next tried was to synthesise a compound in which any “unnecessary” protons were eliminated. The structure chosen was the 5,17-di(9H-fluoren-9-yl)-25,26,27,28-tetrapropoxy calix[4]arene (**15**), see ***Figure 2.21***.

Starting with the halogen-metal exchange reaction followed by reaction with 9-fluorenone produced 5,17-di(9-fluorenol-9-yl)-25,26,27,28-tetrapropoxy calix[4]arene (**14**) in 76 % yield. The alcohol was reduced by triethylsilane (Et_3SiH) in trifluoroacetic acid (TFA) at ambient temperature resulting in **15** in 87 % yield. The corresponding reaction with phenylmagnesiumbromide and 9-

fluorenone, e.g. 9-phenyl-fluoren-9-ol (**61**), followed by reduction with $Et_3SiH/BF_3{*}Et_2O$ in CH_2Cl_2, e.g. 9-phenyl-9H-fluorene (**62**) proceed in 97 % and 70 % yield respectively.

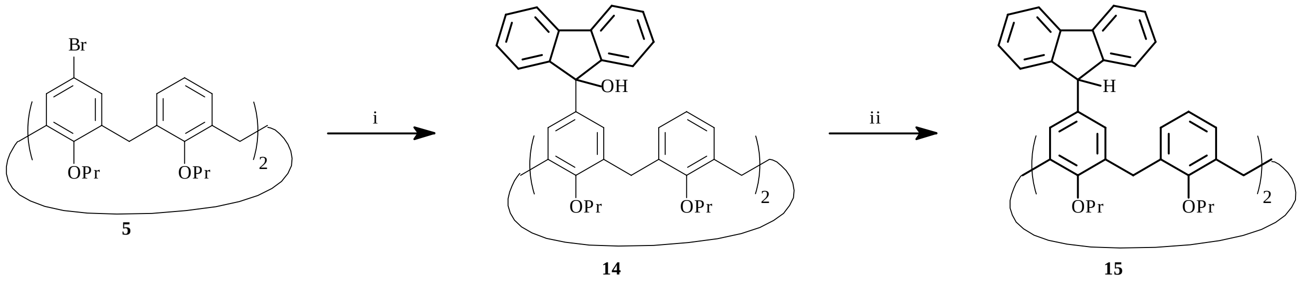


*Figure 2.21. Synthesis of 5,17-di(9H-fluoren-9-yl)-25,26,27,28-tetrapropoxy calix[4]arene (**15**). The reaction conditions used were: i) 4 eqv. Bu^tLi/THF/-78 °C/15 min, 2 eqv. 9-fluorenone/THF/RT; ii) Et_3SiH/TFA/RT.*

It was possible to obtain X-ray quality crystals of **15** by recrystallisation from toluene and solving the structure showed that **15** crystallizes without solvent in a conformation where the aryl groups holding the fluorenyl moieties are pinched together while the fluorenyl groups themselves are bent outwards away from the calix[4]arene center, see ***Figure 2.22***. The *pinched cone* conformation is also confirmed by ^{1}H-NMR in which two different propoxy-groups exists with a $\Delta\delta = 0.15$ ppm between the OCH_2 protons situated at the 25/27 and the 26/28 positions. The larger this difference is the more *pinched cone* is the conformation.

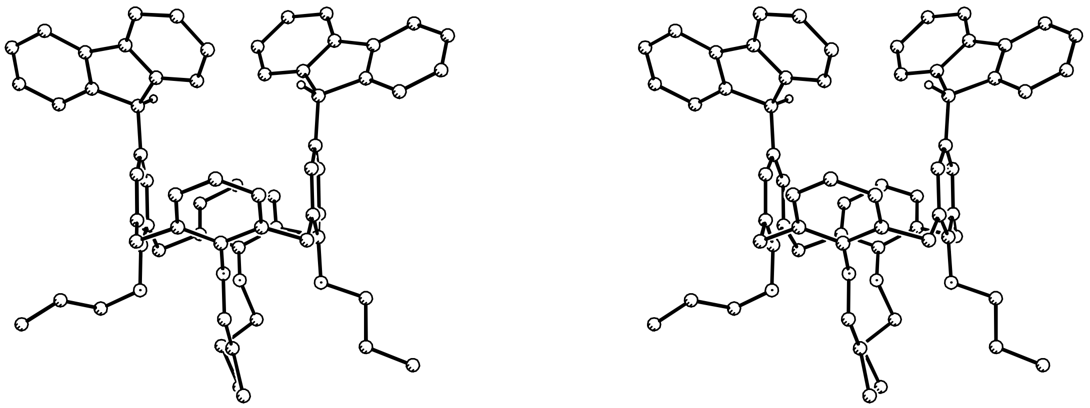


*Figure 2.22. Stereoview of the molecular conformation of **15**. The well-known pinched cone conformation is observed with the fluorenyl substituents together.*

The angle between the fluorenyl planes is 81.22(4) degrees giving rise to a zigzag interdigitation between layers of calix[4]arenes of opposite orientation. The unit cell belong to the monoclinic space group $P_{2/c}$ consisting of 4 molecules in each cell, see *Appendix 1* for full crystallographic data and ***Figure 2.23*** for stereoview of the unit cell.

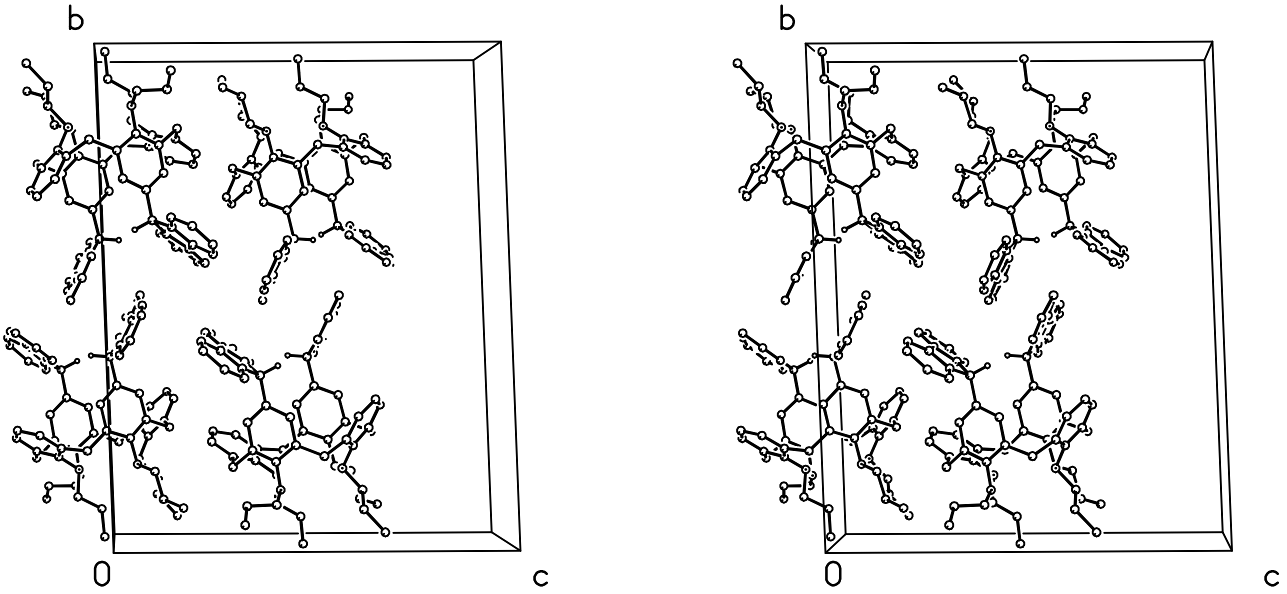


Figure 2.23. Stereoview of the $P_{2/c}$ *unit cell of* ***15****.*

It was anticipated that deprotonation at the 9-positions of both fluorene moieties followed by reaction with MCl_4 (M = Ti, Zr or Hf) would result in the formation of a bis-fluorenyl metallocene dichloride system positioned at the *upper rim* of a calix[4]arene template, see ***Figure 2.24***. This was attempted using Bu^tLi as base in dry THF at -78 °C producing a very intensely orange colored solution which was cannulated into a solution of MCl_4*2THF in THF. The bis tetrahydrofuran complexes of the transition metal tetrachloride were used due to the increased stability towards moisture (mostly in the case of titanium tetrachloride) but also as a way of purifying the transition metal tetrachloride (in the case of zirconium and hafnium)[*].

---

[*] Easily prepared by addition of 2 equivalents of dry THF to a solution or suspension of MCl_4 in hexane, followed by either stirring for 1 hour ($TiCl_4$) or overnight ($ZrCl_4$ or $HfCl_4$) depending on which metal that is used.

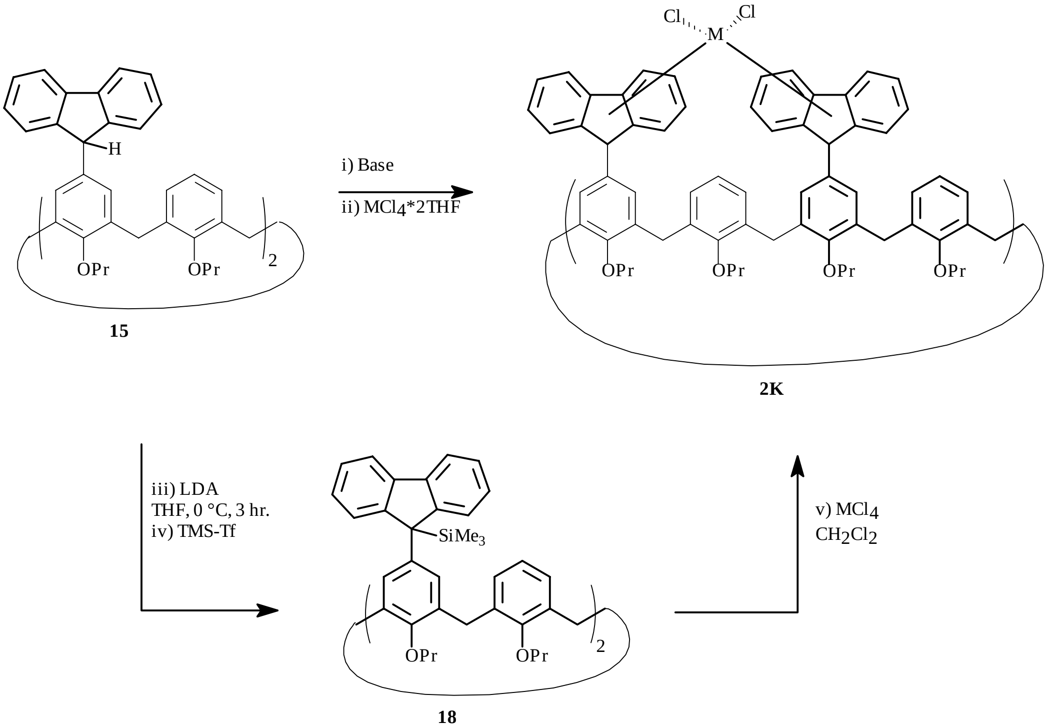


Figure 2.24. Strategy for the synthesis of upper rim metallocene dichloride systems from ***15*** *or* ***18****, M= Ti, Zr, Hf.*

In order to verify that formation of the dianion had taken place using these conditions samples were drawn with appropriate intervals of time, quenched with D_2O and ^{1}H-NMR spectra were recorded. The disappearance of the resonance situated at 4.89 ppm, assigned to the proton in the 9-position of the fluorenyl moiety, could be monitored as a function of time and was near completion after one hour, see ***Figure 2.25***.

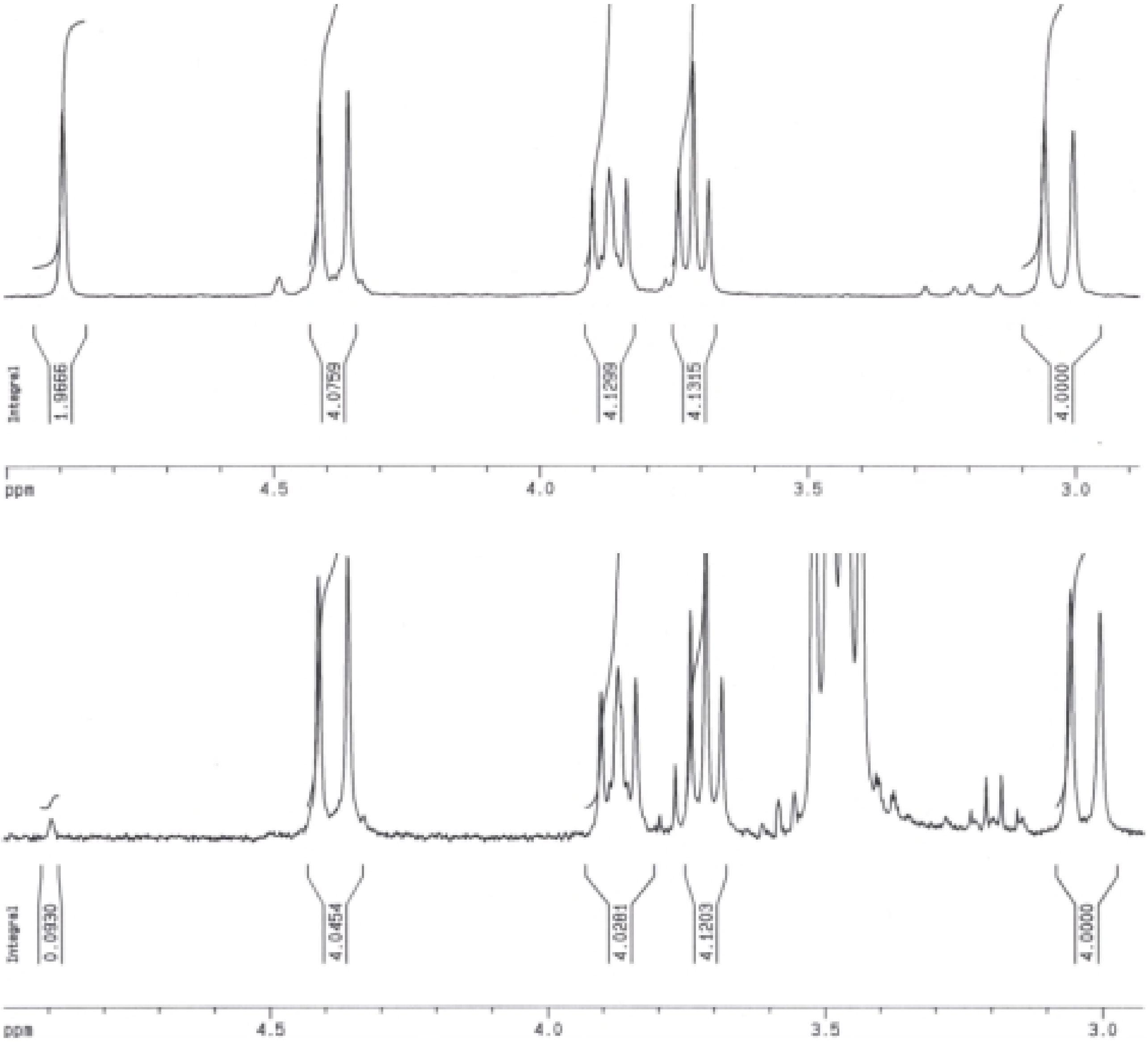
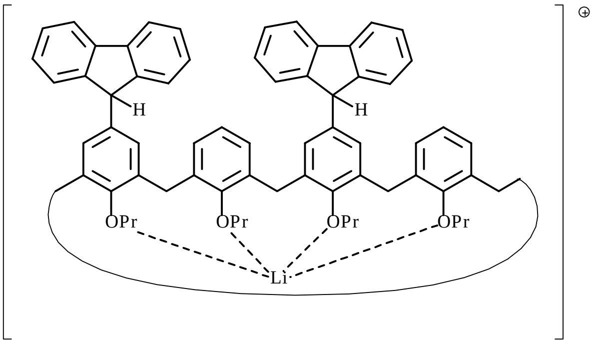


*Figure 2.25. ^{1}H-NMR spectrum of **15** before (upper) and after (lower) reaction with Bu^{t}Li in dry THF at –78 °C for one hour, quenched with D_2O.*

When the dianion was cannulated into a solution of $TiCl_4$ * 2THF the orange color was immediately changed to dark brown indicative of some sort of decomposition taken place. No product could be isolated in this case.

When $ZrCl_4$ * 2THF was used instead, the orange color still disappeared but more slowly and the final color was more yellow than orange. The solution was refluxed overnight and evaporated under argon. Treatment with toluene, filtration using Schlenk technique followed by standing under argon for several days produced crystals suitable for X-ray crystallography. The crystals were found to be very unstable when exposed to air properly both loosing solvent and reacting with the air. It was however possible to harvest crystals from the solution, quickly transferring them to a drop of oil thereby covering and protecting the crystals from the air, mounting one crystal on the glass capillary and rapidly transfer the mounted crystal to the cooling nitrogen stream and collecting data at 120 K. The compound isolated was unexpectedly found to be the salt **77**, see ***Figure 2.26***.



77

Figure 2.26. The salt isolated from the reaction between the dianion of **15** *and* $ZrCl_4$**2THF.*

The lithium-ion binds to the ether groups and thereby opens up the structure, e.g. making **77** a less *pinched cone* than the parent calix[4]arene **15**. This was however not possible to confirm whether this confinement also apply in solution by ^{1}H-NMR studies. Strangely, both the fluorenyl substituents were protonated and the unusual but previously observed[71,72] zirconium pentachloride tetrahydrofuran anion had been formed. The observed product may be explained by partial cleavage of the calix[4]arene ether functions with the Lewis acid $ZrCl_4$, see ***Figure 2.27***.

$$\mathrm{ArOPr} + 2\,\mathrm{ZrCl_4} \longrightarrow \mathrm{ArOZrCl_3} + \mathrm{ZrCl_5^{\ominus}} + \mathrm{Pr^{\oplus}}$$

Figure 2.27. Proposed reaction path for the formation of the zirconium pentachloride tetrahydrofuran anion.

---

[71] Polamo, M., Leskelä, M.; *Acta Chem. Scand.*, 1997, **51**, 44

This reaction of $ZrCl_4$, which though being a Lewis acid, was not expected since normally stronger Lewis acids are required for this type of ether cleavage, e.g. $TiBr_4$ or BBr_3. The propyl cation can decompose and in this process forming a proton that neutralizes the lithium salt of the fluorenyl moiety.

An experiment was run in a sealed NMR tube in order to verify this proposed reaction path; mixing 34 mg 25,26,27,28-tetrapropoxy calix[4]arene (**3**), 14 mg $ZrCl_4$ (1.1 eqv.) and two drops of THF in deutero benzene (C_6D_6), sealing the tube and heating overnight at 350 K. By ^{1}H-NMR almost total conversion was observed, see ***Figure 2.28***.

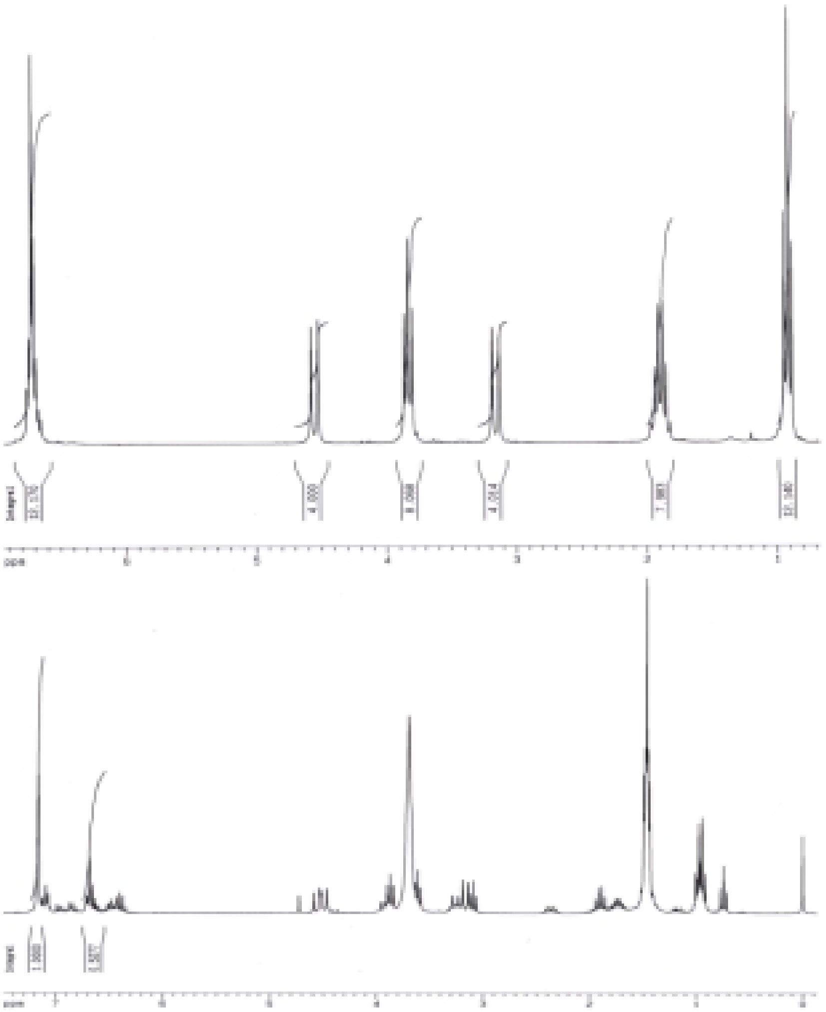


*Figure 2.28. ^{1}H-NMR spectrum of the reaction mixture before (upper spectrum) and after (lower spectrum) reaction overnight at 350 K in a sealed NMR tube, e.g. 34 mg 25,26,27,28-tetrapropoxy calix[4]arene (**3**), 14 mg $ZrCl_4$ and two drops of THF in deutero benzene (C_6D_6).*

---

[72] Scholz, J., Richter, B., Goddard, R., Krüger, C.; *Chem. Ber.*, 1993, **126**, 57

The sealed NMR tube was then opened and the mixture was analyzed by MALDI-TOF, see ***Figure 2.29***, where it was found that peaks corresponding to cleavage of four (**2**, m/z= 424.5), two (**2L**, m/z= 508.6) or one (**2M**, m/z= 550.7) propoxy groups. The compound **2N** having the molecular weight of 747.3 g/mol is included because it seems highly reasonable to assume that the peak centered at m/z= 750.5 can be attributed to this compound. When careful inspection of the spectrum is done, one will see that the peak-selecting routine in the software of the MALDI-TOF program has chosen the maximum at a slightly higher weight than actually is the case.

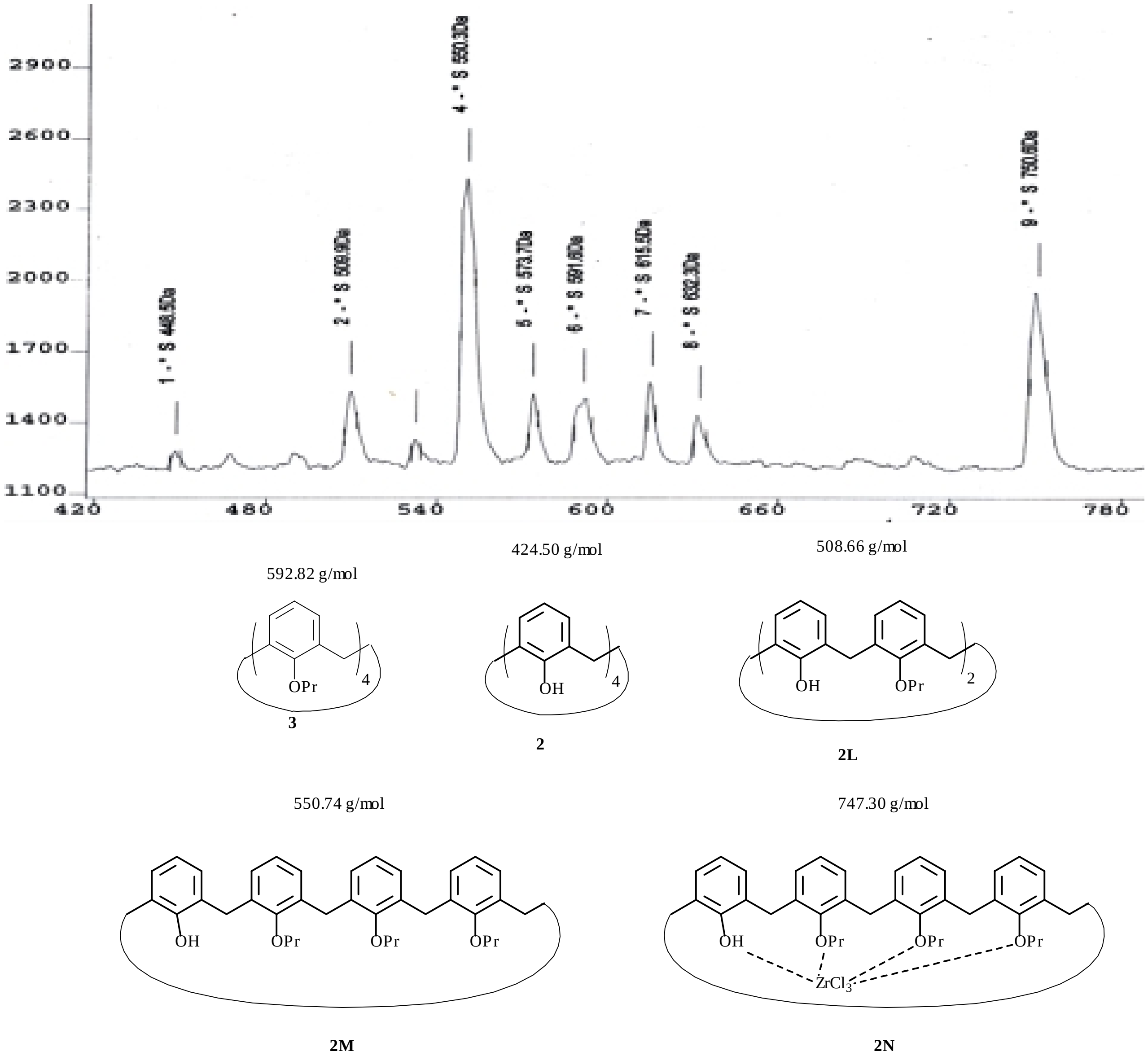


*Figure 2.29. MALDI-TOF spectrum of the reaction mixture after reaction overnight at 350 K in a sealed NMR tube, e.g. 34 mg 25,26,27,28-tetrapropoxy calix[4]arene (**3**), 14 mg $ZrCl_4$ and two drops of THF in deutero benzene (C_6D_6).*

In the structure of the salt **77**, see ***Figure 2.30*** a dramatic change has occurred in the calix[4]arene on complexation with the lithium ion as mentioned above, e.g. the change from *pinched cone* to a regular *cone* conformation.

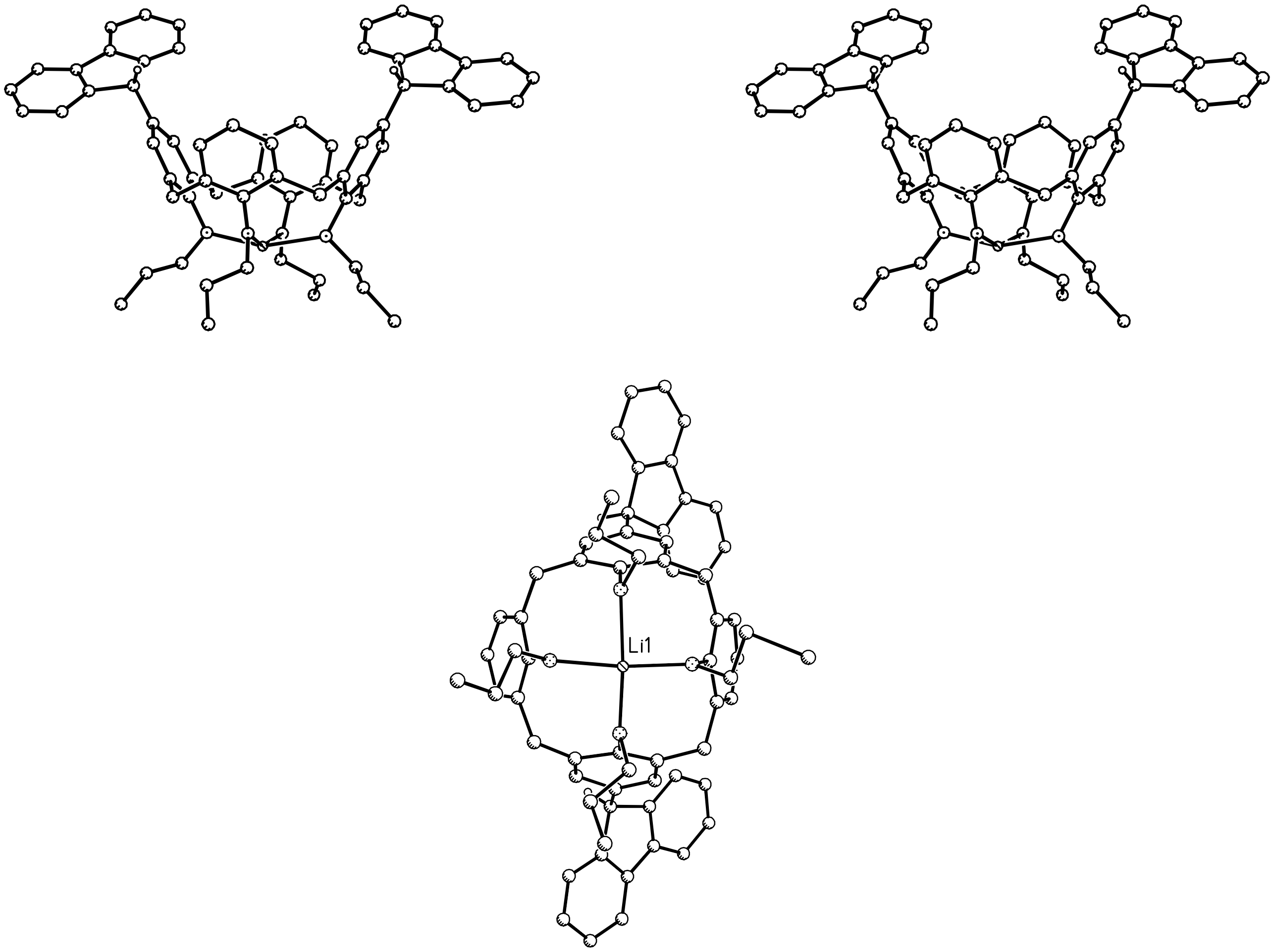


Figure 2.30. The molecular conformation of ***77*** *where the lithium ion is bound between the four oxygen atoms of the propoxy groups, upper: stereoview from side, lower: viewed from the lower rim. This forces the calix[4]arene into the cone conformation (pseudo* C_{4v}*).*

This forces the fluorenyl substituents outwards and into a plane inclined with respect to the C_{2v} axis, thereby allowing an efficient π-π overlap with another calix[4]arene, see ***Figure 2.31***. The interplanar fluorenyl-fluorenyl distance in the dimer is about 4.15(5) Å indicating a substantial intermolecular π-π overlap. The result of this dimerization is a formation of an egg-shaped cavity large enough to accommodate a solvent molecule of toluene. The ability of incorporating solvent molecules into a dimer of calixarenes have been constructed previously relying on hydrogen bonding interactions[73] proved only by the change in chemical shift of the solvent molecule before and after the entrapment. Other ways of decreasing the pinching, e.g. opening the cavity making complexation of guest molecules possible, has been investigated. Either by crown-ether functionalization at the *lower rim* constraining the geometry to open up the cavity[74] or by binding a metal ion to the four oxygen atoms imposing C_{4v} symmetry on the calixarene skeleton. However in the latter case only few examples are known[75] where an alkali metal ion is bound to a simple calixarene ether.

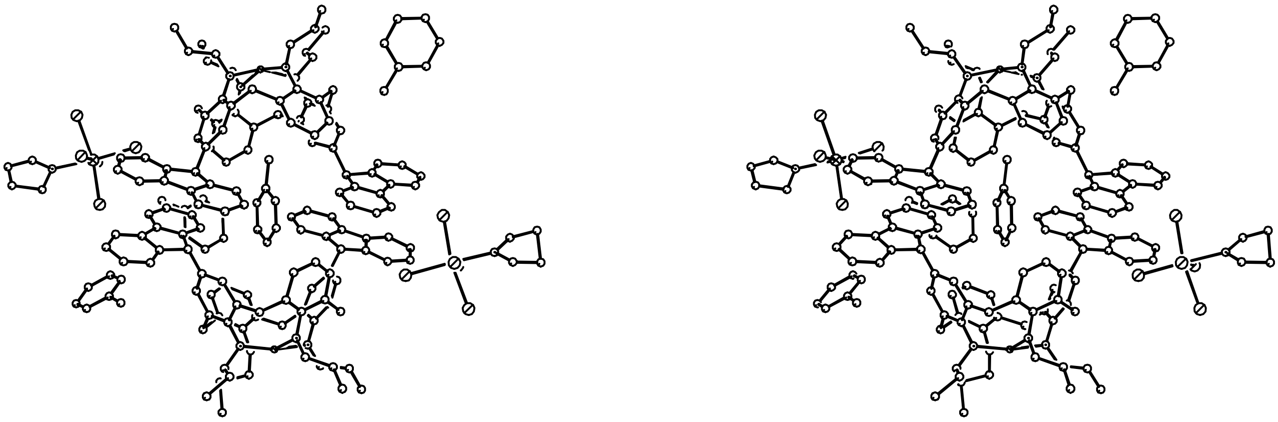


Figure 2.31. Stereoview of the dimer clathrate with the lithium-ions bound between the oxygen atoms of the propoxy groups and the included toluene solvent molecule.

The more open calix[4]arene structure produces an egg-shaped cavity large enough to hold a disordered toluene molecule resulting in a crystal structure of the salt **77** which is a simple packing of egg-shaped dimers interspersed with solvent toluene and tetrahydrofuran pentachlorozirconate anions, see ***Figure 2.32***. The unit cell belong to the triclinic space group P*1* consisting of 2 molecules in each unit cell, see *Appendix 1* for full crystallographic data. This work has been published, see *Appendix 4*.

---

[73] Heinz, T., Rudkewich, D.M, Rebek, J.; *Nature*, 1998, **394**, 164

[74] Arduini, A., Fabbi, M., Mantovani, M., Mirone, L., Pochini, A., Secchi, A., Ungaro, R.; *J. Org. Chem.*, 1995, **60**, 1454

[75] Bott, S.G., Coleman, A.W., Atwood, J.L.; *J. Am. Chem. Soc.*, 1986, **108**, 1709

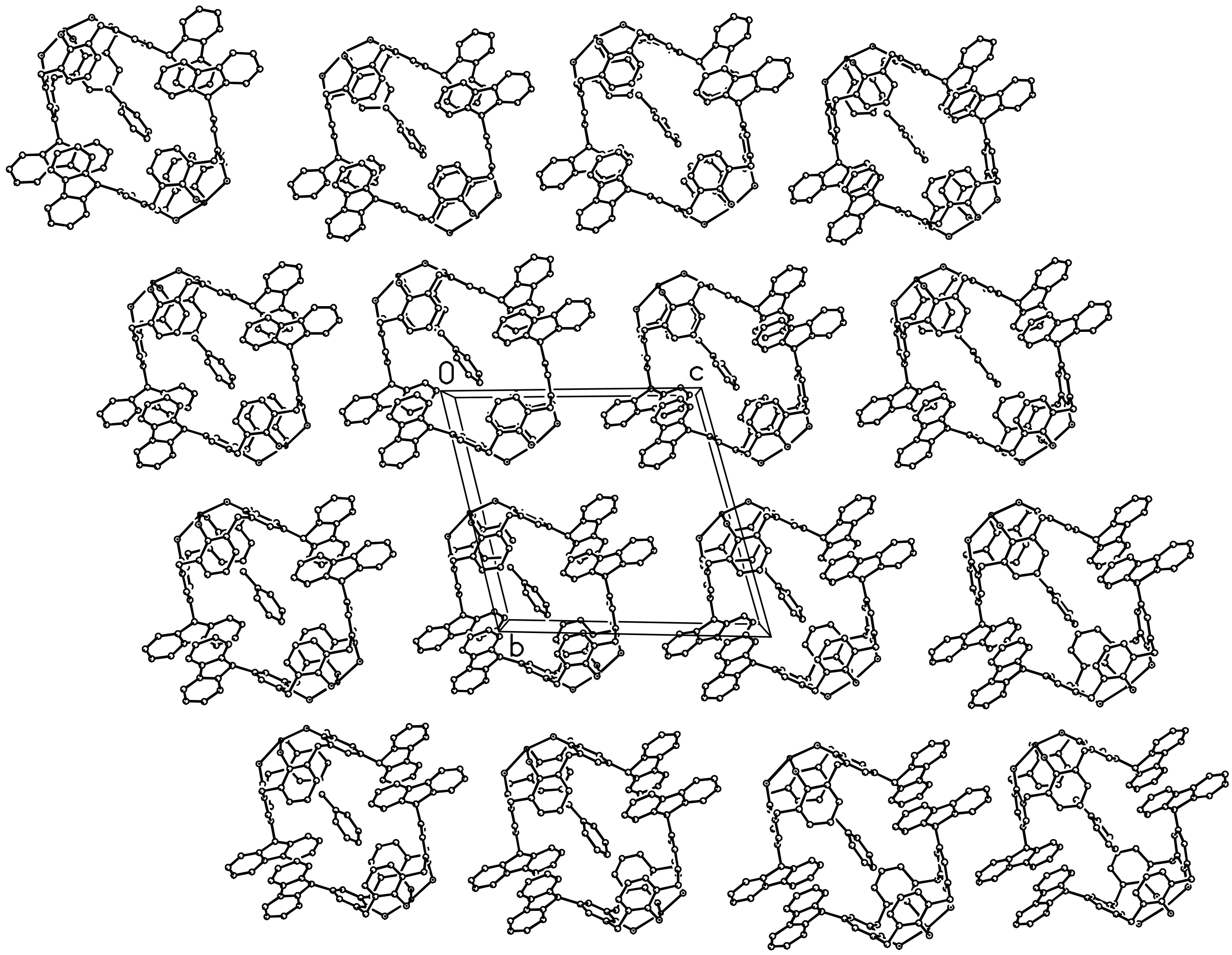


Figure 2.32. The packing of egg-shaped dimers in the crystal.

2.4 Lower rim functionalized calix[4]arene

After the depressing attempts to functionalize the *upper rim* of tetrapropoxy-calix[4]arene with a metallocene, it was decided to investigate the use of crown ethers and calix[4]arenes in the living anionic polymerization of styrene. The idea was to bind the lithium-ion and thereby provide an environment that would influence the tacticity of the polymer. The results and experimental details was discussed previously in *Chapter 1* but the compounds **3**, **22**, **24, 26** and **29** were synthesised, see ***Figure 2.33***.

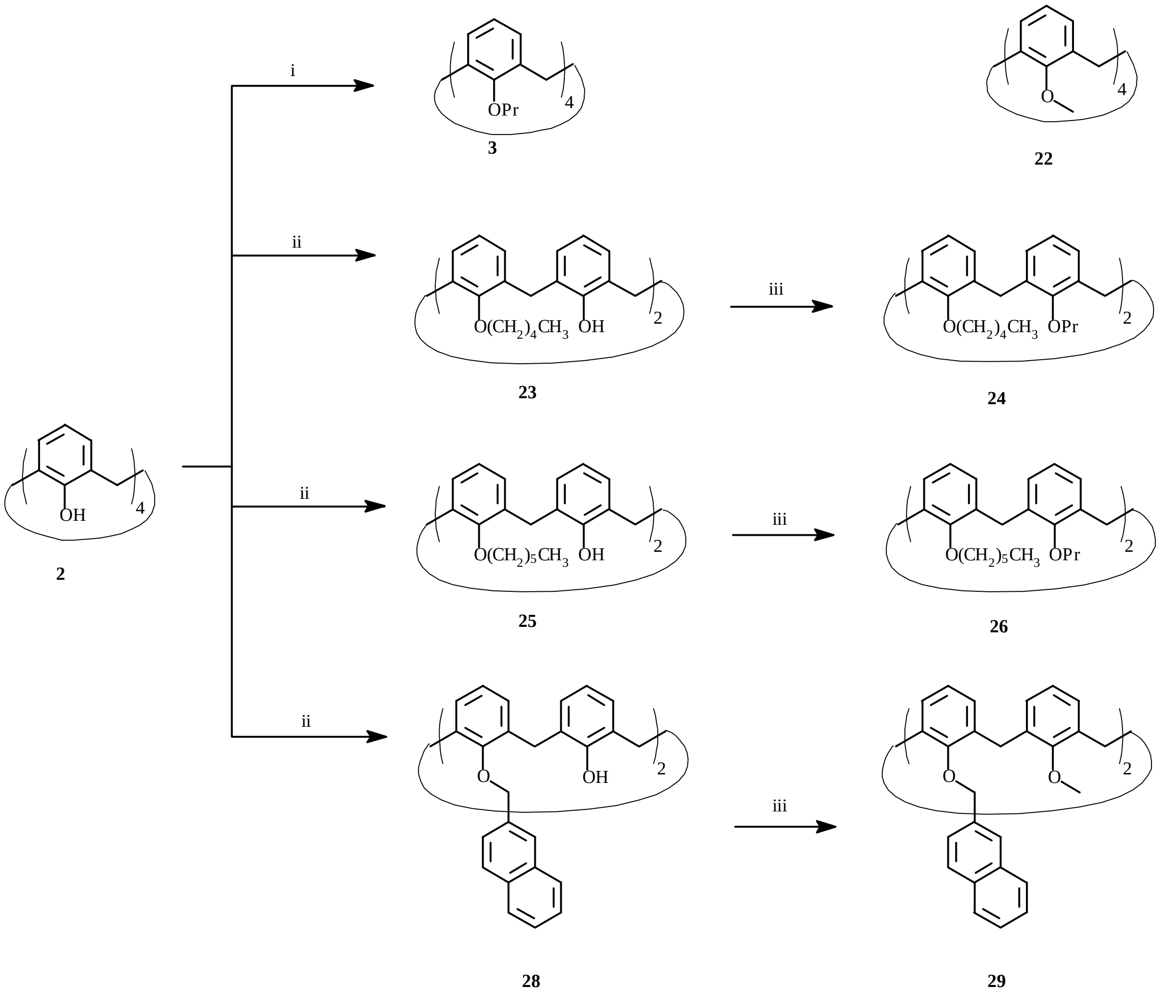


*Figure 2.33. Synthetic route used in preparation of **3**, **22**, **24, 26** and **29** from **2**. Conditions used is: i) 1) NaH/DMF/RT/90 min 2) n-PrI or MeI/RT/overnight; ii) K_2CO_3/alkyl-iodide (in the case of **28** the bromide was used)/acetone/reflux/2 days (in the case of **28** one hour); iii) 1) NaH/DMF/RT/30 min 2) alkyl-iodide/60 °C/overnight.*

2.5 ***Conclusion***

The lesson learned from the above has been that the chemistry available in order to derivatives the *upper rim* of calix[4]arenes seems to fail when applied to reagents possessing labile protons like cyclopentadiene or indene. While it is absolutely necessarily to have at least one labile proton to synthesise the wanted metallocene in mind these limits are counteracting, making calix[4]arenes a poor choice as a template for these systems. Another problem is the reaction between calix[4]arene and the Group 4 metals (and properly also Group 5) resulting in the cleavage of the ether groups.

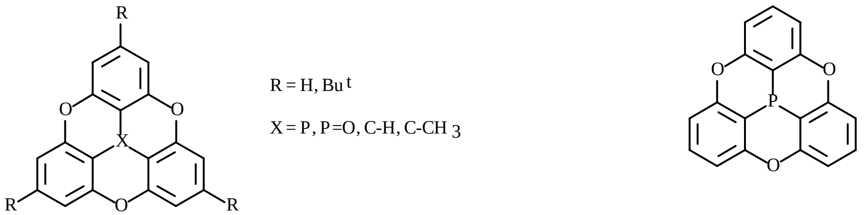
The work above lead to the conclusion that 25,26,27,28-tetraalkoxy calix[4]arenes simply is a poor template for the use in metallocene catalysts at least when the transition metal atom used is either titanium, zirconium or hafnium. ^{1}H-NMR analysis using a sealed NMR tube as explained above but with $HfCl_4$ instead of $ZrCl_4$ showed the same result as in the later case though the destruction not as complete. One could also argue that even if the synthesis of a metallocene based on a calixarene had been successful the ease with which the calixarenes makes complexes with moderate Lewis acids probably would have rendered the activation necessary by methylaluminoxane (MAO). This being a very strong Lewis acid, would most certainly again have led to destruction of the catalyst.

3 Other projects

This chapter will focus on the work concerning two compounds namely 2,6,10-tri-tert-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene and 7,8-dioxa[6]helicene. The two projects do not concern the metallocenes but represent time spent on more fruitful synthetic work. Both projects has resulted in publications, see *Appendix 6-8*.

3.1 Trioxatriangulene system

This project was initiated by the work of Krebs *et al*[1] who synthesised 4,8,12-trioxa-12c-phospha-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene (**3A**) and solved the crystal structure finding that was shaped like a Chinese hat with C_{3v} symmetry exhibiting pyroelectric properties. In order to investigated how an alteration of the spatial extent by molecular substitution of the trioxatriangulene skeleton correlates with the space group symmetry observed in the crystalline phase and the subsequent dielectric properties, see ***Figure 3.1***.



3A

Figure 3.1. 4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[cd,mn]pyrene system (also called trioxatriangulene) with the R substituents at the 2,6,10-positions and the substituent X at the 12c-position.

The synthesis of trioxatriangulene, e.g. R= H and X= C-H in ***Figure 3.1***, was first published by Martin and Smith[2] through the reduction of the cation by $LiAlH_4$.

---

[1] Krebs, F.C., Larsen, P.S., Larsen, J., Jacobsen, C.S., Boutton, C., Thorup, N.; *J. Am. Chem. Soc.*, 1997, **119**, 1208

[2] Martin, J.C., Smith, R.G.; *J. Am. Chem. Soc.*, 1964, **86**, 2252

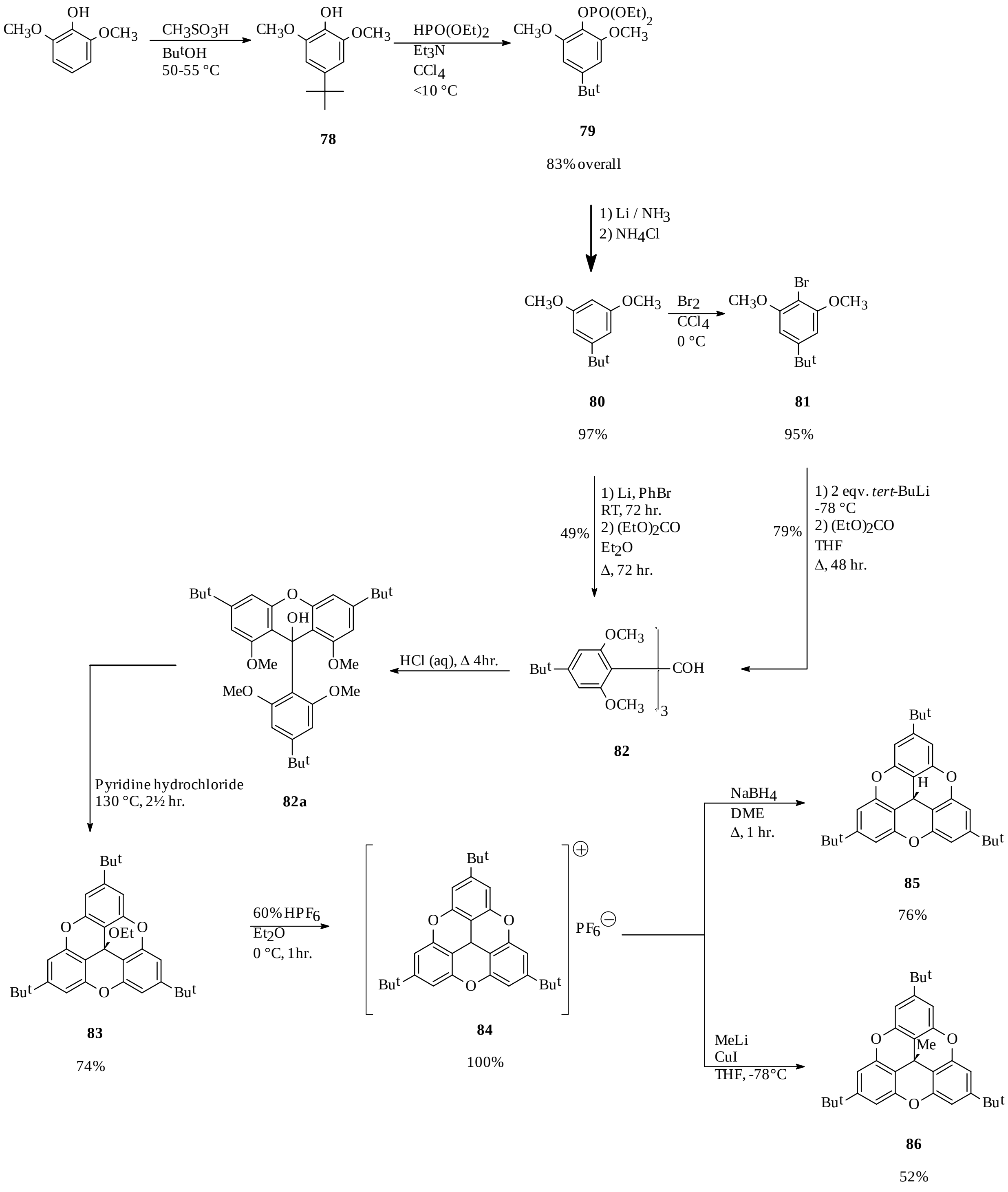


Figure 3.2. The synthetic route for the preparation of ***85*** *and* ***86****.*

The synthesis of 2,6,10-tri-*tert*-butyl trioxatriangulene (**85**) has been described previously[3] but the method developed here gives a much higher overall yields combined with a considerable reduction in time used for the total synthesis, see ***Figure 3.2***. The synthesis starts with the commercially available 2,6-dimethoxyphenol, which was *tert*-butylated under Friedel-Crafts conditions producing **78**. The crude **78** was reacted directly with diethyl phosphite giving **79** in 83 % overall yield, this was reduced by lithium in liquid ammonia producing **80** quantitatively.

The next step, e.g. the formation of **82**, was found to be accomplished by two different routes. Either by direct lithiation of **80** using phenyllithium for 3 days followed by nucleophilic substitution on diethyl carbonate in refluxing Et_2O for another 3 days giving the product in 49 % yield. First it was assumed that the lithiation was incomplete due to the low yield but it was found that using commercial phenyllithium in Et_2O under identical conditions followed by quenching with D_2O resulted in 61 % lithiation, determined by ^{1}H-NMR spectroscopy. If however freshly prepared phenyllithium was used the lithiation was 77 %, determined in the same manner. When applying the procedure by Brandsma and Verkruijsee[4] used for the quantitative lithiation of dimethylresorcinol only 12 % had been lithiated, indicating that the lithiation of **80** is not trivial and is probably governed by both base-strength and steric demands of the organometallic compound in use.

The other way of formation of **82** was using a halogen-metal exchange reaction. Synthesis of **81** by bromination of **80** was found to be nearly quantitative and the halogen-metal exchange reaction was complete, e.g. 100 %, after only one hour (determined by quenching and analysis as above). Also the nucleophilic substitution was more rapid probably due to the use of THF instead of Et_2O and after two days **82** was obtained in 79 % yield.

The formation of the xanthol **82a** was accomplished by reflux for 4 hours in hydrochloric acid where after the crude product was reacted directly with neat pyridine hydrochloride at 130 °C giving **83**. The conversion of **83** to the intensely yellow colored 2,6,10-tri-*tert*-butyl trioxatriangulene cation (**84**) was quantitative when HPF_6 in Et_2O was used.

The reduction of **84** by sodium borohydride runs smoothly giving the colorless 2,6,10-tri-*tert*-butyl trioxatriangulene (**85**) in moderate yield. It was then anticipated that the reaction of **84** with methyllithium in THF similarly would result in 2,6,10-tri-*tert*-butyl 12c-methyl-trioxatriangulene (**86**). It did, but only in 7 % yield, which was unsatisfactory, and the yield was found to greatly

---

[3] Peters, N.J.; *Ph.D. Dissertation*, University of Illinois, 1980, pp 10-15

[4] Brandsma, L., Verkruijsse, H.D.; *Preparative Polar Organo-metallic Chemistry*, Springer-Verlag, Berlin, Heidelberg, 1987, **1**, 203

improve to 36 % if catalytic amount of CuI was added. Even better yield was obtained if the dimethylcopperlithium reagent was produced *in situ* and reacted with **84** giving **86** in 52 % yield. Recrystallisation from ethyl acetate formed high quality and very beautiful crystals suitable for X-ray crystallography, see *Appendix 2* for crystallographic details.

Compound **85** crystallizes in the exceptionally high symmetry space group cubic I-43*d* having 16 molecules in the unit cell but since a center of symmetry is absence pyroelectric properties are thus not possible while piezoelectric properties in theory should be observable. An unsuccessful attempt was made using the method of Giebe and Shiebe[5] to measure the piezoelectric response. In ***Figure 3.3*** is the packing of compound **85** shown and in ***Figure 3.4*** is an ORTEP drawing shown.

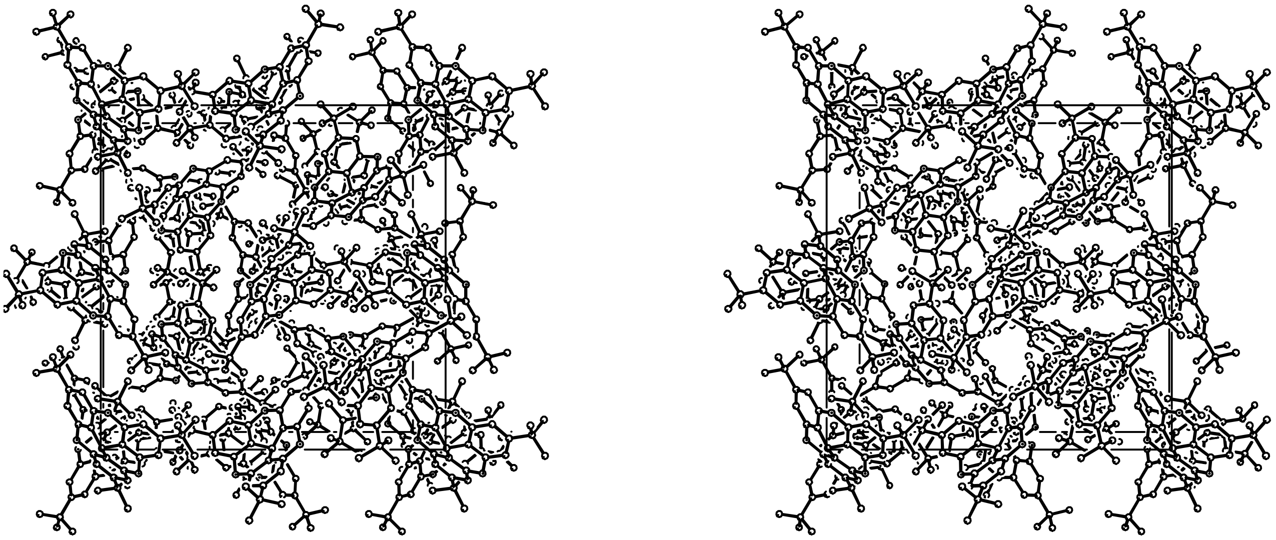


Figure 3.3. Stereoview of the packing for compound ***85*** *as a projection along one of the crystallographic axes. The molecules stack in a staggered manner along the three-fold crystallographic symmetry axes.*

---

[5] Mason, W.P; *Piezoelectric Crystals and Their Application to Ultrasonics*, Van Nostrand, New York, 1950, 47-48

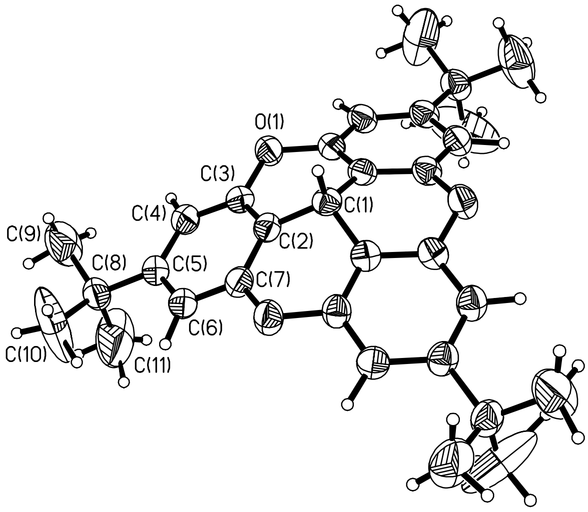


Figure 3.4. ORTEP drawing of the molecule for compound ***85*** *where only the asymmetric unit has been labeled.*

Compound **86** crystallizes in an orthorhombic P*na*2_1 space group with 4 molecules in the unit cell. The structure of **86** belongs to the *mm2* point group and is thus polar and should in principle also be pyroelectric, see ***Figure 3.5*** and ***Figure 3.6***.

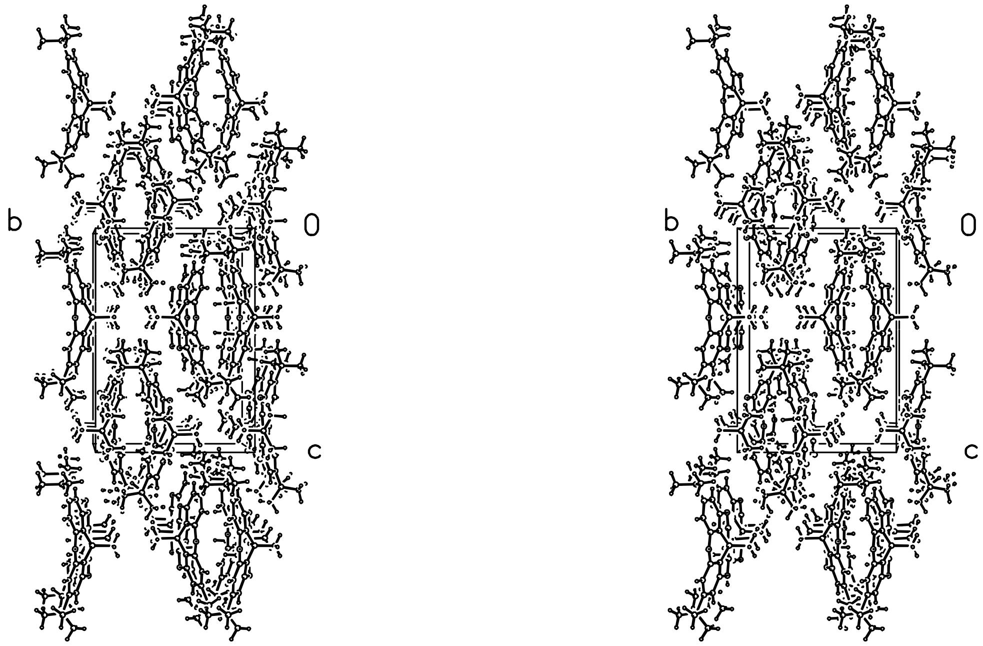


Figure 3.5. Stereoview of the packing for compound ***86*** *along the a-axis. The molecules do not form stacks; they are arranged in layers.*

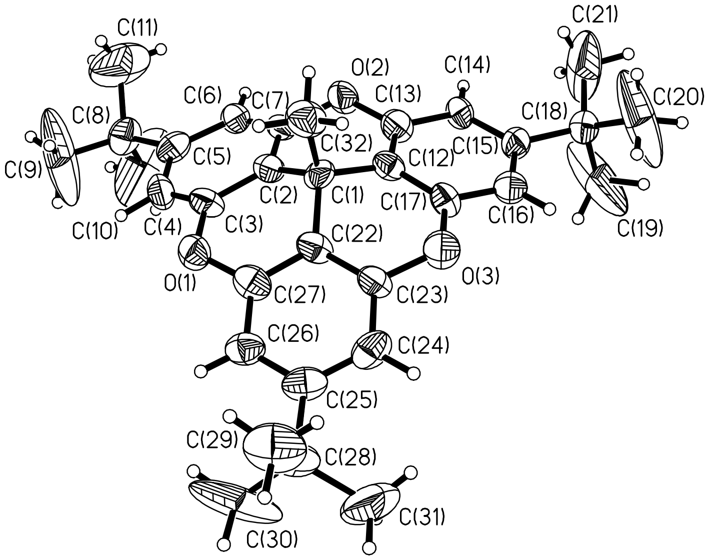


Figure 3.6. ORTEP drawing of the molecule for compound ***86*** *with labeling of the atoms.*

In ***Figure 3.5*** it can be seen that the molecules are all opposing each other with respect to the direction of their individual molecular dipole moments, along the molecular C_3 axis, thereby excluding the possibility of a large permanent dielectric polarization. More carefully inspection of the molecular dipole moments shows that they all form an angle of 0.2 degree with the *ab*-plane in the negative *c*-direction. There is therefor a small amount of dielectric polarization in the solid along the *c*-axis but the magnitude of the pyroelectric coefficient would be very small when considering values of thermal expansion and dipole moments typical measured for organic compounds. The substituent at the 12c-position of **86** prevents stacking, forming a layered structure instead.

As seen the ellipsoids representing the *tert*-butyl groups are rather large due to some degree of disorder common for both compounds **85** and **86**. This is explained by the fact the neither molecules gives rise to a dense packing in the crystalline state, evidenced by their low densities in the order of 1.1 g/cm^3 compared to other trioxatriangulenes having densities around 1.5 g/cm^3.

Comparing the substitution pattern and the resulting crystalline structures resulted in the conclusion that when hydrogen or lone pair was present at the central position, e.g. 12c-position, the compound belonged to a non-centrosymmetric space group forming stacks (as in the case of compound **85**). When the central position was substituted with larger substituents (e.g. methyl or P=O) the compound belonged to a centrosymmetric space group. The substitution at the periphery, e.g. 2,6,10-positions, with substituents as bulky as *tert*-butyl had little effect on the nature of packing when the central substituent was hydrogen or lone-pair. If however both the central and the periphery positions were substituted with methyl and *tert*-butyl groups respectively a non-centrosymmetric structure is also observed but no stacking occur due to the presence of molecules of opposite chirality in the unit cell (as in the case of compound **86**).

Compound **84** was also used to introduce other substituents, see ***Figure 3.7***, but high quality crystals suitable for X-ray crystallography has not been achieved. These compounds were only synthesised for academic interest, one could expect some interesting crystalline structures resembling molecular "hand-weights" in the case of **88**.

Compound **83** were used to prepared a molybdenum chloride cluster **3B** which together with **84** was used in a study of the structures of planar cations with various monovalent and divalent anions, see *Appendix 6*.

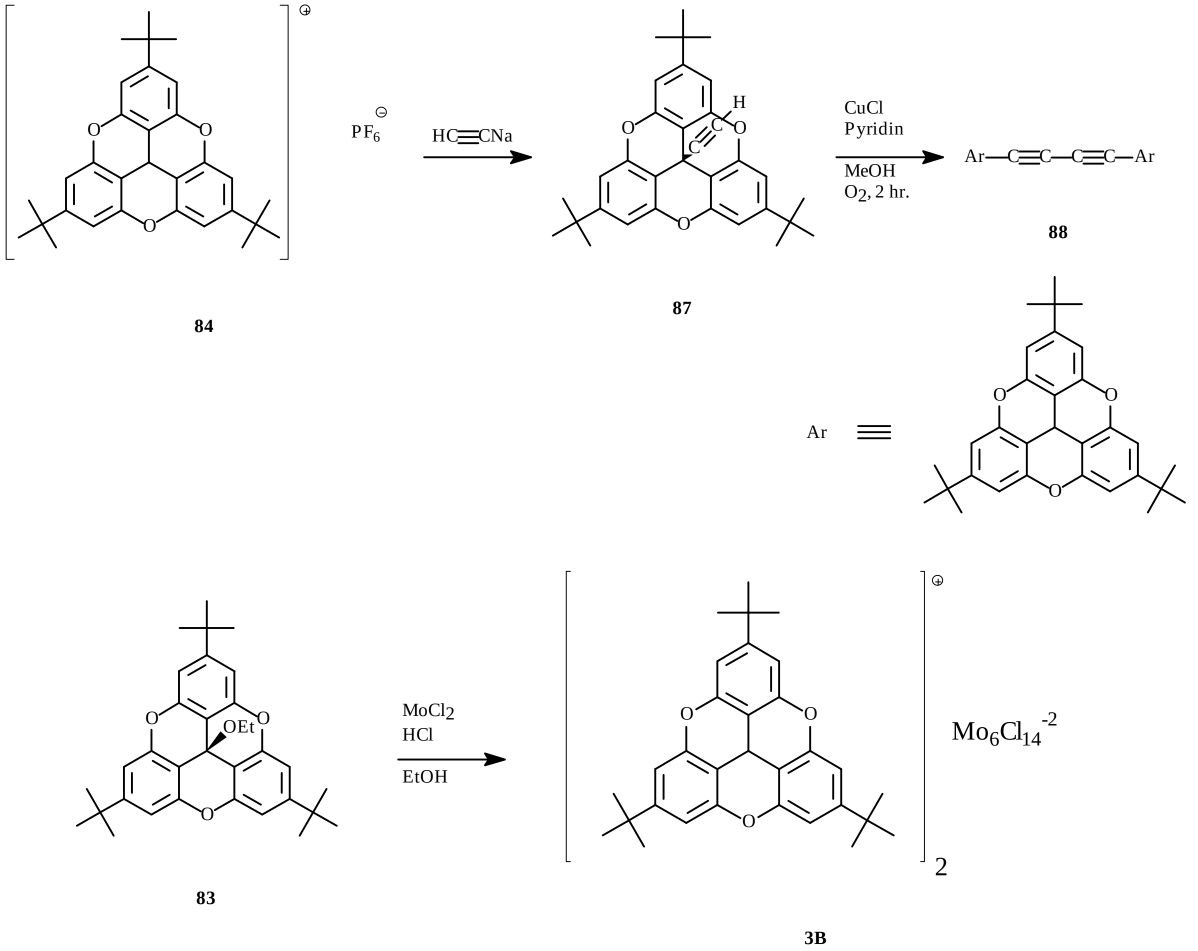


*Figure 3.7. The synthetic route used for preparation of compound **87** and **88** from **84** and **3B** from **83**.*

3.2 7,8-Dioxa[6]helicene

The interest in synthesising the 7,8-dioxa[6]helicene (**89**)[*] arose from simple theoretical models indicating the a low inversion barrier excisted between the helical enantiomers. The horseshoe shaped **89** is a six ring heterohelicene having a rather complex crystal structure and is prepared from the 7a,14c-dihydro-7,8-dioxa[6]helicene (**3C**), see ***Figure 3.8***. Compound **3C** is synthesised from the regioselective condensation of 2 moles of 2-naphthol and glyoxal[6]. The synthesis and crystal structure has been published, see *Appendix 7* and *Appendix 8*.

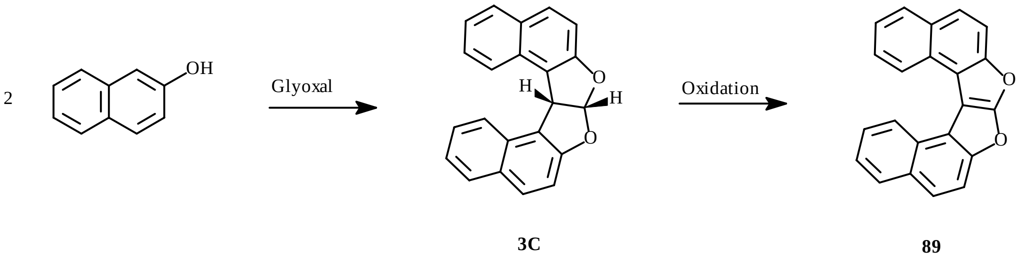


*Figure 3.8. Synthesis of 7,8-dioxa[6]helicene (**89**).*

The oxidation reaction was first attempted by heating in neat selenium or sulfur, neither resulted in dehydrogenation[7] of **3C** as was the case when refluxing **3C** in mesitylene with palladium on carbon passing air though the reaction mixture in order to remove hydrogen from the reaction mixture. When 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was applied in refluxing benzene if was found that some dehydrogenation had taken place and when the solvent was changed to 1,2-dichlorobenzene thereby increasing the temperature **89** was collected in 40 % yield. The collected product was however found by HPLC to be a mixture of three compounds, **3C**, **89** and **3D**. Using semipreparative HPLC it proved possible to separate the three compounds and by NMR the starting material **3C** and product **89** was identified. By NMR it was not possible to identity the compound **3D** but growing high quality crystals was achieved, and by X-ray crystallography it was found that the by-product **3D** had the structure shown in ***Figure 3.9***.

---

[*] IUPAC name is naphtho[2,1-*b*]naphto[1',2':4,5]furo[3,2-*d*]furan

[6] Dischendorfer, O.; *Monatsh. Chem.*, 1940, **73**, 45

[7] Jackman, L.M.; *Adv. Org. Chem.*, 1960, **2**, 329-366

This unexpected formation of the 5-chloro-7,8-dioxa[6]helicene (**3D**) turned out to be rather significant in the discussion of the parent helicene structure **89**, which exhibits very unusual structural properties. While the crystal structure of **3D** is orthorhombic belonging to the $Pna2_1$ space group and perfectly ordered, see *Appendix 3* and ***Figure 3.10***, the crystal structure of **89** exhibit varying pitch of the helixes in the crystal and a disordered structure with eight different molecules in the asymmetric unit.

It was later found that **89** could by synthesised in 82 % yield, and without formation of the above-mentioned by-product, by reaction with N-bromosuccinimide and UV radiation in refluxing carbontetrachloride. The reaction most likely proceeds by Wohl-Ziegler radical bromination of the "benzylic" 14c-position in **3C**, followed by E_1 elimination of hydrogenbromide. The E_1 type elimination is proposed since X-ray studies have shown that the two hydrogen at the 7a and 14c positions are in a *cis* geometry, see *Appendix 8*.

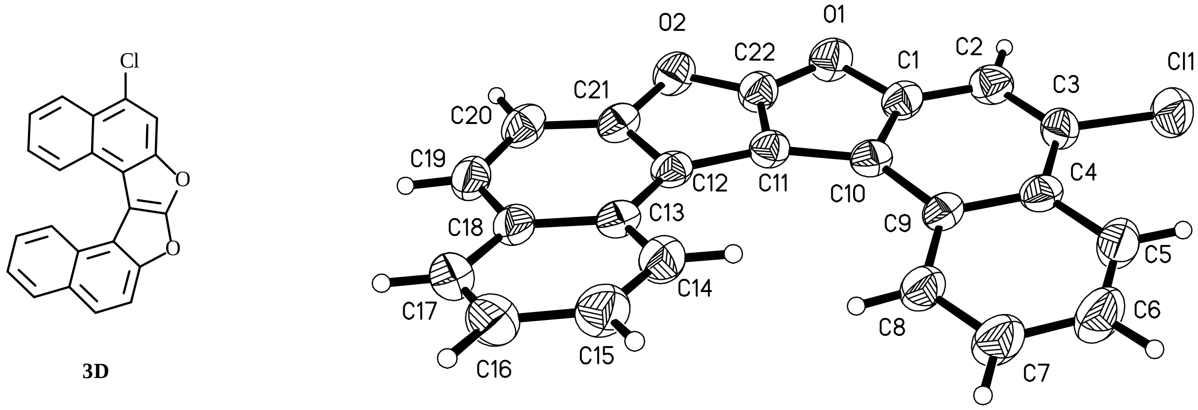
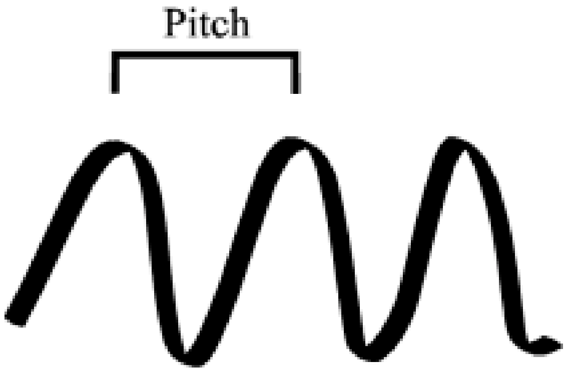


*Figure 3.9. Structure of 5-chloro-7,8-dioxa[6]helicene (**3D**), left, and right ORTEP drawing of the molecule.*

*Figure 3.10. Stereoview of **3D** shows the helical nature of the 7,8-dioxa[6]helicene.*

In compound **89** the geometrical features of the two five-membered furane rings resulting in interconversion of the two helical enantiomeric forms, e.g. racemisation, occurs readily at room temperature in solution. This property is responsible for the unsuccessfully attempts to resolve the two enatiomeric forms by NMR using chemical shift reagents and by using chiral column chromatography. In the crystal structure using synchrotron X-ray diffraction 8 different enantiomeric pairs, two of which are disordered, was observed having varying enantiomer geometry. The so-called *inner pitch*[8] characterizes the helicity of the molecules and was found to be around 1.3 Å where in a "normal" helicene the inner pitch is around 3 Å, see ***Figure 3.11***.



Molecule	Pitch /Å
A 57 % s.o.f.	1.3
B	1.3
C	1.5
D	1.3
E 57 % s.o.f.	1.1
F	1.1
G	1.3
H	1.2
A(U) 43 % s.o.f.	1.0
E(U) 43 % s.o.f.	1.2

*Figure 3.11. Illustration of the inner pitch, left, where the curve should illustrate the screw arising within a stack of helicenes; the pitch is then the distance required for one full turn. Right is shown the variation of the inner pitch for **89**.*

The crystal system of **89** is monoclinic and the space group is C*c*, see *Appendix 3*, having 32 molecules in the unit cell, which in a simpler representation can be reduced to 8 enantiomeric pairs, see ***Figure 3.12***.

---

[8] Navaza, J., Tscoucaris, G., le Bas, G., de Rango, C.; *Bull. Soc. Chim. Belg.*, 1979, **88**, 863

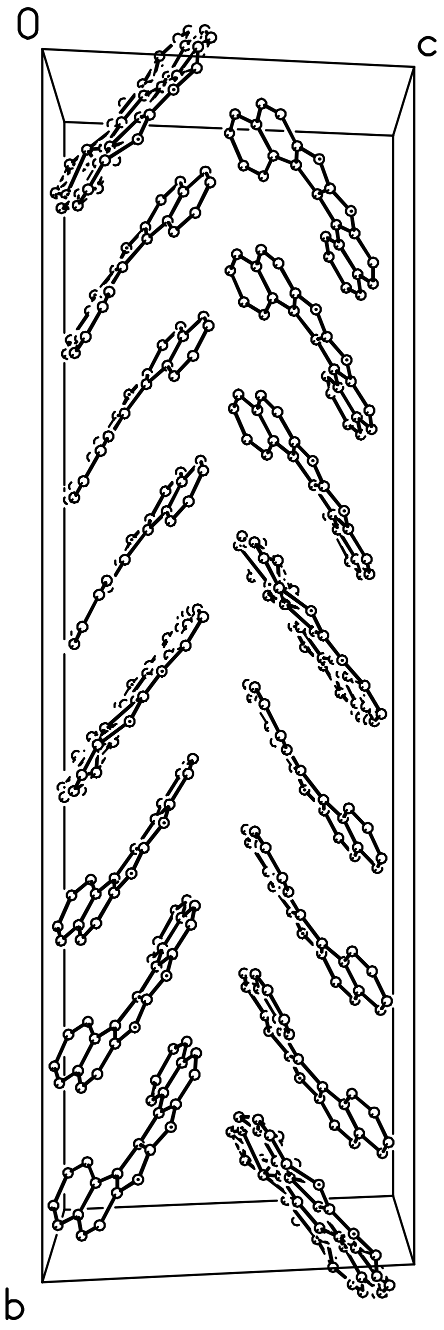


Figure 3.12. The unit cell of compound ***89****.*

The two enantiomeric forms is denoted P (+) and M (-) which are distributed in the following manner when running along a stack in the crystal; a triad of P helicity, the next molecule is disordered (P or M), then a triad of M helicity and finally another disordered molecule (P or M) is observed, see ***Figure 3.13***.

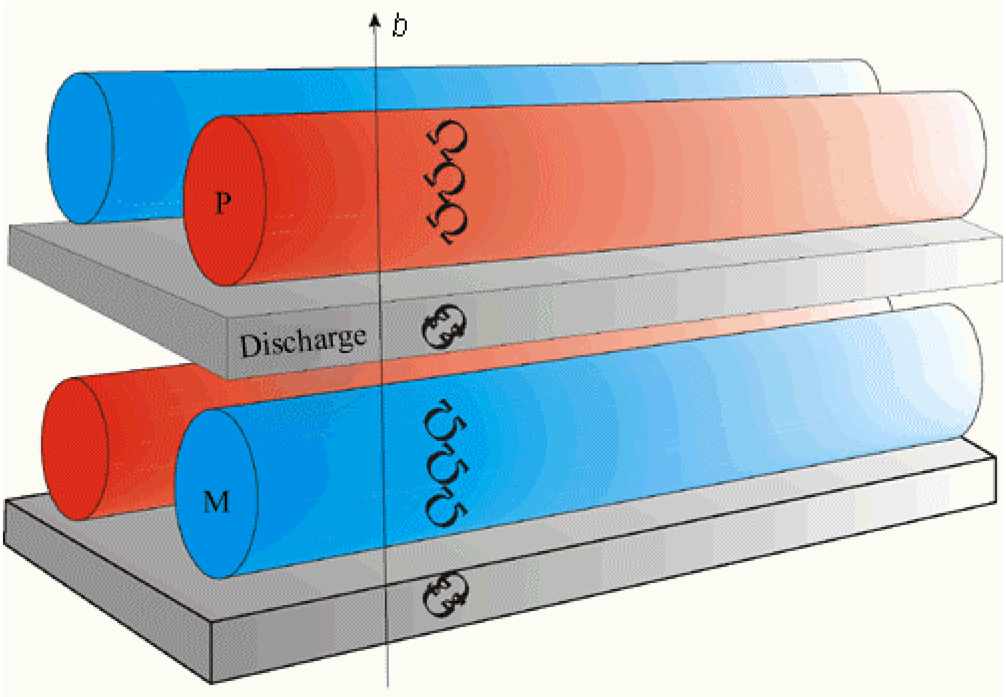


Figure 3.13. Structure model. The helical molecules (Ω) are stacked along the b axis.

The observed disorder gives rise to polymorphic crystals where each macroscopic crystal appears as an individual. Along the stacking direction, taking 8 individual molecules (the asymmetric unit) the static order will appear as {4 4}, {5 3}, {3 5}, {3 4 1} or {4 3 1}. This means that small domains of the crystal can exhibit enantiomeric excess but it was however not possible to investigate experimentally the size of the microdomains. The P and M helicity occurs with a 57/43 s.o.f. (site occupation factor) with orientation related to their underlying triad which is assumed to be the origin of the low symmetry, lacking inversion symmetry, observed for this compound.

Experimental

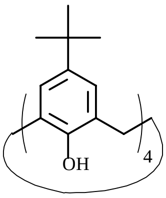
Synthetic methods and materials. All reagents used were standard grade unless otherwise mentioned. THF and diethylether was dried by distillation from Na/benzophenone under argon. The 1,2-dimethoxyethane (DME) was treated with and stored over CaH_2 before use. All operations using lithium was conducted under an atmosphere of argon. The concentration of *n*-BuLi in hexane and *tert*-BuLi in pentane was determined by titration of *N*-(2-methylphenyl)-2,2-dimethylpropanamide[1] in the appropriate dry solvent (e.g. THF or diethylether) before usage in reactions where the stoichiometry was critical.

Spectroscopy and analysis. NMR spectra were recorded on a BRUKER Advance DPX 250 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Unless otherwise stated all NMR spectra was performed using $CDCl_3$ as solvent and was dried over basic Al_2O_3 (70-230 mesh) prior to use. Melting points was determined using a BÜCHI 510 melting point apparatus. Mass spectra were determined using a Hewlett Packard 6890 Series GC-MS system with a 5% phenyl methyl siloxane column and Hewlett Packard G2025A MALDI-TOF mass spectrometer. DSC spectra were recorded on a Perkin Elmer DSC Pyris 1. SEC/GPC analyses were performed using a Viscotek 200 with refractive index and viscosity detectors. Elemental analysis were performed at DB Lab, Stenhuggervej 9, DK-5230 Odense M, Denmark and Mikro Kemi AB, Seminariegatan 29, 75228 Uppsala, Sweden.

Synthesis of precursors and catalysts

*1 5,11,17,23-Tetra(tert-butyl)-25,26,27,28-tetrahydroxyCalix[4]arene (**1**)*

648.92 g/mol



1

In three liter round bottom bottle was placed 4-*tert*-butylphenol (250 g; 1.66 mol), formaldehyde wt-37% in water (155 ml; 2.07 mol) and NaOH (1.2 g; 0.03 mol) dissolved in water (3 ml). The mixture was mechanically stirred at 120 °C for ca. 30 min until a very viscous mixture formed (be cautionary happens very quickly!). The solid was cooled to RT, added diphenyl ether (2000 ml) and toluene (100 ml) followed by heating without cooling the condenser to 260 °C for 3 hours. In the beginning the heating was performed carefully in order to control the distilling rate of the water/toluene azeotrop. The heating was continued with the condenser for another 3 hours, which caused the solution to become homogenous and dark brown. The solution was cooled to 60 °C, added ethylacetate (1500 ml), cooled to RT and stirred overnight. The solution was filtered, and the white solid washed with ethylacetate (50 ml), triturated with acetic acid

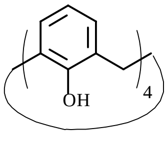
---

[1] Suffert, J. *J. Org. Chem.* **1989**, *54*, 509-510.

(200 ml), filtered, washed with ethylacetate (4 x 50 ml) and recrystallized from toluene (3000 ml). Yield: 62 % (167.19 g). ^{1}H-NMR: 10.33 (s, 4H); 7.04 (s, 8H); 4.23 (br. s, 4H); 3.51 (br. s, 4H); 1.21 (s, 36H). ^{13}C-NMR: 143.7; 127.7; 125.9; 112.0; 77.5; 34.0; 32.6; 31.4

*2 25,26,27,28-TetrahydroxyCalix[4]arene (**2**)*

424.50 g/mol

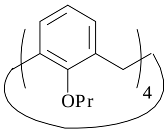


2

A solution of **1** (155.24 g; 0.239 mol), phenol (124.19 g; 1.32 mol) and toluene (1550 ml) was cooled to 10 °C and added anhydrous $AlCl_3$ (170.76 g; 1.28 mol). The temperature raised to 22 °C during the addition and after 2 hours of stirring a precipitation started. Finally the reaction mixture was stirred overnight at room temperature. The light brown reaction mixture was poured onto 2 M HCl (1000ml)/ice, stirred vigorously for ca. 15 min. after which the organic phase was separated and evaporated to a mixture of liquid and solid material. This suspension was added $CHCl_3$ (ca. 700 ml), refluxed shortly and added MeOH (ca. 1000 ml) which trigged a precipitation of the white product. The mixture was filtered after 4 hours in the cold and dried in vacuum overnight at 50 °C. Yield: 81% (81.93 g). ^{1}H-NMR: 10.19 (s, 4H, OH); 7.04 (d, 8H, J= 7.6 Hz); 6.72 (t, 4H, J= 7.6 Hz); 4.23 (br. s, 4H); 3.56 (br. s, 4H). ^{13}C-NMR: 148.8; 129.0; 128.3; 122.2; 31.7

*3 25,26,27,28-TetrapropoxyCalix[4]arene (**3**)*

592.82 g/mol

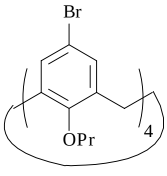


3

To a solution of **2** (70.00 g; 0.165 mol) in DMF (800 ml) under argon was added slowly NaH wt.-60% dispersion in oil (40.00 g; 24.00 g; 1.00 mol) at RT and stirred mechanical for 30 min. The solution was cooled to 5 °C and added n-propylbromide (240 ml; d= 1.354 g/ml; 324.96 g; 2.80 mol) in one portion. The mixture was stirred for 18 hr. at 10-15 °C. The solution changed color from white to greenish blue to brown. The reaction mixture was quenched slowly by adding MeOH (250 ml) and evaporated as much as possible. The residue was poured into 2 M HCl (1000 ml), stirred for 10 min. and extracted with $CHCl_3$ (5 x 100 ml). The yellow organic phases were collected and washed with water (4 x 200 ml), dried (Na_2SO_4), and concentrated in vacuum to yellow solid. Addition of boiling $CHCl_3$ (ca. 200 ml) followed by addition of MeOH (ca. 700 ml) coursed the product to precipitate as a white powder. Yield: 88 % (86.12 g). ^{1}H-NMR: 6.57 (m, 12H); 4.45 (d, 4H, J= 13.3 Hz); 3.84 (t, 8H, J= 7.4 Hz); 3.14 (d, 4H, J= 13.3 Hz); 1.92 (m, 8H, J= 7.5 Hz); 0.99 (t, 12H, J= 7.4 Hz). ^{13}C-NMR: 156.6; 135.1; 128.1; 121.8; 76.7; 31.0; 23.2; 10.3

*4 5,11,17,23-Tetrabromo-25,26,27,28-tetrapropoxyCalix[4]arene (**4**)*

908.40 g/mol

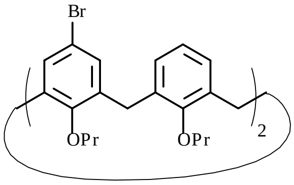


4

A solution of **3** (20.00 g; 33.74 mmol), N-bromosuccinimide (53.21 g; 0.299 mol; +120 %) and two drops of 6 M HCl in methylethylketone (420 ml) was stirred 1 day at RT. The orange reaction mixture was added Na_2SO_3 (300 ml) and 6 M HCl (1 ml) and stirred for 10 min. The yellow organic phase was separated and the aqueous phase was washed with $CHCl_3$ (100 ml). The organic phases was collected and washed with water (3 x 200 ml), sat. $NaHCO_3$ (200 ml), water (200 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was dissolved in boiling $CHCl_3$ (ca. 150 ml), added MeOH (ca. 300 ml), cooled in ice, filtered and the white product was dried at 70 °C overnight in vacuum. mp: 271-273 °C, litt.: 280-282 °C. Yield: 90 % (27.57 g). ^{1}H-NMR: 6.80 (s, 8H); 4.35 (d, 4H, J= 13.5 Hz); 3.80 (t, 8H, J= 7.5 Hz); 3.08 (d, 4H, J= 13.5 Hz); 1.87 (m, 8H, J= 7.5 Hz); 0.96 (t, 12H, J= 7.5 Hz). ^{13}C-NMR: 155.6; 136.5; 131.09; 115.3; 77.3; 30.8; 23.2; 10.3

*5 5,17-Dibromo-25,26,27,28-tetrapropoxyCalix[4]arene (**5**)*

750.61 g/mol

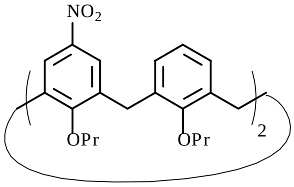


5

4 (87.81 g; 96.66 mmol) was dissolved in dry THF (1000 ml), cooled to -78 °C, added 1.6 M n-BuLi (157 ml; 28.62 mol; +30 %) and stirred for 15 min. at -78 °C. Methanol (450 ml) was added quickly and the reaction mixture was stirred for an additional 10 min. before it was evaporated to dryness. The solid was dissolved in $CHCl_3$ (200 ml) and water (200 ml). The organic phase was separated, the aqueous phase washed with $CHCl_3$ (2 x 100 ml). The organic phases was collected, washed with 2 M HCl (100 ml), sat. Na_2CO_3 (100 ml), water (100 ml), dried (Na_2SO_4) and evaporated to dryness giving a pale yellow solid. This solid was dissolved in a minimum of hot $CHCl_3$ (ca. 75 ml) and addition of methanol (ca. 250 ml) coursed the product to precipitate as a white solid which was filtered, washed with methanol and dried at 70 °C in vacuum overnight. mp: 227-230 °C, litt.: 243-245 °C. Yield: 87 % (64.35 g). ^{1}H-NMR: 6.77 (s, 4H); 6.63 (s, 6H); 4.40 (d, 4H, J= 13.3 Hz); 3.83 (t, 4H, J= 7.5 Hz); 3.81 (t, 4H, J= 7.5 Hz); 3.11 (d, 4H, J= 13.3 Hz); 1.90 (q, 4H, J= 7.6 Hz); 1.89 (q, 4H, J= 7.4 Hz); 0.98 (t, 6H, J= 7.4 Hz); 0.97 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 156.4; 155.7; 137.2; 134.4; 130.8; 128.4; 122.5; 114.7; 76.9; 76.8; 30.9; 23.2; 10.3; 10.3 (fewer carbon signals than expected because of accidentally isochrony)

*6 5,17-Dinitro-25,26,27,28-tetrapropoxyCalix[4]arene (**6**)*

682.82 g/mol

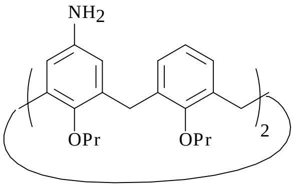


6

3 (10.00 g; 16.87 mmol) was dissolved in CH_2Cl_2 (400 ml), AcOH (5 ml) and fuming 100 % HNO_3 (5.00 ml; d= 1.52 g/ml; 7.60 g; 0.121 mol; 3.5 eqv.) was added at RT. The reaction mixture changed color to dark violet. Stirring was continued for ½ hour at RT (or until a TLC (CH_2Cl_2) show that dinitro-calixarene (R_f= 0.62) has reached a maximum) and quenched with ice/water (400 ml). The green dispersion was stirred for 10 min. and the organic phase was separated, washed with sat. Na_2CO_3 (2 x 300 ml), water (50 ml), dried (Na_2SO_4) and evaporated to an orange solid. This solid was treated with boiling EtOH (100 ml) and the residue was filtered and washed with boiling EtOH (4 x 10 ml) producing an off white solid which was dried in vacuum. Yield: 72 % (8.30 g). ^{1}H-NMR: 7.42 (s, 4H); 6.73 (s, 6H); 4.47 (d, 4H, J= 13.7 Hz); 3.88 (q, 4H, J= 7.3 Hz); 3.86 (q, 4H, J= 7.3 Hz); 3.25 (d, 4H, J= 13.7 Hz); 1.90 (m, 8H); 1.03 (t, 6H, J= 7.4 Hz); 0.98 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 162.3; 156.7; 142.9; 136.7; 134.6; 129.3; 123.8; 123.5; 77.6; 31.5; 23.7; 23.5; 10.7; 10.6

*7 5,17-Diamino-25,26,27,28-tetrapropoxyCalix[4]arene (**7**)*

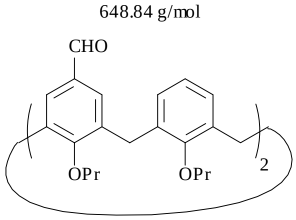
622.85 g/mol



7

A suspension of **6** (2.00 g; 2.93 mmol) and Raney Nickel 50 % slurry in water (1.50 ml; 0.75 g) in 96 % EtOH (50 ml) was added hydrazine hydrate (1.00 ml; d= 1.03 g/ml; 1.03 g; 20.58 mmol) was added slowly. The reaction mixture was stirred for 2 hours at RT followed by reflux for 15 min. producing a colorless suspension. The suspension was filtered and washed with $CHCl_3$ (2 x 50 ml). The combined organic phases was washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from acetonitrile resulted in a white product. mp: 265-267 °C, litt.: 268-270 °C. Yield: 68 % (1.25 g). ^{1}H-NMR: 6.70 (m, 4H); 6.60 (m, 2H); 5.93 (s, 4H); 4.37 (d, 4H, J= 13.3 Hz); 3.83 (t, 4H, J= 7.5 Hz); 3.73 (t, 4H, J= 7.4 Hz); 3.10 (br. s, 4H, NH_2); 3.03 (d, 4H, J= 13.3 Hz); 1.88 (m, 8H); 0.98 (accidental collapsing to a q, 12H, J= 7.6 Hz). ^{13}C-NMR: 157.6; 150.5; 141.1; 136.2; 136.0; 128.8; 122.4; 116.4; 77.4; 77.3; 31.8; 23.9; 11.1; 10.9

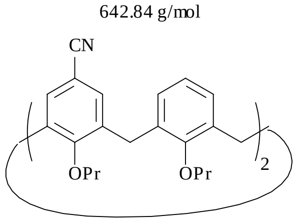
*8 5,17-Diformyl-25,26,27,28-tetrapropoxyCalix[4]arene (**8**)*



8

To a stirred solution of **5** (7.50 g; 9.99 mmol) in dry THF (150 ml) at –78 °C was added 1.35 M n-BuLi (45 ml; 60.00 mmol). The yellow solution was stirred at –78 °C for 15 min, quenched with DMF (82 ml; d= 0.944 g/ml; 82.10 g; 1.123 mol) and stirred for another 10 min. The reaction mixture was poured into ice-cold 6 M HCl (600 ml) and extracted with $CHCl_3$ (3 x 200 ml). The organic phases were collected and washed with water (100 ml), $NaHCO_3$ (100 ml), water (4 x 250 ml), dried (Na_2SO_4) and evaporated to dryness. The white solid was recrystallized from n-hexane (400 ml). mp: 204-208 °C, litt.: 216-218 °C (MeOH). Yield: 79 % (5.13 g). ^{1}H-NMR: 9.50 (s, 2H); 7.03 (s, 4H); 6.76 (m, 6H); 4.50 (d, 4H, J= 13.6 Hz); 3.92 (m, 8H); 3.26 (d, 4H, J= 13.6 Hz); 1.94 (m, 8H); 1.03 (accidental collapsing to a q, 12H, J= 7.4 Hz). ^{13}C-NMR: 192.4; 162.6; 157.3; 136.6; 135.5; 131.7; 130.5; 129.5; 123.3; 77.5; 32.0; 31.3; 23.8; 23.0; 10.8; 10.6

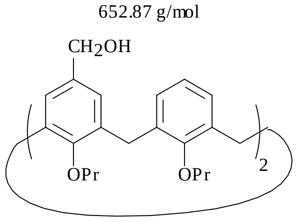
*9 5,17-Dicyano-25,26,27,28-tetrapropoxyCalix[4]arene (**9**)*



9

5 (4.00 g; 5.34 mmol), CuCN (1.92 g; 21.32 mmol) in NMP (200 ml) was mixed and refluxed overnight under argon. The reaction mixture was cooled to 100° C and added a solution of $FeCl_3$ (3.46 g; 21.32 mmol) dissolved in 3 M HCl (100 ml). The solution was stirred for 2 hours at RT. The mixture was filtered and the solid was recrystallized from EtOH (ca. 400 ml) giving an off-white product. mp: 267 °C dec. Yield: 69 % (2.36 g). ^{1}H-NMR: 6.83 (s, 4H); 6.75 (s, 6H); 4.43 (d, 4H, J= 13.3 Hz); 3.83 (m, 8H); 3.16 (d, 4H, J= 13.3 Hz); 1.89 (m, 8H); 0.95 (m, 12Hz). ^{13}C-NMR: 160.0; 157.2; 136.3; 134.5; 132.0; 128.8; 128.6; 125.9; 122.9; 122.7; 119.0; 105.7; 77.2; 76.8; 30.9; 30.7; 23.3; 23.1; 10.4; 10.1

*10 5,17-Di(hydroxymethyl)-25,26,27,28-tetrapropoxyCalix[4]arene (**10**)*

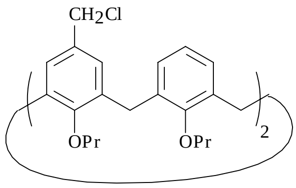


10

To a suspension of **8** (5.13 g; 7.91 mmol) in EtOH (1000 ml) was added slowly $NaBH_4$ (5.98 g; 0.158 mol) at 0 °C. The addition was finished after 10 min and the reaction mixture was stirred at RT for 4 hours. Addition of 2 M HCl (40 ml) quenched the reaction followed by evaporation to dryness. The solid was dissolved in $CHCl_3$ (100 ml) and water (100 ml). The organic phase was separated and the aqueous phase was washed with $CHCl_3$ (4 x 100 ml). The organic phases were collected and washed with sat. $NaHCO_3$ (100 ml), water (100 ml), drying (Na_2SO_4) and evaporation to a white solid. This solid was recrystallized from n-hexane (100 ml) and upon cooling a white precipitate formed. This solid was collected and dried. Yield: 77 % (3.96 g). ^{1}H-NMR: 6.91 (d, 4H); 6.77 (m, 2H); 6.37 (s, 4H); 4.44 (d, 4H, J= 13.2 Hz); 4.16 (s, 4H); 3.97 (t, 4H); 3.72 (t, 4H); 3.14 (d, 4H, J= 13.2 Hz); 1.90 (m, 8H); 1.27 (s, 2H); 1.05 (t, 6H); 0.93 (t, 6H). ^{13}C-NMR: 157.2; 155.6; 136.0; 134.4; 134.2; 128.7; 126.4; 122.2; 76.6; 64.9; 31.9; 31.0; 23.4; 23.1; 22.7; 10.6; 10.0

*11 5,17-Di(chloromethyl)-25,26,27,28-tetrapropoxyCalix[4]arene (**11**)*

689.76 g/mol

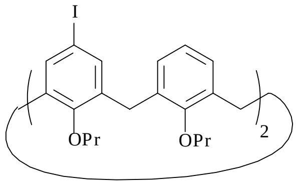


11

To a solution of **10** (3.96 g; 6.07 mmol) in $CHCl_3$ (300 ml) was added $SOCl_2$ (6.2 ml; d= 1.63 g/ml; 10.00 g; 84.06 mmol) slowly at RT. The reaction mixture was stirred for another hour at RT. Evaporation in vacuum produced a pink solid, which was recrystallized from n-hexane. mp: 186-188 °C, litt.: 153 °C. Yield: 87 % (3.63 g). ^{1}H-NMR: 6.65 (m, 6H); 6.58 (s, 4H); 4.43 (d, 4H, J= 13.3 Hz); 3.82 (m, 8H); 3.14 (d, 4H, J= 13.3 Hz); 1.90 (m, 8H); 0.97 (m, 12H). ^{13}C-NMR: 158.3; 158.1; 136.8; 136.5; 132.1; 129.9; 129.9; 123.7; 78.4; 78.3; 48.3; 32.5; 24.8; 24.7; 11.9; 11.8

*12 5,17-Diiodo-25,26,27,28-tetrapropoxyCalix[4]arene (**12**)*

844.61 g/mol

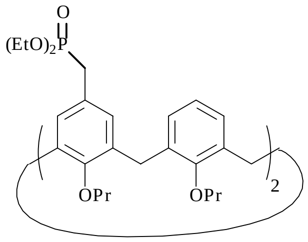


12

A solution of **5** (5.00 g; 6.66 mmol) in dry THF (100 ml) at –78 °C was added 1.20 M n-BuLi (16.7 ml; 20.00 mmol) and stirred at –78 °C for 1 hour. After 1 hour $B(OMe)_3$ (3.0 ml; d= 0.915 g/ml; 2.75 g; 26.50 mmol) was added and the temperature was raised to RT where the reaction mixture was stirred 1 hour. Conc. NaOH (50 ml) and I_2 (20.34 g; 80.14 mmol) were added followed by reflux for 2 hours under argon. The reaction mixture was transferred to a separation funnel and the organic phase collected. The aqueous phase was washed with $CHCl_3$ (2 x 50 ml), the organic phases was collected and washed with sat. Na_2SO_3 (50 ml), sat. NaCl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was treated with boiling $CHCl_3$ (50 ml) and added MeOH (150 ml) and the precipitated white crystals were collected. mp: 229-231 °C. Yield: 61 % (3.42 g). ^{1}H-NMR: 7.11 (s, 4H); 6.48 (, 6H); 4.36 (d, 4H, J= 13.3 Hz); 3.86 (t, 4H, J= 7.6 Hz); 3.76 (t, 4H, J= 7.3 Hz); 3.06 (d, 4H, J= 13.4 Hz); 1.90 (q, 4H, J= 7.6 Hz); 1.89 (q, 4H, J= 7.3 Hz); 0.97 (quintet (two triplets that accidentally collapse to a quintet), 12H, J= 7.4 Hz). ^{13}C-NMR: 157.0; 155.9; 138.3; 137.1; 133.7; 128.2; 122.5; 85.5; 76.9; 76.8; 30.6; 23.3; 23.1; 10.4; 10.1

*13 5,17-Di(diethylphosphonatmethylester)-25,26,27,28-tetrapropoxyCalix[4]arene (**13**)*

893.05 g/mol

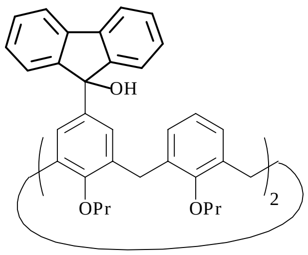


13

A solution of **11** (2.17 g; 3.15 mmol) in $(EtO)_3P$ (70 ml) was refluxed for 24 hours under argon. The mixture was evaporated to an oil and stirred overnight with hexane (50 ml). The white precipitate was collected and dried. Yield: 73 % (2.05 g). ^{1}H-NMR: 6.88 (d, 4H, J= 2.5 Hz); 6.30 (t, 6H, J= 3.7 Hz); 4.41 (d, 4H, J= 13.2 Hz); 3.99 (m, 12H); 3.71 (t, 4H, J= 7.0 Hz); 3.11 (d, 4H, J= 13.3 Hz); 3.02 (d, 4H, J= 21.2 Hz); 1.89 (m, 8H); 1.25 (t, 12H, J= 7.1 Hz); 1.05 (t, 6H, J= 7.4 Hz); 0.91 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 156.5; 155.6; 136.4; 136.4; 133.7; 130.1; 129.9; 127.7; 125.9; 124.4; 124.2; 121.8; 62.1; 62.0; 30.9; 23.4; 23.0; 16.5; 16.4; 10.6; 10.0

*14 5,17-Di(9-fluorenol-9-yl)-25,26,27,28-tetrapropoxyCalix[4]arene (**14**)*

953.22 g/mol

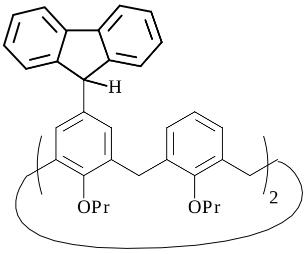


14

5 (10.00 g; 13.32 mmol) was dissolved in dry THF (250 ml) and cooled to –78 °C under argon. To this solution was added 1.5 M Bu^{t}Li (40 ml; 60 mmol), stirred for 15 min. at –78 °C and added 9-fluorenone (10.81 g; 60 mmol) dissolved in dry THF (100 ml) followed by heating to RT. The color changed from dark yellow to dark red when the electrophile was added. The color fainted slowly to red-orange during the first couple of hours. The dark red solution was stirred overnight at RT. To the reaction mixture was added MeOH (250 ml) and evaporated to a yellow solid. The solid was dissolved in $MeCl_2$ (150 ml), washed with water (50 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was treated with boiling $CHCl_3$ (50 ml), added hexane (600 ml) and the $CHCl_3$ was removed using a rotary evaporator. After the removal the yellow suspension was placed in the freezer for 2 hours, filtered, the white solid washed with hexane (20 ml) and dried. Yield: 76 % (9.62 g). ^{1}H-NMR: 7.63 (d, 4H, J= 7.1 Hz); 7.25-7.7.41 (m, 12H); 7.03 (s, 4H); 6.32 (m, 2H); 6.17 (d, 4H, J= 7.5 Hz); 4.55 (d, 4H, J= 13.2 Hz); 3.86 (t, 4H, J= 7.9 Hz); 3.67 (t, 4H, J= 7.0 Hz); 3.03 (d, 4H, J= 13.2 Hz); 2.58 (s, 2H); 1.80-1.93 (m, 8H); 1.01 (t, 6H, J= 7.4 Hz); 0.88 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 157.0; 155.5; 150.3; 139.5; 135.8; 133.8; 128.8; 128.2; 127.5; 126.1; 125.9; 125.0; 122.1; 120.0; 83.5; 76.7; 31.0; 23.4; 23.1; 10.6; 10.0

*15 5,17-Di(9-H-fluorene-9-yl)-25,26,27,28-tetrapropoxyCalix[4]arene (**15**)*

921.23 g/mol

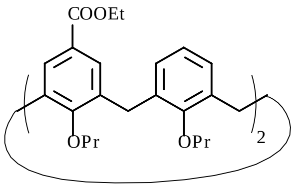


15

To the nearly black solution of **14** (8.51 g; 8.93 mmol) in TFA (250 ml) was added dropwise Et_3SiH (5.72 ml; d= 0.728 g/ml; 4.17 g; 35.72 mmol) at RT under argon, after the addition the reaction mixture was stirred for 1 hour. There started a precipitation of a white compound after addition of the first drop. The reaction mixture was evaporated to dryness, the solid treated with boiling MeOH (100 ml), placed in the freezer for 4 weeks, filtered and dried. This resulted in a white product. mp: 308 °C dec. Yield: 87 % (7.16 g). Found: C, 86.2; H, 7.2. Cal. for $C_{66}H_{64}O_4$: C, 86.0; H, 7.0%. ^{1}H-NMR: 7.74 (d, 4H, J= 7.4 Hz); 7.24-7.37 (m, 12H); 6.68 (s, 4H); 6.35 (m, 6H); 4.89 (s, 2H); 4.37 (d, 4H, J= 13.2 Hz); 3.86 (t, 4H, J= 7.7 Hz); 3.71 (t, 4H, J= 7.0 Hz); 3.03 (d, 4H, J= 13.2 Hz); 1.89 (q, 8H, J= 7.4 Hz); 1.02 (t, 6H, J= 7.4 Hz); 0.91 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 156.4; 155.7; 148.1; 140.9; 136.0; 134.0; 133.9; 128.5; 127.6; 127.1; 127.0; 125.3; 122.2; 119.7; 76.7; 76.6; 53.9; 30.9; 23.3; 23.1; 10.6; 10.0

*16 5,17-Di(carboxyl ethylester)-25,26,27,28-tetrapropoxyCalix[4]arene (**16**)*

736.95 g/mol

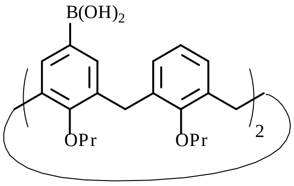


16

To a solution of **5** (10.00 g; 13.32 mmol) in dry THF (200 ml) was added 1.41 M Bu^{t}Li (46 ml; 64.86 mmol; +20 %) at –78 °C. The yellow solution was stirred 15 min at –78 °C followed by addition of CO_2 (g) at a rapid rate. The mixture was slowly poured into ice-cold 2 M HCl (200 ml) and stirred for 15 min. The white solid was collected, washed with petroleum ether (2 x 50 ml), dried in vacuum, placed in a one necked bottle, added $SOCl_2$ (150 ml) and refluxed for 2 hours. Excess of $SOCl_2$ was evaporated and the oil was refluxed with 99 % EtOH (200 ml) for 30 min followed by evaporation to dryness. The solid was first dissolved in boiling EtOH (100 ml) then allowed to cool to RT where the crystals were collected and dried. Yield: 49 % (4.82 g). ^{1}H-NMR: 7.74 (s, 4H); 6.20 (m, 6H); 4.45 (d,4H, J= 13.4 Hz); 4.367 (q, 4H, J= 7.1 Hz); 4.05 (t, 4H, J= 7.8 Hz); 3.70 (t, 4H, J= 6.9 Hz); 3.23 (d, 4H, J= 13.5 Hz); 1.90 (m, 8H); 1.40 (t, 6H, J= 7.1 Hz); 1.07 (t, 6H, J= 7.4 Hz); 0.91 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 166.9; 162.1; 155.3; 136.7; 132.9; 130.3; 127.8; 123.9; 122.3; 77.0; 76.7; 60.6; 30.9; 23.5; 23.2; 14.4; 10.7; 10.0

*17 5,17-Diboronic acid-25,26,27,28-tetrapropoxyCalix[4]arene (**17**)*

680.45 g/mol

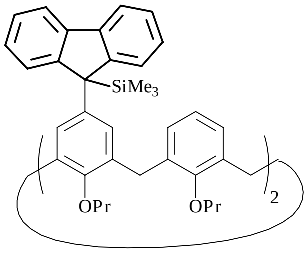


17

To a stirred solution of **5** (8.00 g; 10.66 mmol) in dry THF (400 ml) at –78 °C was added 1.5 M n-BuLi (18.5 ml; 27.71 mmol) under argon. The yellow solution was stirred for 15 min. at –78 °C, quenched with $B(OMe)_3$ (10.0 ml; d= 0.915 g/ml; 9.15 g; 88.06 mmol) and stirred for another 2 hours. The reaction mixture was poured into ice-cold 2 M HCl (400 ml) and extracted with $CHCl_3$ (4 x 100 ml). The organic phase washed with water (100 ml), dried (Na_2SO_4), evaporated to dryness. The crude dried boronic acid was suspended in benzene (250 ml), added 1,3-propandiol (3.0 ml) and reflux until no more water was collected in the distillate. The slightly yellow solution was diluted with $CHCl_3$ (200 ml), washed with water (200 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was recrystallized from heptane (400 ml) and placed in the freezer. The white solid was collected and dried in vacuum for 2 hours. The boronic ester (1.85 g) was refluxed in THF/water (80 and 30 ml; respectively) where the pH was adjusted to 4 using 0.1 M HCl for 1 hour. The solution was evaporated until only water was present, the residue was washed with $CHCl_3$ (3 x 100 ml), the organic phases were collected, dried (Na_2SO_4), evaporated to dryness and recrystallized from acetone. mp: 269-271 °C. Yield: 15 % (1.05 g). ^{1}H-NMR: 7.83 (s, 4H); 7.56 (s, 4H); 6.3-6.1 (m, 6H); 4.36 (d, 4H, J= 13.1 Hz); 4.01 (t, 4H, J= 7.7 Hz); 3.63 (t, 4H, J= 6.5 Hz); 3.13 (d, 4H, J= 13.1 Hz); 2.1-1.7 (m, 8H); 1.09 (t, 6H, J= 7.4 Hz); 0.89 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 159.1; 154.7; 135.1; 135.0; 132.7; 127.1; 121.5; 76.6; 75.8; 30.3; 23.0; 22.5; 10.6; 9.7

*18 5,17-Di(9-trimethylsilyl-fluorene-9-yl)-25,26,27,28-tetrapropoxyCalix[4]arene (**18**)*

1065.59 g/mol

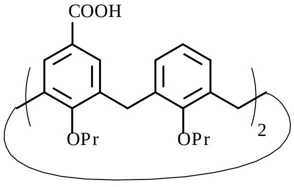


18

A solution of 1.6 M n-BuLi (8.1 ml; 13.08 mmol) in dry THF (60 ml) was cooled to –15 °C followed by addition of a solution of diisopropylamine (1.8 ml; d= 0.722 g/ml; 1.32 g; 13.08 mmol) in dry THF (15 ml). The solution was stirred for 10 min and addition of a solution of **15** (3.00 g; 3.27 mmol) in dry THF (200 ml) was slowly added at 0 °C. The color changed from colorless to orange immediately after addition of the first drop. The solution was stirred for 2 hours and added TMS-Tf (3.90 ml; d= 1.228 g/ml; 4.65 g; 21.00 mmol) and stirred for 2 hours at 0 °C. The mixture became homogenous and almost colorless. The solution was poured into ice-cold water (100 ml), the organic phase collected, the aqueous phase washed with $CHCl_3$ (2 x 50 ml), the organic phases were collected, washed with water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The oil was dissolved in CH_2Cl_2 (10 ml), added MeCN (150 ml) and placed in the freezer overnight. The white product was collected and dried in vacuum without heat! Yield: 57 % (2.00 g). ^{1}H-NMR: 7.89 (dd, 2H, J^1= 5.3 Hz, J^2= 2.0 Hz); 7.75 (d, 2 H, J= 6.8 Hz); 7.55 (m, 2H); 7.40-7.28 (m, 10H); 7.10 (d, 2H, J= 3.0 Hz); 6.88 (d, 2H, J= 3.0 Hz); 6.30-6.08 (m, 2H); 6.02 (t, 2H, J= 7.5 Hz); 5.86 (t, 2H, J= 7.6 Hz); 4.40-4.27 (m, 4H); 3.97-3.87 (m, 4H); 3.62-3.55 (m, 4H); 2.97 (td, 4H, J^1= 13.5 Hz, J^2= 4.3 Hz); 1.90-1.77 (m, 8H); 1.09-0.97 (m, 6H); 0.87-0.77 (m, 6H); -0.03 (s, 9H); -0.08 (s, 9H). ^{13}C-NMR: 155.4; 152.3; 149.5; 140.7; 140.1; 136.8; 136.5; 133.0; 128.9; 127.3; 127.1; 126.9; 126.3; 125.6; 125.0; 124.3; 119.8; 77.2; 76.5; 62.5; 58.4; 55.6; 31.2; 26.5; 23.4; 22.9; 10.8; 9.7; -0.5; -1.9

*19 5,17-Dicarboxylic acid-25,26,27,28-tetrapropoxyCalix[4]arene (**19**)*

680.98 g/mol

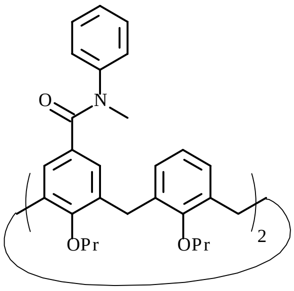


19

To a solution of **5** (5.00 g; 6.66 mmol) in dry THF (200 ml) was added 1.6 M n-BuLi (10.00 ml; 16.00 mmol) at –78 °C. The solution was stirred for 10 min, added CO_2 (excess) and stirred at RT for 2 hours. The solution was added 2 M HCl (50 ml), the organic phases collected, washed with water (100 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was treated with EtOH (50 ml), cooled, filtered and dried. Yield: 53 % (2.40 g). ^{1}H-NMR: 12.87 (br. s, 2H); 7.17 (d, 4H, J= 7 Hz); 7.03 (t, 2H, J= 7 Hz); 6.77 (s, 4H); 4.42 (d, 4H, J=14 Hz); 4.00 (t, 4H, J= 9 Hz); 3.66 (t, 4H, J= 6 Hz); 3.14 (d, 4H, J= 14 Hz); 1.90 (m, 8H); 1.10 (t, 6H, J= 7 Hz); 0.86 (t, 6H, J= 7 Hz). ^{13}C-NMR: 172.4; 160.1; 158.0; 137.0; 134.1; 130.1; 129.8; 123.6; 123.2; 77.3; 76.9; 31.3; 23.9; 23.3; 11.2; 10.2

*20 5,17-Di(N,N-methylphenylamide)-25,26,27,28-tetrapropoxyCalix[4]arene (**20**)*

859.26 g/mol

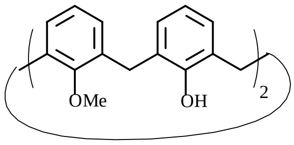


20

A solution of **19** (2.39 g; 2.00 mmol) was refluxed in $SOCl_2$ (30 ml) for 1 hour, the $SOCl_2$ was removed in vacuum, first at the evaporator then using the oil pump for 30 min. The acid chloride was dissolved in $MeCl_2$ (30 ml) and slowly added to a solution of N-methylaniline (0.53 g; 5.00 mmol) and pyridine (5 ml) in $MeCl_2$ (20 ml). The solution was stirred at RT for 1 hour, poured into ice cold 2 M HCl (100 ml), the organic layer separated, dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from hexane resulted in colorless crystals. mp: 158-160 °C. Yield: 55 % (0.94 g). Found: C, 77.8; H, 7.3; N, 3.3. Cal. for $C_{60}H_{62}N_2O_6$: C, 79.4; H, 6.9; N, 3.1%. ^{1}H-NMR: 7.15-7.35 (m, 10H); 7.05 (s, 3H); 6.03 (t, 2H, J= 7.6 Hz); 5.50 (d, 4H, J= 7.6 Hz); 4.25 (d, 4H, J= 13.3 Hz); 3.88 (t, 4H, J= 8.0 Hz); 3.45-3.60 (m, 10H); 2.93 (d, 4H, J= 13.5 Hz); 1.70- 1.87 (m, 8H); 1.03 (t, 6H, J= 7.4 Hz); 0.82 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 171.6; 159.1; 154.9, 145.8; 136.7; 132.4; 129.5; 129.2; 127.4; 127.3; 126.1; 121.7; 76.9; 76.4; 38.4; 31.6; 30.7; 23.4; 22.9; 22.7; 14.1; 10.7; 9.8

*21 25,27-Dihydroxy-26,28-dimethoxyCalix[4]arene (**21**)*

452.55 g/mol

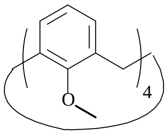


21

A mixture of **2** (5.00; 11.78 mmol), K_2CO_3 (6.50 g; 47.11 mmol) and MeI (2.2 ml; d= 2.27 g/ml; 5.00 g; 35.34 mmol) in MeCN (200 ml) was refluxed under argon overnight. The slightly purple mixture was diluted with CH_2Cl_2 (100 ml), washed with water (100 ml), the organic phase was washed with 2 M HCl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was dissolved in CH_2Cl_2 (30 ml) and added MeOH (300 ml). The solid was collected by filtration and dried in vacuum. Yield: 59 % (3.12 g). ^{1}H-NMR: 6.83 (d, 8H, J= 7.2 Hz); 6.62 (t, 4H, J= 7.2 Hz); 3.4-3.8 (br. m, 16H). ^{13}C-NMR: 158.6; 134.9; 129.4; 122.7; 60.9; 34.8

*22 25,26,27,28-TetramethoxyCalix[4]arene (**22**)*

480.61 g/mol

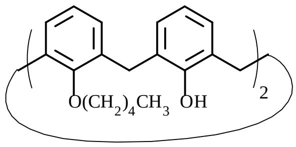


22

A suspension of **2** (5.10 g; 12.0 mmol) and NaH 60 %-wt. (15.0 g; 0.375 mol) in DMF (400 ml) was stirred at RT under argon for 1½ hour. Methyliodide (20.44 g; 0.144 mol) was added and stirring was continued overnight at RT. Addition of another portion of methyliodide (20.44 g; 0.144 mol) was added and the suspension was stirred another day at RT. Addition of MeOH (200 ml) quenched the reaction, the mixture was evaporated to dryness, dissolved in $CHCl_3$ (400 ml) and water (300 ml), the organic phase collected and the aqueous phase washed with $CHCl_3$ (2 x 100 ml). The organic phases were collected, washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was recrystallized twice from $CHCl_3$ (50 ml) and MeOH (500 ml) producing a white product. mp: 226-228 °C, litt.: 234-235 °C. Yield: 71 % (4.12 g). ^{1}H-NMR (DMSO-d_6): 6.86 (d, 8H, J= 7.2 Hz); 6.65 (t, 4H, J= 7.2 Hz); 3.72 (s, 8H); 3.56 (s, 12H). ^{13}C-NMR (DMSO-d_6): 158.4; 134.9; 129.4; 122.8; 62.0; 31.0

*23 25,27-Dihydroxy-26,28-dipentyloxyCalix[4]arene (**23**)*

564.78 g/mol



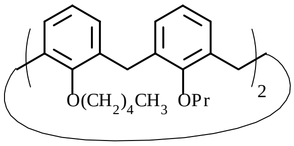
23

A mixture of **2** (2.00 g; 4.71 mmol), K_2CO_3 (7.00 g; 50.60 mmol) and n-pentyliodide (10.00 g; 50.76 mmol) in acetone (200 ml) was refluxed for 2 days. The reaction mixture was evaporated to dryness, treated with $CHCl_3$ (250 ml), filtered and evaporated to about 50 ml. The residue was added MeOH (300 ml), the $CHCl_3$ was removed and placed in the freezer for crystallization. Yield: 64 % (1.71 g). ^{1}H-NMR: 8.19 (s, 2H); 7.04 (d, 4H, J= 7.4 Hz); 6.89 (d, 4H, J= 7.3 Hz); 6.60-6.75 (m, 4H); 4.31 (d, 4H, J= 12.9 Hz); 3.99 (t, 4H, J= 6.7 Hz); 3.36 (d, 4H, J= 12.9 Hz); 2.06 (qv., 4H,

J^1= 7.4 Hz; J^2= 6.7 Hz); 1.68 (qv., 4H, J^1= 7.9 Hz, J^2= 6.9 Hz); 1.35-1.56 (m, 4H); 0.99 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 153.4; 152.0; 133.4; 129.2; 128.4; 128.2; 125.2; 118.9; 77.2; 76.8; 31.4; 29.7; 28.2; 22.5; 14.1

*24 25,27-Dipentyloxy-26,28-dipropyloxyCalix[4]arene (**24**)*

648.93 g/mol

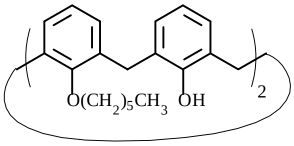


24

To a solution of **23** (1.00 g; 1.97 mmol) in DMF (100 ml) was added NaH-60% dispersion in mineral oil (1.58 g; 39.40 mmol) at RT. The mixture was stirred 30 min at RT, added pentyliodide (7.80 g; 39.40 mmol) and stirred overnight at 60 °C. The solution was added MeOH (200 ml), evaporated to dryness, added CH_2Cl_2 (200 ml) and washed with water (100 ml). The aqueous phase was washed with CH_2Cl_2 (100 ml), the organic phases collected, washed with water (2 x 200 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was dissolved in CH_2Cl_2 (50 ml), added MeCN (100 ml) and left in the freezer overnight. The crystals were collected and dried in vacuum. mp: 80-82 °C. Yield: 69 % (0.88 g). ^{1}H-NMR: 6.67-6.51 (m, 12H); 4.44 (d, 4H, J= 13.3 Hz); 3.86 (t, 8H, J= 7.5 Hz); 3.13 (d, 4H, J= 13.3 Hz); 2.00-1.86 (m, 8H); 1.52-1.38 (m, 8H); 1.09-0.83 (m, 12H). ^{13}C-NMR: 156.8; 156.5; 135.4; 135.0; 128.2; 128.0; 121.9; 121.8; 76.7; 75.1; 31.0; 30.0; 29.7; 28.5; 23.3; 22.8; 14.2; 10.3. MALDI-TOF: 670 (M^++ Na)

*25 25,27-Dihydroxy-26,28-dihexyloxyCalix[4]arene (**25**)*

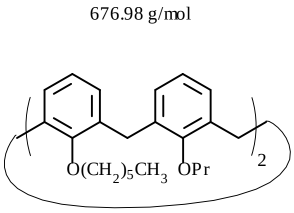
592.76 g/mol



25

A mixture of **2** (2.00 g; 4.71 mmol), K_2CO_3 (7.00 g; 50.60 mmol) and n-hexyliodide (10.86 g; 50.76 mmol) in acetone (200 ml) was refluxed for 2 days. The reaction mixture was evaporated to dryness, treated with $CHCl_3$ (250 ml), filtered and evaporated to about 50 ml. The residue was added MeOH (300 ml), the $CHCl_3$ was removed and placed in the freezer for crystallization. Yield: 62 % (1.74 g). ^{1}H-NMR: 8.23 (s, 2H); 7.08 (d, 4H, J= 7.4 Hz); 6.93 (d, 4H, J= 7.6 Hz); 6.65-6.79 (m, 4H); 4.34 (d, 4H, J= 12.9 Hz); 4.06 (t, 4H, J= 6.7 Hz); 3.40 (d, 4H, J= 12.9 Hz); 2.10 (qv., 4H, J^1= 7.0 Hz; J^2= 6.7 Hz); 1.73 (qv., 4H, J^1= 7.2 Hz, J^2= 6.8 Hz); 1.35-1.53 (m, 8H); 0.98 (t, 6H, J= 6.9 Hz). ^{13}C-NMR: 153.8; 152.4; 133.9; 129.3; 128.8; 128.6; 125.6; 119.3; 77.6; 77.2; 32.2; 31.8; 30.4; 26.1; 23.1; 14.5

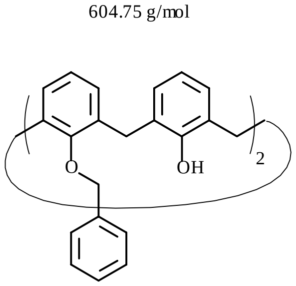
*26 25,27-Dihexyloxy-26,28-dipropyloxyCalix[4]arene (**26**)*



26

To a solution of **25** (1.74 g; 2.94 mmol) in DMF (100 ml) was added NaH-60% dispersion in mineral oil (1.58 g; 39.40 mmol) at RT. The mixture was stirred 30 min at RT, added n-propyliodide (6.70 g; 39.40 mmol) and stirred overnight at 60 °C. The solution was added MeOH (200 ml), evaporated to dryness, added CH_2Cl_2 (200 ml) and washed with water (100 ml). The aqueous phase was washed with CH_2Cl_2 (100 ml), the organic phases collected, washed with water (2 x 200 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was dissolved in CH_2Cl_2 (50 ml), added MeCN (100 ml) and left in the freezer overnight. The crystals were collected and dried in vacuum. mp: 99-101 °C. Yield: 84 % (1.67 g). ^{1}H-NMR: 6.66-6.49 (m, 12H); 4.44 (d, 4H, J= 13.3 Hz); 3.86 (dt, 8H, J^1= 7.3 Hz; J^2= 7.2 Hz); 3.13 (d, 4H, J= 13.3 Hz); 1.99-1.82 (m, 8H); 1.52-1.25 (m, 12H); 0.98 (t, 6H, J= 7.4Hz); 0.91 (t, 6H, J= 6.4 Hz). ^{13}C-NMR: 156.7; 156.5; 135.3; 135.2; 128.2; 128.1; 121.9; 76.7; 75.1; 32.8; 31.0; 29.7; 29.4; 25.9; 23.3; 22.8; 14.1; 10.4. MALDI-TOF: 698 (M^++ Na)

*27 25,27-Dihydroxy-26,28-dibenzyloxyCalix[4]arene (**27**)*

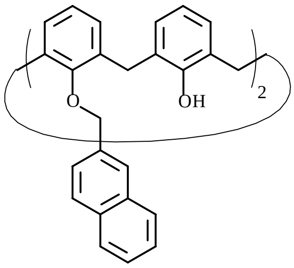


27

A mixture of **2** (5.22 g; 12.3 mmol) and anhydrous K_2CO_3 (3.74 g; 27 mmol) in acetone (300 ml) was refluxed for 1 hour under argon. Benzylbromide (4.61 g; 27 mmol) was added and reflux was continued overnight. The purple suspension was evaporated to dryness, dissolved in water (300 ml) and $CHCl_3$ (300 ml). The aqueous phase was washed with $CHCl_3$ (50 ml), the combined organic phases were washed with water (200 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in $CHCl_3$ (100 ml), added MeOH (600 ml) and the $CHCl_3$ was removed. The slurry was placed in the freezer overnight, the white compound was collected and dried in vacuum. mp: 221-223 °C. Yield: 66 % (4.91 g). ^{1}H-NMR: 7.78 (s, 2H); 7.62 (t, 4H, J= 4.1 Hz); 7.36 (t, 6 H, J= 2.2 Hz); 7.03 (d, 4 H, J= 7.5 Hz); 6.87 (d, 4H, J= 7.4 Hz); 6.77-6.62 (m, 4H); 5.05 (s, 4H); 4.31 (d, 4H, J= 13.0 Hz); 3.33 (d, 4H, J= 13.1 Hz). ^{13}C-NMR: 153.0; 151.5; 136.4; 132.8; 128.6; 128.4; 128.1; 127.6; 127.1; 125.5; 125.0; 118.5; 78.0; 76.6; 31.0

*28 25,27-Dihydroxy-26,28-dinaphthyloxyCalix[4]arene (**28**)*

704.86 g/mol

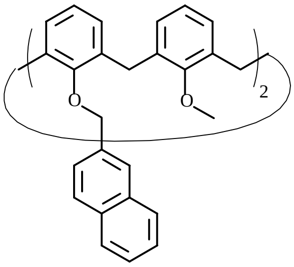


28

A mixture of **2** (5.22 g; 12.3 mmol) and anhydrous K_2CO_3 (3.74 g; 27 mmol) in acetone (300 ml) was refluxed for 1 hour under argon. 2-Bromomethylnaphthalene (5.97 g; 27 mmol) was added and reflux was continued overnight. The suspension was evaporated to dryness, dissolved in water (300 ml) and $CHCl_3$ (300 ml). The aqueous phase was washed with $CHCl_3$ (50 ml), the combined organic phases were washed with water (200 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in $CHCl_3$ (100 ml), added MeOH (600 ml) to cause a precipitation. The slurry was placed in the freezer overnight, the white compound was collected and dried in vacuum. Yield: 75 % (6.48 g). ^{1}H-NMR: 8.00 (s, 2H); 7.87 (s, 2H); 7.80 (d, 2H, J= 8.4 Hz); 7.71 (d, 2H, J= 8.4 Hz); 7.44 (t, 2H, J= 7.0 Hz); 7.35 (t, 2H, J= 7.8 Hz); 7.04 (d, 4H, J= 7.4 Hz); 6.87 (d, 4H, J= 7.5 Hz); 6.73 (t, 2H, J= 7.4 Hz); 6.64 (t, 2H, J= 7.4 Hz); 5.20 (s, 4H); 4.36 (d, 4H, J= 13.1 Hz); 3.33 (d, 4H, J= 13.1 Hz). ^{13}C-NMR: 154.0; 152.7; 134.9; 134.0; 133.9; 133.8; 129.8; 129.3; 129.2; 128.8; 128.7; 128.5; 127.2; 126.8; 126.7; 126.2; 126.1; 119.6; 79.3; 77.8; 32.2

*29 25,27-Dimethyloxy-26,28-dinaphthyloxyCalix[4]arene (**29**)*

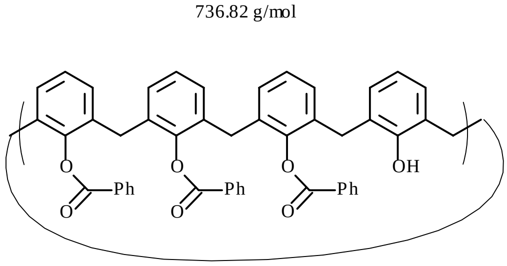
732.91 g/mol



29

A suspension of **28** (2.00 g; 2.84 mmol) and NaH 60 %-wt. (6.0 g; 0.15 mol (washed twice with petroleum ether (100 ml)) in dry THF (200 ml)/DMF (30 ml) was stirred at RT under argon for 1½ hour. Methyliodide (21.30 g; 0.15 mol) was added to the suspension and refluxed for 1 hour and stirred overnight at RT. Addition of MeOH (100 ml) quenched the reaction, the mixture was evaporated to dryness, dissolved in $CHCl_3$ (200 ml) and water (200 ml), the organic phase collected and the aqueous phase washed with $CHCl_3$ (2 x 100 ml). The organic phases were collected, washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was dissolved several times in $CHCl_3$ (50 ml), added MeOH (300 ml) followed by evaporation until a solid formed. This method finally produced a white product. mp: 124-126 °C. Yield: 51 % (1.05 g). ^{1}H-NMR (DMSO-d_6,350K): 8.13 (s, 2H); 8.04 (d, 4H, J= 8.7 Hz); 7.96 (m, 2H); 7.75 (d, 2H, J= 9.4 Hz); 7.68-7.62 (m, 4H); 7.23 (d, 4H, J= 7.4 Hz); 6.94 (t, 2H, J= 7.4 Hz); 6.70-6.50 (m, 6H); 5.07 (s, 4H); 4.20 (br. s, 4H); 3.60 (br. s, 6H); 3.40 (d, 4H, J= 12.5 Hz). ^{13}C-NMR (DMSO-d_6,350K): 159.0; 156.4; 137.0; 136.4; 133.8; 133.5; 130.1; 128.8; 128.5; 128.5; 127.3; 127.0; 126.8; 122.8; 77.0; 60.5; 32.8. MALDI-TOF: 731, 754 (M^+ + Na), 770 (M^+ + K)

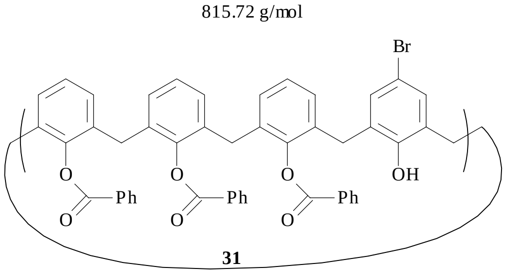
30 25-Hydroxy-26,27,28-tribenzoylCalix[4]arene (**30**)



30

A solution of **2** (4.24 g; 10.00 mmol) in pyridine (50 ml) was cooled to 0 °C under argon and benzoylchloride (9.4 ml; d= 1.211 g/ml; 11.38 g; 81.00 mmol) was added and stirring was continued for 2 hours at 0 °C. The solution change color from colorless to yellow. The yellow suspension was added to water (300 ml), stirred for 10 min. and filtered. The solid was dissolved in a minimum of hot $CHCl_3$ (ca. 50 ml) and added methanol (ca. 250 ml) to trigger a precipitation. The solution was placed in the freezer overnight. Filtration, washing with methanol (2 x 20 ml) and drying in vacuum at 50 °C resulted in light yellow flakes. Yield: 88 % (6.51 g). ^{1}H-NMR: 8.08-6.51 (m, 27H, ArH); 5.43 (s, 1H,OH); 3.90-3.45 (m, 8H, $ArCH_2Ar$). ^{13}C-NMR: 164.4; 163.8; 152.8; 148.3; 146.7; 133.7; 133.4; 133.2; 132.9; 132.6; 131.3; 130.8; 130.3; 129.5; 129.2; 128.8; 128.6; 128.1; 127.8; 127.7; 125.1; 119.7; 37.4; 32.4. MALDI-TOF: 736 (M^+); 759 (M^++ Na); 775 (M^++ K)

31 5-Bromo-25-hydroxy-26,27,28-tribenzoylCalix[4]arene (**31**)

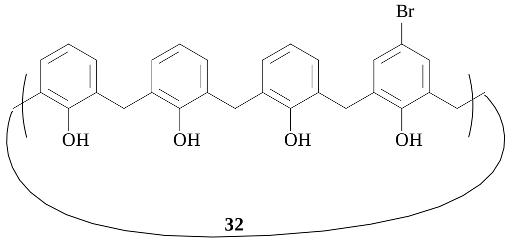


31

A solution of Br_2 (2.86 ml; d= 3.102 g/ml; 8.88 g; 55.60 mmol; 1.1 eqv.) in CH_2Cl_2 (200 ml) was slowly added dropwise during 2 hours to **30** (37.24 g; 50.54 mmol) dissolved in CH_2Cl_2 (300 ml) under argon at RT. The red reaction mixture was stirred for 18 hours at RT. The mixture was poured into a separation funnel and extracted with a 5 % aqueous sodium thiosulphate solution (300 ml), water (2 x 300 ml), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from hot CH_2Cl_2 (ca. 200 ml) followed by addition of methanol (700 ml) to trigger the precipitation of the white product. The suspension was placed in the freezer for 2 hours, filtered and dried. Yield: 89 % (36.65 g). ^{1}H-NMR: 8.01 (d, 4H, J= 7.2 Hz, ArH); 7.75 (t, 2H, J= 7.4 Hz, ArH); 7.56 (m, 5H, ArH); 7.30 (d, 4H, J= 4.6 Hz, ArH); 7.05 (m, 4H, ArH); 6.84 (d, 2H, ArH ortho to bromine); 6.63 (m, 5H, ArH); 5.24 (s, 1H, OH); 3.83-3.47 (m, 8H, $ArCH_2Ar$). ^{13}C-NMR: 165.0; 164.6; 152.8; 148.9; 147.7; 134.5; 134.4; 134.0; 133.9; 132.6; 132.3; 132.0; 131.6; 131.5; 131.4; 130.5; 130.2; 129.5; 129.3; 128.8; 128.5; 126.7; 125.8; 112.2; 38.0; 33.8. MALDI-TOF: 815 (M^+); 837 (M^++ Na); 854 (M^++ K)

*32 5-Bromo-25,26,27,28-tetrahydroxyCalix[4]arene (**32**)*

503.39 g/mol

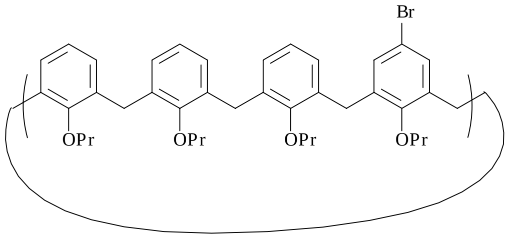


32

31 (36.00 g; 44.13 mmol) was suspended in a 10 wt-% KOH in a 1:1 EtOH/H_2O (700 ml) solution and refluxed for 4 hours followed by stirring for 4 days at RT under argon. To the yellow homogenous solution there was added $CHCl_3$ (100 ml) and the organic phase were separated. The aqueous phase was extracted with $CHCl_3$ (3 x 100 ml). The organic phases was collected and washed with 5 wt-% KOH (2 x 50 ml), 2 M HCl (100 ml), sat. $NaHCO_3$ (3 x 50 ml), water (2 x 50 ml), dried (Na_2SO_4) and evaporated to dryness. The residue solid was recrystallized from hot $CHCl_3$ (200 ml) and added methanol (800 ml). After filtration and several washings with methanol, the slightly yellow compound was dried in vacuum. Yield: 91 % (20.20 g). ^{1}H-NMR: 10.10 (s, 4H, OH); 7.15 (s, 2H, ArH); 7.06 (m, 6H, ArH); 6.76 (t, 3H, J= 7.4 Hz, ArH); 4.22 (br. s, 4H, $ArCH_2Ar$); 3.54 (br. s, 4H, $ArCH_2Ar$). ^{13}C-NMR: 148.8; 148.6; 148.1; 131.5; 130.4; 129.3; 129.1; 129.0; 128.4; 128.1; 127.4; 122.5; 122.4; 113.9; 31.7; 31.5. MALDI-TOF: 503 (M^+); 526 (M^++ Na); 542 (M^++ K)

33 *5-Bromo-25,26,27,28-tetrapropoxyCalix[4]arene (**33**)*

671.71 g/mol

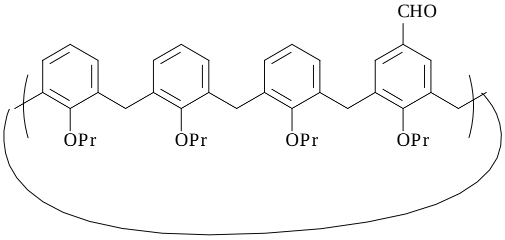


33

32 (19.41 g; 38.56 mmol) was dissolved in DMF (800 ml) under argon and there was added a 60 wt-% NaH (12.80 g; 0.320 mol) suspension in oil followed by the addition of n-PrI (32.0 ml; d= 1.743 g/ml; 56.00 g; 0.328 mol). The solution was stirred overnight under argon at RT. After a few hours, the solution became nearly homogenous and yellow. The solution was added water (1000 ml) and washed with $CHCl_3$ (5 x 200 ml). The combined organic phases was washed with water (4 x 200 ml), 1 M HCl (2 x 300 ml), 5 % $Na_2S_2O_3$ (200 ml), water (2 x 200 ml), dried (Na_2SO_4) and evaporated to dryness. The oil was added hot $CHCl_3$ (ca. 100 ml), methanol (1000 ml) and stirred slowly overnight. The white product was collected as white crystals. mp: 146-148 °C, litt.: 151-153 °C. Yield: 64 % (16.48 g). ^{1}H-NMR: 6.55-6.84 (m, 7H); 6.48 (s, 2H, ortho to bromine); 6.41 (s, 1H); 6.37 (s, 1H); 4.42 (pair of d that accidental looks like a triplet, 4H, $ArCH_2Ar$, J= 13.0 Hz); 3.70-3.95 (m, 8H, OCH_2); 3.16 (d, 2H, $ArCH_2Ar$, J= 13.5 Hz); 3.09 (d, 2H, $ArCH_2Ar$, J= 13.5 Hz); 1.87 (m, 8H, CH_2); 1.03 (pair of triplets, 6H, CH_3, J= 7.4 Hz); 0.94 (t, 6H, CH_3, J= 7.4 Hz). ^{13}C-NMR: 157.5; 156.4; 155.7; 137.3; 136.4; 135.4; 134.8; 130.8; 129.2; 128.7; 128.2; 126.3; 122.5; 122.4; 115.1; 77.2; 77.1; 77.0; 31.4; 31.3; 23.8; 23.7; 23.5; 10.9; 10.8; 10.5. MALDI-TOF: 671 (M^+); 694 (M^++ Na); 710 (M^++ K)

34 *5-Formyl-25,26,27,28-tetrapropoxyCalix[4]arene (**34**)*

620.83 g/mol

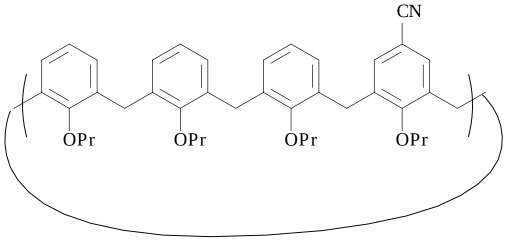


34

To a stirred solution of **33** (3.00 g; 4.47 mmol) in dry THF (100 ml) at –78 °C was added 1.275 M n-BuLi (4.2 ml; 5.36 mmol). The yellow solution was stirred at –78 °C for 15 min, quenched with DMF (17 ml; d= 0.944 g/ml; 16.34 g; 0.224 mol; 50 eqv.) and stirred for another 20 min. The reaction mixture was poured into ice-cold 2 M HCl (400 ml) and extracted with $CHCl_3$ (2 x 200 ml). The organic phases was collected and washed with water (2 x 200 ml), dried (Na_2SO_4) and evaporated to a white compound. This solid was recrystallized from MeCN (ca. 100 ml) and placed in the freezer overnight. The white crystals was collected by filtration and dried in vacuum. mp: 140-142 °C. Yield: 89 % (2.47 g). ^{1}H-NMR: 9.60 (s, 1H, CHO); 7.03 (s, 2H); 6.70 (m, 7H); 6.45 (m, 3H); 4.50 (t, 4H, J= 13.1 Hz); 3.91 (m, 8H); 3.22 (dd, 4H, J= 13.6 Hz); 1.95 (m, 8H); 1.13 (m, 12Hz). ^{13}C-NMR: 192.4; 162.7; 157.5; 156.9; 136.7; 136.5; 135.8; 135.4; 135.3; 131.6; 130.6; 129.5; 129.0; 128.8; 128.6; 122.9; 122.5; 77.6; 77.3; 31.6; 24.1; 24.0; 23.8; 11.2; 11.1; 11.0; 10.9

35 *5-Cyano-25,26,27,28-tetrapropoxyCalix[4]arene (**35**)*

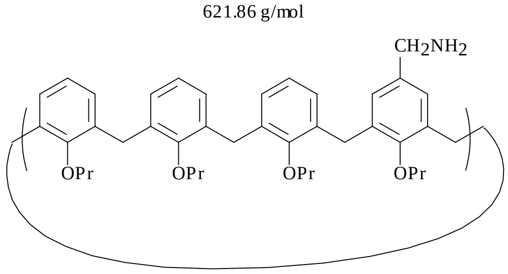
617.83 g/mol



35

33 (2.00 g; 2.98 mmol) and CuCN (0.54 g; 6.03 mmol; + 100%) was mixed in NMP (100 ml) followed by reflux overnight under argon. The reaction mixture was cooled to 100° C and added a solution of $FeCl_3$ (0.97 g; 6.03 mmol) dissolved in 3 M HCl (50 ml). The solution was stirred for 2 hours at RT. The mixture was filtered and the solid was recrystallized from EtOH (ca. 200 ml) giving an off-white product. Yield: 87 % (1.60 g). ^{1}H-NMR: 6.20-7.10 (m, 11H); 4.43 (d, 4H, J= 13.1 Hz); 3.89 (m, 8H); 3.15 (d, 4H, J= 13.1 Hz); 1.90 (m, 8H); 1.00 (m, 12H). ^{13}C-NMR: 159.6; 157.4; 155.6; 136.8; 136.0; 135.2; 135.0; 133.8; 131.7; 130.5; 129.4; 128.8; 128.5; 128.3; 127.8; 122.3; 122.2; 119.8; 105.5; 76.8; 76.6; 31.0; 30.8; 23.4; 23.4; 23.1; 10.7; 10.6; 10.1; 10.0

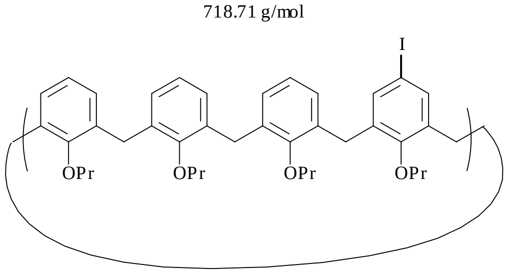
36 *5-Methylamino-25,26,27,28-tetrapropoxyCalix[4]arene (**36**)*



36

To a mixture of **35** (1.50 g; 2.43 mmol) and $NaBH_4$ (0.69 g; 18.21 mmol) in dry THF (200 ml) was added dropwise BF_3*Et_2O (3.06 ml; d= 1.12 g/ml; 3.43 g; 48 % wt.; 1.65 g; 24.28 mmol) at 0° C under argon. After final addition, the reaction mixture was heated to reflux overnight. After the mixture was cooled to RT there was added 1 M HCl (40 ml) slowly and the mixture was stirred for an additional hour. The solution was evaporated to dryness and the residue was dissolved in $MeCl_2$ (100 ml) and extracted with 1 M HCl (100 ml). The aqueous phase was made basic with 4 M NaOH and extracted with $MeCl_2$ (3 x 50 ml). The combined organic phases was dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from n-hexane (30 ml) gave the product as white crystals. Yield: 59 % (0.89 g). ^{1}H-NMR: 7.40 (br. s, 2H, NH_2); 6.39-6.82 (m, 11H); 4.44 (d, 2H, J= 4.6 Hz); 4.39 (d, 2H, J= 4.6 Hz); 3.82 (septet, 8H); 3.68 (s, 2H, CH_2); 3.16 (d, 2H, J= 3.6 Hz); 3.11 (d, 2H, J= 3.6 Hz); 1.87 (m, 8H); 0.95 (m, 12H). ^{13}C-NMR: 157.3; 156.7; 156.5; 136.0; 135.3; 134.9; 128.8; 128.5; 128.1; 125.3; 122.3; 121.5; 76.8; 76.7; 43.7; 31.0; 30.9; 23.3; 23.2; 10.4; 10.3; 10.2

37 *5-Iodo-25,26,27,28-tetrapropoxyCalix[4]arene (**37**)*

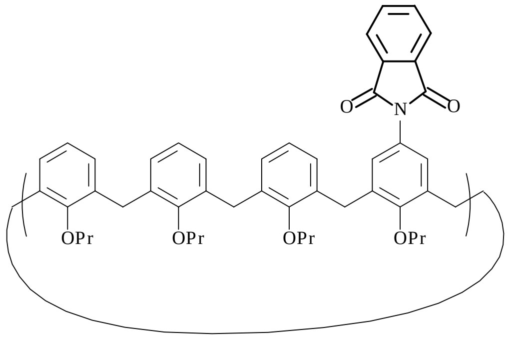


37

A solution of **33** (1.00 g; 1.49 mmol) in dry THF (50 ml) under argon at –78 °C was added 1.20 M n-BuLi (2.0 ml; 2.40 mmol) and stirred at –78 °C for 1 hour. After 1 hour $B(OMe)_3$ (0.60 ml; d= 0.915 g/ml; 0.52 g; 5.00 mmol) was added and the reaction mixture was stirred at –78 °C for 2 hours. Conc. NaOH (10 ml) and I_2 (3.78 g; 14.90 mmol) were added followed by reflux for 2 hours under argon. The reaction mixture was transferred to a separation funnel and the organic phase collected. The aqueous phase was washed with $CHCl_3$ (2 x 50 ml), the organic phases was collected and washed with sat. Na_2SO_3 (50 ml), sat. NaCl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The solid was treated with boiling $CHCl_3$ (50 ml) and added MeOH (150 ml) and the precipitated white crystals were collected. Yield: 61 % (0.65 g). ^{1}H-NMR: 6.58-6.77 (m, 9H); 6.45 (d, 2H, J= 7.5 Hz); 4.42 (pair of d, 4H, J= 13.4 Hz, $ArCH_2Ar$); 3.73-3.90 (m, 8H, OCH_2); 3.11 (pair of d, 4H, J= 13.5 Hz, $ArCH_2Ar$); 1.89 (m, 8H, CH_2); 0.91-1.05 (m, 12H, CH_3). ^{13}C-NMR: 156.9; 156.3; 156.2; 137.5; 136.6; 135.9; 135.1; 134.8; 134.5; 128.8; 128.2; 128.1; 127.8; 122.3; 122.1; 121.9; 85.8 (C-I); 76.8; 76.7; 31.0; 30.7; 23.3; 23.3; 23.1; 10.5; 10.4; 10.3; 10.2

38 *5-Phthalimid-25,26,27,28-tetrapropoxyCalix[4]arene (**38**)*

737.93 g/mol

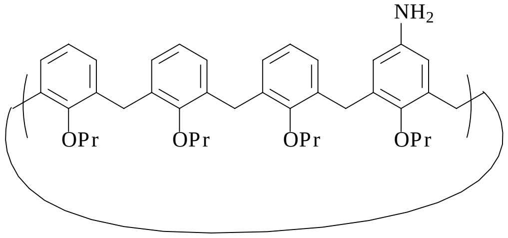


38

33 (4.38 g; 6.52 mmol), potassium phthalimid (3.62 g; 19.62 mmol), CuI (3.73 g; 19.62 mmol) were suspended in 2,4,6-Collidine (100 ml) and flushed with argon for 10 min. The mixture was refluxed for 3 days. The solution was cooled and diluted with $MeCl_2$ (300 ml). The organic phase was washed with 2 M HCl (2 x 50 ml), 2.5 M NaOH (50 ml), dried (Na_2SO_4) and evaporated to an oil. The product was isolated by column chromatography on silica with n-hexane/AcOEt (9:1, v/v) as eluent, to give the product as slightly yellow oil. The oil was treated with boiling MeOH (50 ml), cooled and filtered. The white crystals were dried in vacuum. Yield: 27 % (1.31 g). ^{1}H-NMR: 7.93-7.89 (m, 2H); 7.76-7.72 (m, 2H); 6.90 (s, 2H); 6.77 (d, 2H, J= 7.4 Hz); 6.70-6.50 (m, 7H); 4.49 (d, 2H, J= 13.3 Hz); 4.46 (d, 2H, J=13.3 Hz); 4.00-3.73 (m, 8H); 3.19 (d, 2H, J= 13.3 Hz); 3.16 (d, 2H, J= 13.3 Hz); 2.05-1.80 (m, 8H); 1.15-0.9 (m, 12H). ^{13}C-NMR: 167.3; 156.9; 156.5; 156.1; 136.2; 135.6; 134.6; 134.1; 133.8; 131.9; 128.5; 128.1; 127.9; 126.0; 125.2; 123.4; 122.2; 122.0; 76.8; 76.6; 31.0; 23.3; 23.2; 23.1; 10.5; 10.2; 10.1

39 *5-Amino-25,26,27,28-tetrapropoxyCalix[4]arene (**39**)*

610.59 g/mol

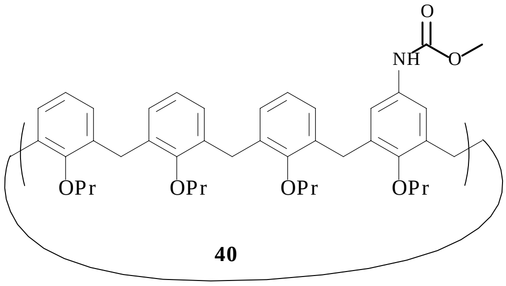


39

To a suspension of **38** (1.31 g; 1.78 mmol) in MeOH (100 ml) was added hydrazinhydrate (3 ml; 61 mmol) and refluxed overnight. The clear solution was cooled and evaporated to dryness. The solid was partially dissolved in 1 M NaOH (50 ml), washed with Et_2O (3 x 50 ml), the organic phases were collected, dried (Na_2SO_4) and evaporated to dryness. The white solid was recrystallized from low boiling petroleum ether. The white crystals were collected and dried. mp: 208-210 °C, litt.: 195-196 °C. Yield: 80 % (0.87 g). ^{1}H-NMR: 6.80-6.50 (m, 9H); 5.93 (s, 2H); 4.46 (d, 2H, J= 13.3 Hz); 4.37 (d, 2H, J= 13.3 Hz); 3.90-3.70 (m, 8H); 3.14 (d, 2H, J= 13.3 Hz); 3.09 (s, 2H); 3.02 (d, 2H, J= 13.3 Hz); 2.00-1.80 (m, 8H); 1.05-0.90 (m, 12H). ^{13}C-NMR: 156.8; 156.7; 149.8; 140.3; 135.6; 135.2; 135.1; 128.1; 121.8; 121.5; 155.4; 76.7; 76.6; 31.02; 31.0; 23.23; 23.20; 23.15; 10.37; 10.32; 10.28

40 *5-Methylureatane-25,26,27,28-tetrapropoxyCalix[4]arene (**40**)*

668.59 g/mol

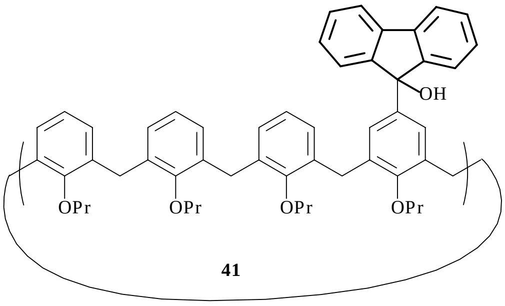


40

To a solution of **39** (1.00 g; 1.64 mmol) in pyridine (75 ml) was added dropwise chloromethylformiate (2 ml; d= 1.28 g/ml; 2.56 g; 27.4 mmol) at 0 °C. The solution was stirred for 1 hour at 0 °C and then 2 hours at RT. The reaction mixture was evaporated to dryness, added $CHCl_3$ (100 ml) and washed with water (2 x 50 ml). The aqueous phase was collected, washed with $CHCl_3$ (50 ml), the organic phases were collected, washed with $NaHCO_3$ (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was treated with boiling MeOH (50 ml) and placed in the freezer for four days. Yield: 72 % (0.78 g). Found: C, 75.8; H, 7.9; N, 2.2. Cal. for $C_{42}H_{51}NO_6$: C, 75.8; H, 7.7; N, 2.1%. ^{1}H-NMR: 6.60-6.72 (m, 6H); 6.43-6.48 (br. d, 5H); 6.09 (br. s, 1H); 4.46 (d, 2H, J= 6.7 Hz); 4.40 (d, 2H, J= 6.7 Hz); 3.74-3.89 (m, 8H); 3.68 (s, 3H); 3.14 (d, 2H, J= 8.4 Hz); 3.09 (d, 2H, J= 8.4 Hz); 1.83-1.98 (m, 8H); 1.00 (t, 6H, J= 7.4 Hz), 0.96 (t, 6H, J= 7.4 Hz). ^{13}C-NMR: 156.9; 152.9; 135.5; 135.4; 135.2; 134.9; 131.4; 128.4; 128.3; 128.0; 121.9; 121.5; 119.3; 76.7; 76.6; 52.1; 31.1; 31.0; 23.3; 23.2; 23.1; 10.4; 10.2

*41 5-(9-Fluorenol-9-yl)-25,26,27,28-tetrapropoxyCalix[4]arene (**41**)*

773.02 g/mol

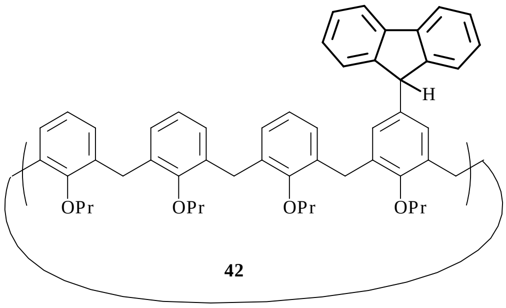


41

33 (11.05 g; 16.45 mmol) was dissolved in dry Et_2O (500 ml) and cooled to –78 °C under argon. To this solution was added 1.5 M Bu^{t}Li (24.1 ml; 36.19 mmol), stirred for 15 min. at –78 °C and added 9-fluorenone (14.82 g; 82.3 mmol) dissolved in dry Et_2O (300 ml) followed by heating to RT. The color changed from yellow to dark red when the electrophile was added. The color fainted slowly to red-orange during the first couple of hours. The dark red solution was stirred overnight at RT. To the reaction mixture was added MeOH (200 ml) and evaporated to a yellow solid. The solid was dissolved in $MeCl_2$ (300 ml), washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was treated with boiling hexane (100 ml), cooled to RT, the white powder was collected, washed with hexane and dried. Yield: 78 % (9.96 g). ^{1}H-NMR: 7.59 (d, 2H, J= 7.3 Hz); 7.31 (td, 2H, J^1= 7.3 Hz, J^2= 1.3 Hz); 7.24 (s, 1H); 7.21 (s, 1H); 7.16 (t, 2H, J= 5.3 Hz); 6.76-6.49 (m, 11H); 4.46 (d, 2H, J= 13.2 Hz); 4.38 (d, 2H, J= 13.3 Hz); 3.88-3.74 (m, 8H); 3.16 (d, 2H, J= 13.2 Hz); 3.05 (d, 2H, J= 13.3 Hz); 2.09 (s, 1H); 1.97-1.83 (m, 8H); 1.02-0.94 (m, 12H). ^{13}C-NMR: 156.8; 156.4; 156.3; 149.8; 139.5; 135.3; 135.2; 135.0; 134.6; 128.6; 128.3; 128.7; 128.0; 125.8; 125.0; 122.2; 119.9; 83.3; 76.9; 76.7; 76.7; 31.0; 23.3; 23.2; 10.3; 10.3

*42 5-(9-H-fluorene-9-yl)-25,26,27,28-tetrapropoxyCalix[4]arene (**42**)*

757.02 g/mol

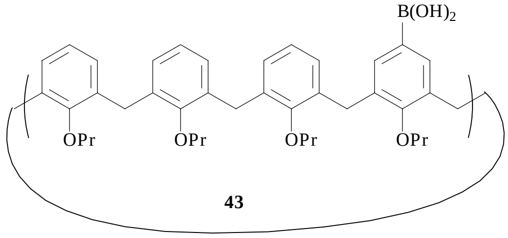


42

To a solution of **41** (9.96 g; 12.89 mmol) in CH_2Cl_2 (100 ml) was added Et_3SiH (2.4 ml; d= 0.75 g/ml; 1.80 g; 15.46 mmol) and BF_3*ET_2O (1.9 ml; d= 1.15 g/ml; 2.19 g; 15.46 mmol) at 0 °C under argon, after the addition the reaction mixture was stirred for 3 hours at 0 °C. The reaction mixture was added 2 M HCl (50 ml), the organic phase separated, washed with water (2 x 50 ml), dried (Na_2SO_4), evaporated to an oil. The oil was treated with boiling CH_2Cl_2 (50 ml), added MeOH (200 ml), the CH_2Cl_2 was removed in vacuum, the residue was cooled in ice for 2 hours before the white crystals were collected. mp: 187-189 °C. Yield: 75 % (7.35 g). ^{1}H-NMR: 7.73 (d, 2H, J= 7.5 Hz); 7.37-7.10 (m, 6H); 6.81-6.42 (m, 11H); 4.73 (s, 1H); 4.46 (d, 2H, J= 13.2 Hz); 4.38 (d, 2H, J= 13.3 Hz); 3.88-3.74 (m, 8H); 3.16 (d, 2H, J= 13.2 Hz); 3.05 (d, 2H, J= 13.3 Hz); 1.97-1.83 (m, 8H); 1.02-0.94 (m, 12H). ^{13}C-NMR: 156.8; 156.4; 155.7; 147.9; 140.8; 135.3; 135.0; 134.9; 133.8; 128.3; 128.1; 128.0; 127.0; 125.5; 122.1; 121.8; 119.6; 76.9; 76.7; 76.7; 53.6; 31.0; 30.9; 23.2; 10.4; 10.3

*43 5-Boronic acid-25,26,27,28-tetrapropoxyCalix[4]arene (**43**)*

636.62 g/mol

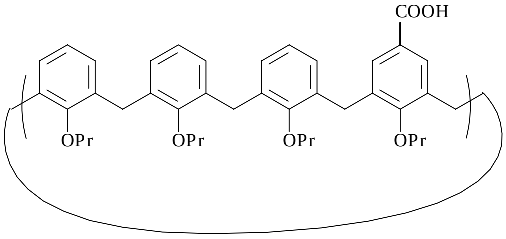


43

A solution of **33** (2.00 g; 2.97 mmol) in dry THF (50 ml) was added 1.6 M n-BuLi (2.4 ml; 3.27 mmol) at –78 °C and stirred for 15 min before adding $B(OPr^i)_3$ (4.6 ml; d= 0.815 g/ml; 3.76 g; 20 mmol) followed by heating to RT and stirred overnight. The solution was poured into ice-cold 2 M HCl (100 ml), the organic phase separated, the aqueous phase washed with $CHCl_3$ (3 x 50 ml), the organic phases were collected, washed with water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The oil was treated with boiling CH_2Cl_2 (20 ml), added MeCN (100 ml) and placed in the freezer for 2 days. Filtered and dried in vacuum. Yield: 60 % (1.14 g). ^{1}H-NMR: 7.62 (s, 2H); 6.83 (d, 2H, J= 7.4 Hz); 6.65 (t, 1H, J= 7.4 Hz); 6.51-6.36 (m, 6H); 4.53 (d, 2H, J= 13.5 Hz); 4.46 (d, 2H, J= 13.4 Hz); 4.04 (t, 2H, J= 7.5 Hz); 3.93 (t, 2H, J= 7.6 Hz); 3.80 (t, 4H, J= 7.1 Hz); 3.34 (d, 2H, J= 13.5 Hz); 3.14 (d, 2H, J= 13.5 Hz); 1.98-1.84 (m, 8H); 1.26-0.83 (m, 12H). ^{13}C-NMR: 161.4; 157.3; 156.0; 136.2; 136.0; 135.7; 134.3; 128.5; 128.0; 127.9; 122.1; 76.8; 31.0; 29.7; 23.4; 23.3; 23.2; 10.6; 10.2

*44 5-Carboxylic acid-25,26,27,28-tetrapropoxyCalix[4]arene (**44**)*

636.82 g/mol

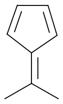


44

To a solution of **33** (7.00 g; 10.42 mmol) in dry THF (200 ml) was added 1.6 M n-BuLi (7.8 ml; 12.51 mmol) at –78 °C. The solution was stirred for 10 min, added CO_2 (excess) over 2 hours. The solution was added water (50 ml), the organic phases collected, washed with water (100 ml), dried (Na_2SO_4) and evaporated to dryness. The white solid was treated with EtOH (100 ml), filtered and dried. Yield: 62 % (4.10 g). ^{1}H-NMR: 7.30 (s, 2H); 6.46-6.67 (m, 9H); 4.44 (dd, 4H, J= 6.5 Hz); 3.79-3.94 (m, 8H); 3.71 (t, 4H, J= 14.1 Hz); 1.85-1.94 (m, 8H); 0-95-1.03 (m, 12Hz). ^{13}C-NMR: 171.4; 156.6; 135.6; 135.4; 135.0; 134.5; 130.5; 128.6; 128.3; 128.2; 122.6; 122.2; 77.2; 76.8; 76.7; 76.6; 31.0; 23.3; 23.2; 10.4; 10.3

*45 5-Isopropylidene-cyclopenta-1,3-diene (**45**)*

106.10 g/mol

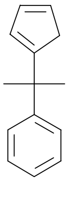


45

To a solution of freshly distilled cyclopentadiene (54.82 g; 0.831 mol), pyrrolidine (40.87 ml; d= 0.87 g/ml; 35.55 g; 0.399 mol) in MeOH (400 ml) was added acetone (24.3 ml; d= 0.79 g/ml; 19.27 g; 0.332 mol) at 0 °C. The yellow solution was stirred for 20 min at RT followed by addition of AcOH (33 ml; 50 vol.-%; 0.588 mol). The reaction mixture was washed with water (300 ml) and n-hexane (200 ml). The organic phase was collected and the aqueous phase was washed with n-hexane (3 x 200 ml). The combined organic phases were washed with water (200 ml) and dried (Na_2SO_4). Fractional distillation resulted in the product as a yellow azeotrop with n-hexane. The boiling point of the first fraction (product and hexane as an azeotrop) was 20 °C with the use of waterpump-vacuum (ca. 12 mmHg) and the second fraction had a boiling point of 62 °C (nearly pure product). Yield: 80 % (70.78 g total yield calculated from GC-MS). ^{1}H-NMR: 6.48 (m, 4H); 2.18 (s, 6H). ^{13}C-NMR: 150.6; 143.1; 131.3; 121.2; 23.7. GC-MS: R_t= 4.78 (method AF5), $M^{+\cdot}$=106 (50 %); 91 (100 %)

*46 (1-Cyclopenta-1,3-dienyl-1-methyl-ethyl)-benzene (**46**)*

184.21 g/mol

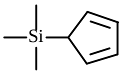


46

45 (70.78 g; 0.667 mol) was dissolved in dry Et_2O (200 ml), cooled to –30 °C under argon and added PhMgBr (0.53 mol) slowly. The reaction mixture was heated to RT, added a catalytic amount of CuI and the reaction mixture was refluxed for 1 hour. Adding water (50 ml) quenched the reaction. The organic phase was separated and the aqueous phase was washed with Et_2O (2 x 50 ml). The organic phases was combined and washed with water (50 ml), sat. $NaHCO_3$ (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to an orange oil. Distillation resulted in the product as a yellow liquid (bp.= 150-155 °C / 12 mmHg). Yield: 10 % (10.19 g total yield calculated from GC-MS). ^{1}H-NMR: 7.10-7.56 (m; 5 H); 6.10-6.40 (m; 2H); 2.99 (d; 1H; J= 1.3 Hz); 2.74 (d; 2H; J= 1.1 Hz); 1.54 (s; 6H). ^{13}C-NMR: 158.1; 155.5; 149.9; 148.9; 133.7; 133.4; 131.7; 131.5; 128.7; 128.0; 127.2; 127.2; 126.3; 125.8; 125.7; 124.2; 40.9; 40.8; 39.9; 30.0; 29.2. GC-MS: R_t= 8.52 (method AF5), $M^{+\cdot}$=184 (45 %); 169 (100 %); 91 (50 %)

*47 Cyclopenta-2,4-dienyl-trimethyl-silane (**47**)*

$C_8H_{14}Si$
138.28
138.086478
C 69.5% H 10.2% Si 20.3%

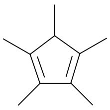


47

A sodium cyclopentadienyl solution in dry THF (0.20 mol) was added slowly during one hour trimethylsilylchloride (26 ml; d= 0.859 g/ml; 22.27 g; 0.205 mol). After the addition the solution was stirred for 3 hours at RT before it was poured into cold water (20 ml). The product was extracted into ether (3 x 50 ml), the organic phases were collected, dried ($MgSO_4$), filtered and concentrated in vacuum. The almost black solution was fractionated distilled under reduced pressure (water pump) and the colorless fraction with boiling range 29-32 °C where collected. Yield: 37 % (10.20 g). Found: C, 67.1; H, 10.3. Cal. for $C_8H_{14}Si$: C, 69.5; H, 10.2%. ^{1}H-NMR: 6.54-6.71 (br. m, 4H); 3.41-3.52 (br. s, 1H); 0.25 (s, 9H). ^{13}C-NMR: 143.5; 139.8; 135.3; 135.0; 132.1; 54.2; 4.0. GC-MS: R_t= 3.44 min (method AF5), $M^{+\cdot}$=138 (20 %); m/z= 123 (30 %); 73 (100 %).

*48 1,2,3,4,5-Pentamethyl-cyclopenta-1,3-diene (**48**)*[2]

136.24 g/mol



48

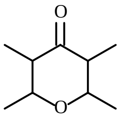
In a three necked bottom was placed lithium wire cut into small flattened pieces (2.66 g; 0.382 mol) in dry Et_2O (40 ml) and to this mixture was added dropwise 2-bromo-2-butene (25 g; 0.185 mol) in such a rate that the mixture was gentle refluxing. When the reaction had started addition of Et_2O (60 ml) took place and the addition of alkene continued. After final addition the yellow-orange reaction mixture was stirred for another hour before adding dropwise AcOEt (8.25 g; 93.75 mmol) diluted with an equal amount of dry Et_2O (10 ml). The reaction mixture was poured into NH_4Cl (sat. 250 ml). The organic phase was separated and the aqueous phase was adjusted to pH 9 with hydrochloric acid. The aqueous phase was washed with Et_2O (3 x 50 ml), the organic phases was collected, dried (Na_2SO_4) and concentrated to 10-20 ml (3,4,5-trimethyl-heptane-2,5-diene4-ol). The concentrate was added dropwise to a solution of p-toluenesulfonic acid monohydrate (1.93 g; 10.10 mmol) in Et_2O (40 ml) as quickly as possible, maintaining a gentle reflux. The reaction mixture was stirred for one hour at RT and then washed with sat. Na_2CO_3 until the washings remained basic. The organic phase was separated and the combined aqueous layers were extracted with Et_2O (3 x 50 ml). The combined organic phases were dried (Na_2SO_4) and evaporated to an orange liquid. This crude product was distilled under reduced pressure. Yield: 24 % (5.93 g). ^{1}H-NMR: 2.45 (br. d, 1H); 1.80 (s, 6H); 1.70 (s, 6H); 1.00 (d, 3H). ^{13}C-NMR: 137.8; 134.2; 51.6; 14.1; 11.6; 11.1

---

[2] Burger, U., Delay, A., Mazenod, F.; *Helv. Chim. Acta*, 1974, **57**, 2106

*49 2,3,4,5-Tetramethyl-tetrahydro-pyran-4-one (**49**)*

$C_9H_{16}O_2$
156.22
156.115029
C 69.2% H 10.3% O 20.5%

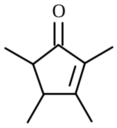


49

A solution of KOH (33.74 g; 0.601 mol) in abs. EtOH (225 ml), diethylketone (158.47 g; 1.840 mol) and LiCl (5.24 g; 0.123 mol) was heated to 30 °C and added very slowly acetaldehyde (220.27 g; 5.006 mol; made from distillation of trialdehyde treated with one drop of conc. H_2SO_4). The reaction mixture was cooled during the addition so the temperature was kept at 30 °C, and the addition took 3 hours. After the addition, the red reaction mixture was stirred overnight at RT. The dark red solution was neutralized by slow addition of conc. HCl (ca. 50 ml) and added Et_2O (300 ml; makes it more easy to perform the washing), the organic phase was washed with water (3 x 250 ml), separated, dried (Na_2SO_4), evaporated to a dark red oil. This oil was distillated under reduced pressure where the fraction boiling up to 100 °C/12 mmHg was collected. Redistillation using a Vigreux and collecting the fraction boiling from 63-89 °C/12 mmHg resulted in the product. Yield: 35 % (103.71 g). GC-MS: R_t= 3.981 min (method AF), M^+ =156, m/z = 56 (100%)

*50 2,3,4,5-Tetramethyl-cyclopent-2-enone (**50**)*

$C_9H_{14}O$
138.20
138.104465
C 78.2% H 10.2% O 11.6%

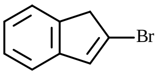


50

To a solution of **49** (103.71 g; 0.655 mol) in benzene (50 ml) was added p-toluenesulfonic acid (44.4 g; 0.233 mol) and the reaction mixture was refluxed for 20 hours collecting the water by azeotropic distillation using a Dean-Stark device. The solution was cooled, added Et_2O (300 ml), washed with $NaHCO_3$ (2 x 400 ml), water (2 x 200 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was distillated at reduced pressure and the colorless fraction boiling at 79-83 °C/12 mmHg was collected. Yield: 26 % (23.72 g). ^{13}C-NMR: 212.0; 211.4; 173.1; 171.9; 154.2; 134.9; 134.6; 130.7; 48.8; 46.7; 43.8; 41.6; 41.0; 32.3; 30.7; 21.7; 18.1; 16.0; 15.4; 15.4; 14.9; 14.9; 11.5; 11.4; 8.5 (mixture of isomers, e.g. 2,3,4,5-tetramethyl-cyclopent-3-enone also formed). GC-MS: R_t= 4.33 min (method AF, M^+=138 (45 %), m/z= 123 (100 %))

*51 2-Bromo-1H-indene (**51**)*[3]

195.06 g/mol

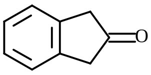


51

To a solution of indene (120.00 g; 1.034 mol) in DMSO (1200 ml), water (40 ml) was added in one portion NBS (384 g; 2.158 mol) at 10 °C. The temperature raised quickly to 75 °C and the solution turned orange in color. The reaction mixture was stirred for 15 min until the temperature had reached 35 °C. Then addition of a solution of Na_2CO_3 (120 g) and AcOH (120 ml) in water (3000 ml), was added slowly. Stirring was continued for another 10 min followed by filtration and washing with water. The yellow solid was dried as much as possible using vacuum without heating. The bright yellow solid was dissolved in toluene (1600 ml), added p-toluenesulfonic acid (4.00 g; 23.52 mmol) and water was removed using azeotropic distillation. The solution was cooled, washed with Na_2CO_3 (200 ml), water (100 ml), dried (Na_2SO_4) and evaporated to a dark nearly black oil. This oil was distillated and the yellow fraction boiling at 74-85 °C/0.3 mmHg was collected and recrystallized from MeOH (100 ml). The slightly yellow crystals were collected and dried. Yield: 48 % (97.72 g). ^{1}H-NMR: 7.11-7.91 (m, 4 H); 6.90 (s, 1H); 3.57 (s, 2H). ^{13}C-NMR: 144.0; 142.6; 133.0; 126.7; 124.9; 124.8; 123.2; 120.2; 45.5. GC-MS: R_t= 5.78 min (M^+=195 (isotopic pattern consisting with a compound containing bromine), m/z= 115 (100%))

*52 2-Indanone (**52**)*

132.16 g/mol



52

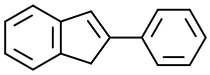
To a solution of 90 % indene (60.00 g; 54.00 g; 0.517 mol; 0.465 mol) in DMSO (600 ml), water (20 ml) was added in one portion NBS (192 g; 1.079 mol) at 10 °C. The temperature raised quickly to 75 °C and the solution turned orange in color. The reaction mixture was stirred for 15 min until the temperature had reached 35 °C. Then addition of a solution of Na_2CO_3 (60 g) and AcOH (60 ml) in water (1500 ml), was added slowly. Stirring was continued for another 10 min followed by filtration and washing with water. The yellow solid was dried as much as possible using vacuum without heating. KOH (25 g) was dissolved in 96% EtOH (400 ml) using reflux. To this solution was added in one portion the raw bromohydrin. The color changed to dark blue/black and the solution was refluxed for 10 min. The KBr was removed using filtration and the filtrate was evaporated to an oil on the rotary evaporator. The residue was partitioned between Et_2O (200 ml) and water (300 ml). The aqueous phase was washed with another portion of Et_2O (100 ml), the organic phases was collected, washed with sat. $NaHCO_3$ (100 ml), water (100 ml), dried (Na_2SO_4) and evaporated to a black oil. This oil was distillated using vacuum. The colorless fraction boiling at 100-105°/12 mmHg was collected in a 39.81 g yield (NMR and GC-MS was consistent with the expected epoxide). A solution of toluene (100 ml) with conc. H_2SO_4 (1.5 ml) was heated to reflux and the epoxide dissolved in toluene (60 ml) was added as fast as the exothermic reaction allowed (caution). After final addition the mixture was refluxed for another 10 min and cooled to RT. The residue was partitioned between Et_2O (200 ml) and water (200 ml). The aqueous phase was washed with another portion of Et_2O (100 ml), the organic phases was collected, washed with sat. $NaHCO_3$ (100 ml), water (100 ml), dried (Na_2SO_4) and evaporated to an orange oil. This oil was distillated using vacuum and the yellow fraction boiling at 106-112 °C/12 mmHg was collected. Yield: 20 % (12.53 g). ^{1}H-NMR: 7.22 (s, 4 H); 3.48 (s, 4H). ^{13}C-NMR: 215.3; 140.7; 127.6; 125.5; 44.7. GC-MS: R_t= 5.15 min, M^+=132, m/z= 104 (100%)

---

[3] Porter, H.D., Suter, C.M.; *J. Am. Chem. Soc.*, 1935, **57**, 2022

*53 2-Phenyl-1H-indene (**53**)*[4]

192.26 g/mol

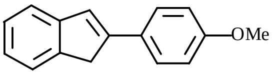


53

A mixture of indene (35.00 g; 0.301 mol), iodobenzene (61.46 g; 0.301 mol), $(PPh_3)_2PdCl_2$ (350 mg) in DMF (140 ml) and Et_3N (140 ml) was refluxed overnight under argon. The red reaction mixture was evaporated to dryness. The solid was dissolved in boiling MeCN (400 ml) followed by cooling in water/ice. The precipitate was collected and washed with cold MeCN producing almost white flakes. Yield: 43 % (24.62 g). ^{1}H-NMR: 7.62 (d, 2H); 7.14-7.47 (m, 8H); 3.78 (s, 2H). ^{13}C-NMR: 146.4; 145.4; 143.2; 136.0; 128.7; 127.5; 126.6; 126.5; 125.9; 125.7; 124.8; 123.7; 121.0; 39.0. GC-MS: R_t= 9.2 min (method AF); M^+=192 (100 %); 165 (20 %); 115 (10 %; indenyl fragment)

*54 2-(4-Methoxybenzene)-1H-indene (**54**)*

222.29 g/mol

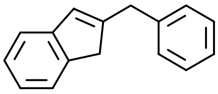


54

A solution of 4-bromanisole (1.97 g; 10.50 mmol) in dry Et_2O (50 ml) was treated with Mg (0.35 g; 14.4 mmol) at RT followed by reflux for 30 min. To this solution was added dropwise a solution of **52** (1.32 g; 10.00 mol) in dry Et_2O (50 ml) at RT. The reaction mixture was heated to reflux for another hour. The reaction mixture was cooled and poured into ice cold sat. NH_4Cl (200 ml). The organic phase was separated, dried (Na_2SO_4) and evaporated to dryness. To the residue was added ethanol (600 ml) and conc. H_2SO_4 (3 ml) followed by reflux for 1 hours. The homogeneous solution was cooled in ice-bath and filtered. The off white solid was washed with ice-cold ethanol (2 x 20 ml) and dried. mp: 207-209 °C, litt.: 206-207 °C. Yield: 37 % (0.83 g). ^{1}H-NMR: 7.05-7.43 (m, 6 H); 6.93 (s, 1H); 6.80 (doublet of triplets, 2H, J^1= 8.9 Hz, J^2= 2.9 Hz); 3.44 (s, 2H); 3.40 (s, 3H). ^{13}C-NMR: 167.3; 154.9; 153.6; 136.4; 134.6; 134.2; 133.5; 132.6; 132.0; 131.1; 128.3; 121.9; 62.3; 46.7. GC-MS: R_t= 10.70 min (method AF), M^+= 222 (100 %), m/z= 207 (35 %), m/z=176 (50 %)

*55 2-Benzyl-1H-indene (**55**)*

206.28 g/mol



55

To a solution of **51** (0.57 g; 2.92 mmol) in dry THF (50 ml) was added 1.33 M n-BuLi (2.4 ml; 3.19 mmol) at –78 °C under argon. The solution was stirred for ½ hour at this temperature and then added benzylbromide (0.72 g; 4.20 mmol). The solution was stirred overnight at RT. The reaction mixture was quenched by addition of water (20 ml), the organic phase was separated and the aqueous phase washed with Et_2O (50 ml). The organic phases were collected and washed with sat. NH_4Cl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to an orange oil, which crystallized upon standing. Yield: 99 % (0.60 g). ^{1}H-NMR: 7.07-7.46 (m, 10H); 4.08 (s, 2H); 3.68 (s, 2H). ^{13}C-NMR: 144.4; 143.0;

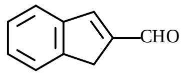
---

[4] Greifenstein, L.G., Lambert, J.B., Nienhuis, R.J., Fried, H.E., Pagani, G.A.; *J. Org. Chem.* ,1981, **46**, 5125

141.7; 138.9; 130.4; 129.2; 127.3; 126.7; 125.7; 124.0; 123.5; 120.2; 45.5; 33.8. GC-MS: R_t= 10.1 min, M^+= 205 (100 %), m/z= 91 (40 %)

*56 2-Formyl-1H-indene (**56**)*

$C_{10}H_8O$
144.17
144.057514
C 83.3% H 5.6% O 11.1%

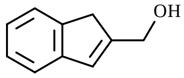


56

To a solution of DMF (62 ml; d=0.95 g/ml; 58.47 g; 0.800 mol) in $CHCl_3$ (400 ml) was added $POCl_3$ (76 ml; d= 1.655 g/ml; 122.80 g; 0.800 mol) slowly at RT. The reaction mixture was stirred 1 hour at RT, followed by addition of indene (92.92 g; 0.800 mol) in $CHCl_3$ (200 ml) dropwise while cooling with ice. The mixture was then allowed to stand for 4 days at RT before it was poured onto ice/water (1200 ml) and stirred using mechanical stirring for 1 hour. The solution was then steam distillated, the collected water/organic phases was separated and the aqueous phase was washed several times with $MeCl_2$ (5 x 100 ml). The organic phases were collected, washed with water (3 x 500 ml), dried (Na_2SO_4) and evaporated to an oil. This oil was fractional distillated under reduced pressure, the colorless fraction boiling at 68 °C /20 mmHg was collected (indene) and the yellow fraction boiling at 142 °C /20 mmHg was also collected (2-formylindene). Yield: 33 % (37.69 g). ^{1}H-NMR: 9.95 (s, 1H); 7.67 (s, 1H); 7.54 (m, 2H); 7.36 (m, 2H); 3.61 (s, 2H). ^{13}C-NMR: 188.0; 147.6; 146.9; 144.9; 142.1; 128.7; 127.0; 124.4; 123.5; 35.3. GC-MS: $R_{t.}$= 5.35 min (method AF), M^+= 144 (25 %), m/z= 115 (100 %), 89 (15 %)

*57 (1H-indene-2-yl)-methanol (**57**)*

$C_{10}H_{10}O$
146.18
146.073165
C 82.2% H 6.9% O 10.9%

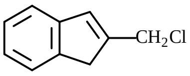


57

A mixture of **56** (1.00 g; 6.94 mmol) in dry isopropyl alcohol (100 ml) and $Al(OPr^i)_3$ (14.17 g; 69.40 mmol) was heated in oil bath to 110 °C. The bottle was equipped with a fractional column and a still head so the distillated acetone could be collected. The mixture was refluxed for 3 hours and evaporated to dryness. The residue was dissolved in $CHCl_3$ (50 ml), washed with 2 M HCl (50 ml), water (2 x 50 ml), dried (Na_2SO_4) and evaporated to dryness. Yield: 100 % (1.01 g). ^{1}H-NMR: 7.11-77.43 (m, 4H); 6.73 (s, 1H); 4.55 (s, 2H); 3.38 (s, 2H); 1.92 (s, 1H). ^{13}C-NMR: 148.7; 143.3; 127.5; 126.3; 125.8; 124.5; 123.7; 120.8; 61.8; 38.8. GC-MS: R_t= 6.10 min (method AF), M^+= 146 (40 %), m/z= 128 (35 %), 115 (100 %)

*58 2-Chloromethyl-1H-indene (**58**)*

$C_{10}H_9Cl$
164.63
164.039278
C 73.0% H 5.5% Cl 21.5%

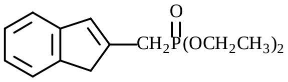


58

To a solution of **57** (1.01 g; 6.90 mmol) in petroleum ether (50 ml) was added $SOCl_2$ (10 ml; d= 1.63 g/ml; 16.3 g; 0.137 mol) and stirred at RT for 3 days. The solution was evaporated to a dark oil. Yield: 92 % (1.05 g). GC-MS: R_t= 5.95 min (method AF), M^+= 164 (15 %), m/z= 129 (100 %)

*59 (1H-indene-2-yl)-methyl-phosphonic acid diethyl ester (**59**)*

$C_{14}H_{19}O_3P$
266.27
266.107183
C 63.2% H 7.2% O 18.0% P 11.6%

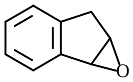


59

58 (1.05 g; 6.38 mmol) in $P(OEt)_3$ (40 ml) was refluxed for 5 hours. The remaining $P(OEt)_3$ was removed in vacuum. Yield: 100 % (1.69 g). ^{1}H-NMR: 7.10-7.42 (m, 4H); 6.71 (d, 1H, J= 4.8 Hz); 4.05-4.17 (m, 4H); 3.87 (q, 2H); 3.07 (d, 2H, J= 22.6 Hz); 1.33 (doublet of triplets, 6H). ^{13}C-NMR: 144.7; 143.4; 138.5; 130.8; 126.2; 124.3; 123.4; 120.4; 63.6; 42.1; 29.4; 16.4. GC-MS: R_t= 9.15 min (method AF), M^+= 266 (8 %), m/z= 210 (6 %), 128 (100 %)

*60 6,6a-Dihydro-1aH-1-oxa-cycloprop[a]indene (**60**)*

C_9H_8O
132.16
132.057514
C 81.8% H 6.1% O 12.1%

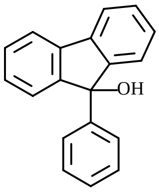


60

To a solution of indene (60.08 g; 54.07 g; 0.465 mol) in DMSO (600 ml), water (20 ml) was added in one portion NBS (192 g; 1.079 mol) at 10 °C. The temperature raised quickly to 75 °C and the solution turned orange in color. The reaction mixture was stirred for 15 min until the temperature had reached 35 °C. Then addition of a solution made from Na_2CO_3 (60 g) and AcOH (60 ml) in water (1500 ml) was added slowly. Stirring was continued for another 10 min followed by filtration and washing with water. The yellow solid was dried as much as possible by pressing a glass stopper into the solid combined with vacuum. KOH (26 g) was dissolved in 96% EtOH (750 ml). To this solution was added in one portion the raw bromohydrin (144.92 g; still water present). The color changed to dark blue/black and the solution was stirred under heating weakly for 15 min. The KBr was removed by filtration and the filtrate was evaporated to an oil by use of a rotary evaporator. This oil was distillated using vacuum. The colorless fraction boiling at 108-110° using water pump was collected. Yield: 29 % (17.78 g). ^{1}H-NMR: 7.46 (d, 1H, J= 7.0 Hz); 7.12-7.26 (m, 3H); 4.22 (dd, 1H, J= 2.6 Hz, J^2= 1.0 Hz); 4.07 (t, 1H, J= 2.9 Hz); 3.17 (d, 1H, J= 18.0 Hz); 2.93 (dd, 1H J= 18.0 Hz, J^2= 2.9 Hz). ^{13}C-NMR: 143.5; 140.8; 128.5; 126.1; 126.0; 125.1; 59.0; 57.6; 34.5

*61 9-Phenyl-fluoren-9-ol (**61**)*[5]

$C_{19}H_{14}O$
258.31
258.104465
C 88.3% H 5.5% O 6.2%

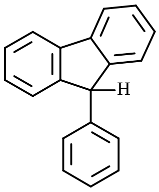


61

A Grignard solution made from magnesium turnings (2.22 g; 91.3 mmol), bromobenzene (15.09 g; 96.2 mmol) in dry Et_2O (225 ml) was prepared. After addition of the halogenide the reaction mixture was refluxed for one hour and cooled to RT. To this solution was added dropwise a solution of 9-fluorenone (15.04 g; 83.46 mmol) in dry Et_2O (100 ml) and the mixture was refluxed overnight. The reaction mixture was cooled to RT and poured into ice-cold NH_4Cl (400 ml). The organic phase was separated, the aqueous phase was washed with Et_2O (100 ml), the organic phases were collected, washed with water (200 ml), dried (Na_2SO_4) and evaporated to an orange oil. Recrystallisation from CCl_4 (150 ml) resulted in nearly colorless crystals after 3 hours in the freezer. Yield: 97 % (20.97 g). ^{1}H-NMR: 7.65 (dd, 2H, J^1= 7.0 Hz, J^2= 0.5 Hz); 7.18-7.38 (m, 11 H); 2.31 (br. s, 1H). ^{13}C-NMR: 150.4; 143.1; 139.6; 129.1; 128.4; 128.2; 127.2; 125.4; 124.8; 120.1; 83.6. GC-MS: R_t= 11.10 min (method AF), M^+=258 (75%), m/z= 241 (46%), 181 (100%), 152 (52%), 119 (15%), 77 (17%)

*62 9-Phenyl-9H-fluorene (**62**)*

$C_{19}H_{14}$
242.32
242.109550
C 94.2% H 5.8%



62

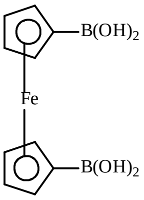
To a solution of **61** (9.73 g; 37.67 mmol) in CH_2Cl_2 (150 ml) was added Et_3SiH (7.0 ml; d= 0.75 g/ml; 5.26 g; 45.20 mmol) and BF_3*ET_2O (5.6 ml; d= 1.15 g/ml; 6.41 g; 45.20 mmol) at 0 °C under argon. After the addition the reaction mixture was stirred for 3 hours at 0 °C. The reaction mixture was added 2 M HCl (50 ml), the organic phase separated, washed with water (2 x 50 ml), dried (Na_2SO_4), and evaporated to dryness. The solid was treated with boiling CH_2Cl_2 (50 ml), added MeOH (200 ml) and cooled in ice for 2 hours before the white crystals were collected. Yield: 70 % (6.34 g). ^{1}H-NMR: 7.78 (d, 2H, J= 7.5 Hz); 7.48-7.21 (m, 9H); 7.08 (dd, 2H, J^1= 7.5 Hz, J^2= 2.0 Hz); 5.03 (s, 1H). ^{13}C-NMR: 147.9; 141.6; 141.0; 128.7; 128.3; 127.3; 126.8; 125.9; 125.3; 119.9; 54.4. GC-MS: R_t= 9.54 min (method AF), M^+=242 (100 %), m/z= 165 (47 %), 119 (40 %)

---

[5] Weber, E., Dörpinghaus, N., Csöregh, I.; *J. Chem. Soc., Perkin Trans. 2,* 1990, 2167

*63 1,1’-Ferrocene-diboronic acid (**63**)*[6]

273.68 g/mol

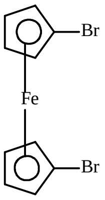


63

To a solution of ferrocene (3.00 g; 16.14 mmol) in dry hexane (200 ml) was added 1.3 M n-BuLi (27 ml; 35.51 mmol; +10 %) and TMEDA (5.4 ml; d= 0.77 g/ml; 4.12 g; 35.51 mmol) at RT. The solution was stirred at RT overnight. To orange heterogeneous solution was added to a solution of $B(OBu)_3$ (11.7 ml; d= 0.853 g/ml; 9.94 g; 43.2 mmol) in hexane (100 ml) at –78 °C. The reaction mixture was stirred for one hour at –78 °C, allowed to heat to RT and stirred at RT for another 12 hours. The solution was poured into 10 % KOH (100 ml), the organic phase was washed with 10 % KOH (4 x 50 ml). The combined aqueous layers were cooled in ice bath and acidified with dilute 10 % H_2SO_4. The precipitate was recovered by filtration, washed with water (500 ml), and dried (P_4O_{10}, 0.10 mbar). Yield: 37 % (1.62 g). ^{1}H-NMR: 7.46 (s, 4H); 4.34 (s, 4H); 4.18 (s, 4H). ^{13}C-NMR: 73.6; 71.6; 68.0

*64 1,1’-Dibromo-ferrocene (**64**)*[7]

343.83 g/mol



64

To a solution of ferrocene (11.63 g; 62.51 mmol) in dry Et_2O (100 ml) was added 1.6 M n-BuLi (86 ml; 0.138 mol; +10 %) and TMEDA (20.75 ml; d= 0.77 g/ml; 15.98 g; 0.138 mol) at RT. The solution was stirred at RT overnight. The solution was cooled to –78 °C for one hour and added 1,2-dibromotetrafluoroethane (16.5 ml; d= 2.17 g/ml; 35.81 g; 0.138 mol) slowly during 30 min. The suspension was stirred at –78 °C for another 4 hours and then stirred at RT for 2 hours. Water (100 ml) was added and the resulting mixture was extracted with CH_2Cl_2 (3 x 100 ml). The combined organic phases were washed with $Na_2S_2O_4$ (3 x 200 ml), dried (Na_2SO_4), evaporated to dryness. The solid was dissolved in MeOH (50 ml) and placed in the freezer for 2 days. Yield: 76 % (16.32 g). ^{1}H-NMR: 4.41 (t, 4H, J= 1.80 Hz); 4.15 (d, 4H, J=2.0 Hz). ^{13}C-NMR: 78.2; 72.6; 69.9. GC-MS: R_t= 7.67 min (method AF); M^+= 344 (30 %), m/z= 128 (100 %)

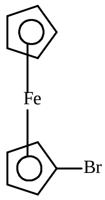
---

[6] Knapp, R., Rehahn, M.; *J. Organomet. Chem.*, 1993, **452**, 235

[7] Dong, T-Y, Lai, L-L; *J. Organomet. Chem.*, 1996, **509**, 131

*65 1-Bromo-ferrocene (**65**)*

264.94 g/mol

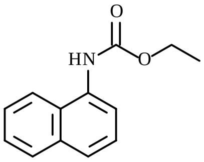


65

To a solution of **64** (3.44 g; 10 mmol) in dry THF (50 ml) was added 1.6 M n-BuLi (6.2 ml; 9.92 mmol) at –25 °C and stirred for 30 min at –25 °C. To the mixture was added water (20 ml) and the mixture was stirred 15 min at RT. The organic phase was collected, the aqueous phase was washed with $CHCl_3$ (3 x 50 ml), the organic phases were collected, washed with water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The oil was treated with boiling petroleum ether (20 ml) and placed in the freezer for 2 days. Yield: 26 % (0.68 g). ^{1}H-NMR: 4.76 (s, 2H); 4.21 (s, 5H); 4.15 (s, 2H). ^{13}C-NMR: 77.6; 70.1; 67.9; 67.1. GC-MS: R_t= 6.35 min (method AF); M^+= 264 (98 %, isotopic pattern consisted with bromine), m/z = 184 (80 %), 128 (100 %), 56 (98 %)

*66 1-Naphtylamine ethyl carbamate (**66**)*

$C_{13}H_{13}NO_2$
215.25
215.094628
C 72.5% H 6.1% N 6.5% O 14.9%

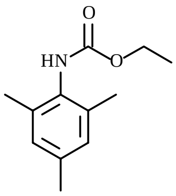


66

To a mixture of 1-naphtylamine (5.00 g; 32.1 mmol) in THF (100 ml) and Na_2CO_3 (4.04 g; 38.11 mmol) in water (50 ml) was added dropwise chloroethylformiate (3.3 ml; d= 1.135 g/ml; 3.79 g; 34.92 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 hours. The organic phase was separated, NaCl (100 ml) was added, the aqueous phase washed with Et_2O (3 x 100 ml). The organic phases were collected, washed with $NaHCO_3$ (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to a dark-red oil. The oil was dissolved in boiling EtOH (150 ml), added charcoal (10 g), reflux for 15 min, filtered hot, evaporated to half the original volume, added water until precipitation took place, heated again to reflux producing a homogeneous phase. The solution was cooled in ice-bath, filtered and the pink solid washed with water and dried in vacuum. Yield: 60 % (4.12 g). ^{1}H-NMR: 7.89-7.83 (m, 3H); 7.65 (d, 1H, J= 8.2 Hz); 7.55-7.7.43 (m, 3H); 6.92 (br. s, 1H); 4.27 (q, 2H, J= 7.2 Hz); 1.34 (t, 3H, J= 7.2 Hz). ^{13}C-NMR: 155.0; 134.1; 132.6; 128.8; 126.2; 126.0; 125.8; 124.9; 120.4; 61.5; 14.6. GC-MS: R_t= 8.53 min (Method AF), M^+= 215 (50 %), m/z= 187 (10 %), 143 (60 %), 115 (100 %)

*67 2,4,6-Trimethylaniline ethyl carbamate (**67**)*

$C_{12}H_{17}NO_2$
207.27
207.125928
C 69.5% H 8.3% N 6.8% O 15.4%

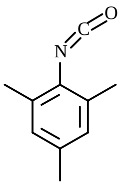


67

To a mixture of 2,4,6-trimethylaniline (4.5 ml; d= 0.963 g/ml; 4.34 g; 32.1 mmol) in THF (100 ml) and Na_2CO_3 (4.04 g; 38.11 mmol) in water (50 ml) was added dropwise chloroethylformiate (3.3 ml; d= 1.135 g/ml; 3.79 g; 34.92 mmol) at 0 °C. The mixture was stirred at 0 °C for one hour. The organic phase was separated, NaCl (100 ml) was added, the aqueous phase washed with Et_2O (3 x 100 ml). The organic phases were collected, washed with $NaHCO_3$ (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was dissolved in boiling petroleum ether (800 ml), filtered hot and cooled in ice-bath, filtered and the white solid washed with water and dried in vacuum. Yield: 77 % (5.14 g). ^{1}H-NMR: 6.87 (s, 2H); 5.97 (br. s, 1H); 4.17 (q, 2H, J= 6.9 Hz); 2.26 (s, 3H); 2.21 (s, 6H); 1.27 (br. s, 3H). ^{13}C-NMR: 154.6; 136.8; 135.6; 131.2; 128.9; 61.2; 20.9; 18.2; 14.7. GC-MS: R_t= 7.04 min (Method AF), M^+=207 (30 %), m/z= 161 (30 %), 134 (100 %), 91 (25 %)

*68 2,4,6-Trimethylphenyl isocyanate (**68**)*

$C_{10}H_{11}NO$
161.20
161.084064
C 74.5% H 6.9% N 8.7% O 9.9%

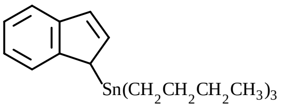


68

A mixture of **67** (1.00 g; 4.82 mmol) in toluene (10 ml) and Et_3N (0.80 ml; d= 0.73 g/ml; 0.59 g; 5.78 mmol; 1.2 eqv.) was refluxed for 5 min. under argon. Chlorocatecholborane (0.89 g; 5.78 mmol; 1.2 eqv.) was added and refluxed for another 5 min. The solution was cooled to RT, evaporated to dryness, treated with boiling hexane (10 ml), filtered hot, the filtrate evaporated to an oil. Yield: 96 % (0.74 g). ^{1}H-NMR: 6.82 (s, 2H); 2.27 (s, 6H); 2.22 (s, 3H). ^{13}C-NMR: 148.6; 136.4; 135.7; 129.6; 122.9; 112.6; 21.4; 18.8. GC-MS: R_t= 4.50 min (Method AF), M^+= 161 (100 %), m/z= 146 (80 %), 132 (45 %), 91 (35 %)

*69 1-Tributylstannyl-indene (**69**)*[8]

$C_{21}H_{34}Sn$
405.19
406.168250
C 62.2% H 8.5% Sn 29.3%

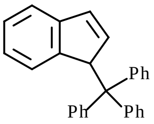


69

A solution of 1.6 M n-BuLi (62.5 ml; 0.100 mol) in dry THF (100 ml) was cooled to –78 °C followed by addition of a solution of diisopropylamine (14.0 ml; d= 0.722 g/ml; 10.12 g; 0.100 mol) in dry THF (50 ml). The solution was stirred for 10 min at –78 °C. To this solution was added a solution of indene (11.7 ml; d= 0.996 g/ml; 11.62 g; 0.10 mol) in dry THF (50 ml) at –78 °C. After the addition the solution was stirred for 15 min at –78 °C, heated to RT and stirred for another 15 min. The solution was cooled again to –78 °C, added chlorotributylstannane (27.9 g/ml; d= 1.20 g/ml; 33.53 g; 0.103 mol) and heated to RT. The mixture was stirred at RT for 3 days. The solution was evaporated to an oil, filtered and distillation under vacuum (0.1 mmHg) resulted in a clear yellow fraction boiling at 140-144 °C. Yield: 24 % (9.64 g). ^{1}H-NMR: 7.47 (br. s, 2H); 7.13 (dd, 2H, J^1=2.9 Hz, J^2=2.3 Hz); 6.75 (t, 1H, J= 3.2 Hz); 4.15 (very br. s, 1H); 0.70-1.5 (m, 27H). ^{13}C-NMR: 135.1; 134.8; 126.2; 124.5; 123.1; 121.2; 29.0; 26.8; 16.4; 13.7; 10.3. GC-MS: R_t=14.3 min (Method AF5), M^+=406 (2 %), m/z= 291 (20 %), 235 (80 %), 179 (100 %), 115 (65 %)

*70 1-Triphenylmethyl-indene (**70**)*[9]

$C_{28}H_{22}$
358.48
358.172150
C 93.8% H 6.2%



70

A solution of 1.6 M n-BuLi (62.5 ml; 0.100 mol) in dry THF (100 ml) was cooled to –78 °C followed by addition of a solution of diisopropylamine (14.0 ml; d= 0.722 g/ml; 10.12 g; 0.100 mol) in dry THF (50 ml). The solution was stirred for 10 min at –78 °C. To this solution was added a solution of indene (11.7 ml; d= 0.996 g/ml; 11.62 g; 0.10 mol) in dry THF (50 ml) at –78 °C. After the addition the solution was stirred for 15 min at –78 °C, heated to RT and stirred for another 15 min. The solution was cooled again to –78 °C, added tritylchloride (27.88 g; 0.10 mol) in dry THF (50 ml) and after the addition the solution was stirred at RT overnight. The reaction mixture was poured into ice-cold NH_4Cl (200 ml), the organic phase separated, the aqueous phase washed with $CHCl_3$ (2 x 100 ml), the organic phases collected, washed with water (100 ml), dried (Na_2SO_4) and evaporated to an oil. The oil was treated with boiling $CHCl_3$ (200 ml) and while hot poured into a rapid stirred solution of MeOH (700 ml). The light yellow precipitate was collected, washed with MeOH (50 ml) and dried in vacuum. Yield: 31 % (11.10 g). ^{1}H-NMR: 7.41 (d, 1H, J= 7.3 Hz); 7.26-7.07 (m, 18H); 6.89 (t, 2H, J= 7.6 Hz); 6.48 (d, 1H, J= 7.7 Hz); 6.24 (t, 1H, J= 2.0 Hz); 3.43 (d, 2H, J= 1.8 Hz). ^{13}C-NMR: 145.1; 144.6; 134.1; 130.9; 130.7; 127.5; 127.2; 126.1; 125.9; 125.3; 124.2; 123.9; 123.4; 60.9; 37.4

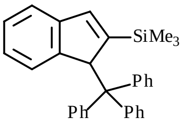
---

[8] Morris, R.J., Bock, P.L., Jefferis, J.M., Goedde, D.M.; *Polyhedron*, 1997, **16**, 3699

[9] Foster, P., Chien, J.C.W., Rausch, M.D.; *Organometallics*, 1996, **15**, 2404

*71 1-Triphenylmethyl-indene-2-trimethylsilane (**71**)*

$C_{31}H_{30}Si$
430.66
430.211679
C 86.5% H 7.0% Si 6.5%

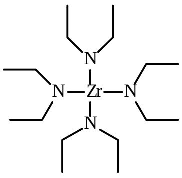


71

To a solution of **70** (8.60 g; 24.0 mmol) in dry THF (100 ml) at –78 °C was added n-BuLi (40 ml; 1.6 M; 64 mmol). The solution was stirred for 30 min at –78 °C during this period the lithio-compound precipitated. To this mixture was added TMS-Cl (8.60 g; 80 mmol) and the solution was stirred overnight at RT. The reaction mixture was quenched with MeOH (500 ml), evaporated to dryness, dissolved in $CHCl_3$ (300 ml), washed with water (50 ml), dried (Na_2SO_4) and evaporated again to dryness. The solid was treated with boiling MeOH (500 ml), cooled, filtered and dried in vacuum. Yield: 85 % (8.74 g). Found: C, 83.1; H, 7.2. Cal. for $C_{31}H_{30}Si$: C, 86.5; H, 7.0%. ^{1}H-NMR: 7.42 (d, 1H, J= 7.7 Hz); 7.26-7.16 (m, 15H); 7.06 (t, 1H, J= 7.4 Hz); 6.89 (t, 1H, J= 7.8 Hz); 6.67 (d, 1H, J= 7.9 Hz); 6.35 (s, 1H); 3.48 (s, 0.5H); -0.07 (s, 9H). ^{13}C-NMR: 149.5; 147.0; 146.4; 144.5; 139.6; 131.7; 127.9; 126.7; 124.8; 123.7; 123.6; 123.4; 62.2; 47.8. GC-MS: R_t= 13.279 min (Method AF), M^+= 414 (10 %), m/z= 337 (10 %), 243 (10 %), 73 (100 %)

*72 Tetrakis(N,N-diethylamino)zirconium (**72**)*

$C_{16}H_{40}N_4Zr$
379.74
378.230005
C 50.6% H 10.6% N 14.8% Zr 24.0%

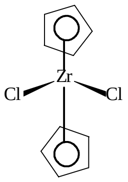


72

To a solution of 1.6 M n-BuLi (100 ml; 0.16 mol) in dry Et_2O (100 ml) was added slowly a solution of diethylamine (16.7 ml; d= 0.70 g/ml; 11.70 g; 0.16 mol) in dry Et_2O (100 ml) at –10 °C. The solution was heated to RT and stirred for another 30 min. Addition of $ZrCl_4$ (9.32 g; 40 mmol) followed by stirring overnight at RT. The mixture was evaporated to dryness, treated with benzene (500 ml), filtered, the filtrate was evaporated and the residue distilled in vacuum. The yellow fraction boiling at 120 °C/0.1 mmHg was collected. Yield: 8 % (1.2 g). ^{1}H-NMR: 3.33 (q, 2H, J= 7.0 Hz); 1.15 (t, 3H, J= 6.9 Hz)

*73 Bis(cyclopentadienyl)zirconium dichloride (**73**)*

292.32 g/mol

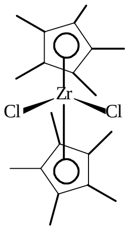


73

To a solution of $ZrCl_4$ (2.00 g; 8.58 mmol) in dry Et_2O (50 ml) was added sodium 2 M cyclopentadienyl (8.60 ml; 17.17 mmol) at RT under argon. After addition the reaction mixture was heated to RT and stirred for 5 days. The reaction mixture was evaporated to dryness, the residue was extracted with boiling $CHCl_3$ (150 ml) saturated with HCl (g) and filtered. The filtrate was evaporated to dryness, extracted with boiling $CHCl_3$ (150 ml) saturated with HCl (g) and filtered again. The filtrate was evaporated to a volume of 50 ml and placed in a cooling-bath (acetone/dry-ice). The precipitate was collected and recrystallized from toluene (30 ml) as white crystals. Yield: 26 % (0.66 g). Found: C, 41.4; H, 3.5. Cal. for $C_{10}H_{10}Cl_2Zr$: C, 41.1; H, 3.5%. ^{1}H-NMR: 6.50 (s). ^{13}C-NMR: 116.0

*74 Bis(1,2,3,4,5-pentamethylcyclopentadienyl)zirconium dichloride (**74**)*

432.59 g/mol

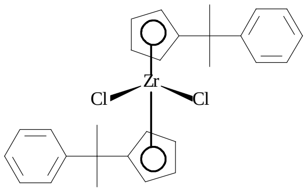


74

To a solution of **48** (2.72 g; 20.00 mmol) in dry THF (100 ml) was added 1.12 M n-BuLi (17.8 ml; 20.00 mmol) at –78 °C under argon after the addition the solution was heated to RT and stirred for 30 min. The yellow solution was cooled again to –78 °C and cannulated to a suspension of $ZrCl_4$ (2.36 g; 10.12 mmol) in toluene (100 ml) and the reaction mixture was stirred for one hour at RT followed by reflux for 3 days. The color changed to dark yellow during the heating. The reaction mixture was evaporated to dryness, and the yellow residue was taken up in $CHCl_3$ (50 ml), washed with 6 M HCl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to almost dryness. The residue was treated with petroleum ether (30 ml) and placed in the freezer overnight. The yellow solid was collected and dried. Yield: 42 % (1.81 g). Found: C, 55.3; H, 7.1. Cal. for $C_{20}H_{30}Cl_2Zr$: C, 55.5; H, 7.0%. ^{1}H-NMR: 1.99 (s). ^{13}C-NMR: 123.7; 12.0

75 *Bis(2-phenyl-2-cyclopentadienyl propane)zirconium dichloride (**75**)*

528.53 g/mol

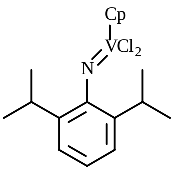


75

To a solution of **46** (1.84 g; 10.00 mmol) in dry THF (50 ml) was added 1.12 M n-BuLi (8.9 ml; 10.00 mmol) at –78 °C under argon after the addition the solution was stirred for 30 min. The slightly orange solution was added $ZrCl_4$ (1.18 g; 5.06 mmol) and the reaction mixture were stirred for 2 hours at RT. The color changed to green yellow with some precipitation during the heating. The reaction mixture was washed with conc. HCl (50 ml), water (50 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was added boiling pentane (30 ml), upon cooling gray crystals precipitated, and was collected. Yield: 20 % (0.52 g). Found: C, 64.6; H, 5.9. Cal. for $C_{28}H_{30}Cl_2Zr$: C, 63.6; H, 5.7%. ^{1}H-NMR: 7.20 (m, 5H); 6.35 (t, 2H, J= 3.7 Hz); 6.00 (t, 2H, J= 3.3 Hz); 1.78 (s, 6H). ^{13}C-NMR: 150.2; 142.4; 128.5; 126.5; 126.5; 117.6; 113.4; 40.8; 29.7

76 *N-(2,6-Diisopropylbenzene)iminium-cyclopentadienyl-vanadium dichloride (**76**)*

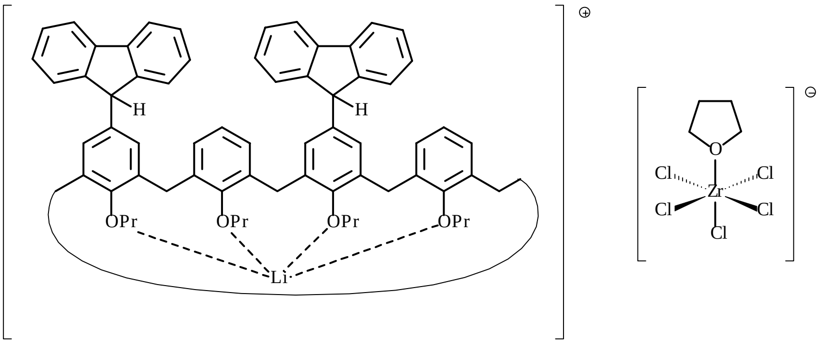
362.09 g/mol



76

A mixture of 2,6-diisopropylaniline isocyanate (2.1 ml; d= 0.951 g/ml; 2.00 g; 9.85 mmol) and $VOCl_3$ (0.92 ml; 1.71 g; 9.85 mmol) in octane (15 ml) was refluxed for 16 hours under argon. The dark green solution was evaporated to dryness, added **47** (3.12 g; 22.5 mmol) and CH_2Cl_2 (60 ml) followed by reflux for 48 hr. The golden brown mixture was filtered, the filtrate was evaporated to dryness, the residue washed with pentane (20 ml) and dried in vacuum. The brown powder was not as expected very hydroscopic. Yield: 50 % (1.77 g). Found: C, 57.5; H, 6.5; N, 3.9. Cal. for $C_{17}H_{22}Cl_2NV$: C, 56.4; H, 6.1; N, 3.9%. ^{1}H-NMR: 7.10-6.99 (t, 3H, J= 4.2 Hz); 6.53 (s, 5H); 3.73 (q, 2H, J= 6.8 Hz); 1.25 (d, 12H, J= 6.8 Hz). ^{13}C-NMR: 150.6; 129.3; 125.9; 122.9; 116.7; 28.2; 24.4

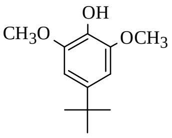
*77 5,17-Bis(9-fluorenyl)-25,26,27,28-tetrapropoxy Calix[4]arene lithium pentachlorozirconate tetrahydrofuran salt (**77**)*



77

To a solution of **15** (1.00 g; 1.09 mmol) in dry THF (100 ml) was added 1.410 M Bu^{t}Li (1.62 ml; 2.28 mmol; 1 eqv. + 5%) at –78 °C. The color changed from colorless to orange immediately after addition of the first drop of base. The solution was stirred for 15 min at –78 °C followed by stirring for another hour at ambient temperature. The colored solution was slowly cannulated into a solution of $ZrCl_4$ * 2THF (0.91 g; 2.40 mmol; + 10%) in dry THF (150 ml) at room temperature. After the addition, the mixture was refluxed overnight. The solution was evaporated to dryness using a flow of argon to exclude moisture. The solid was treated with toluene (70 ml) and filtered using Schlenk technique. The filtrate was evaporated to half its original volume and left at ambient temperature for several days to crystallize.

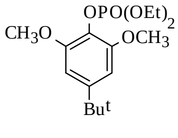
*78 4-(Tert-butyl)-2,6-dimethoxyphenol (**78**)*



78

A solution of 2,6-dimethoxyphenol (99.17 g, 0.64 mol) in CH_3SO_3H (150 ml) was warmed to 40 °C. *tert*-BuOH (185 ml, 1.985 mol) was added slowly during 3½ hours in order to keep the temperature between 50-55 °C. After addition the temperature was maintained at 50 °C for 2 hours. The reaction mixture was poured onto ice (1 kg) followed by extraction with diethylether (3 x 100 ml). The combined organic phases were washed with water (3 x 100 ml), saturated $NaHCO_3$ (2 x 500 ml), water (2 x 50 ml), dried ($MgSO_4$) and concentrated using a rotary evaporator giving a yellow oil **78** that was used without further purification in the preparation of compound **79**.

*79 Diethyl-(4-(tert-butyl)-2,6-dimethoxyphenyl)phosphate (**79**)*

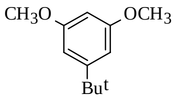


79

Compound **78** (obtained above, entire quantity) was dissolved in a mixture of CCl_4 (100 ml) and diethylphosphite (105 ml, 0.765 mol) at 0 °C under argon. Triethylamine (115 ml, 0.825 mol) was added at such a rate that the temperature was kept below 10 °C followed by stirring overnight at room temperature. The reaction mixture was concentrated on a rotary evaporator and the crude product was dissolved in a mixture of diethylether (500 ml) and water (500 ml). The organic phase was separated, washed with water (100 ml), 1 M HCl (*aq.*) (2 x 100 ml), water (100 ml), 4 M NaOH (*aq.*)

(2 x 100 ml), water (100 ml), dried ($MgSO_4$) and evaporated to dryness. Recrystallisation from *n*-hexane yielded compound **79** (184.74 g, 83% overall yield) as white flakes, mp 74-75 °C, (Found: C, 55.1; H, 7.9; P, 9.25. Cal. for $C_{16}H_{27}O_6P$: C, 55.5; H, 7.9; P, 8.9%); δ_H(250 MHz; $CDCl_3$, TMS) 6.59 (2 H, s, Ar*H*), 4.30 (4 H, q, J_{AB}7.10, $^3J_{PH}$7.20, $POC\mathit{H}_2CH_3$), 3.86 (6 H, s, $OC\mathit{H}_3$), 1.38 (6 H, td, J_{AB}7.10, $^4J_{PH}$1.15, $POCH_2C\mathit{H}_3$), 1.30 (9 H, s, $C(C\mathit{H}_3)_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 151.6 (d, J_{PC}3.5), 148.8 (d, J_{PC}2.0), 127.9 (d, J_{PC}7.9), 103.0 (d, J_{PC}1.5), 64.6 (d, J_{PC}6.0, $PO\mathit{C}H_2CH_3$), 56.5 ($O\mathit{C}H_3$), 35.4, 31.8, 16.5 (d, J_{PC}7.4, $POCH_2\mathit{C}H_3$); *m/z* 346 (M^+, 23%), 331 (M^+ - Me, 23) and 177 (M^+ - $OPO(OEt)_2$, 100).

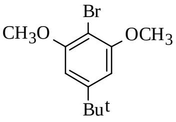
*80 1-(*Tert*-butyl)-2,5-dimethoxybenzene (**80**)*



80

Compound **79** (97.75 g, 0.282 mol) was dissolved in a mixture of dry THF (50 ml) and dry diethylether (250 ml). This solution was added slowly under reflux to metallic lithium (4.50 g, 0.648 mol) in liquid NH_3 (600 ml). The addition took 2 hours. Towards the end of the addition the blue color disappeared. More lithium was added (1.01 g, 0.146 mol) in order to maintain the blue color. After the addition the blue mixture was stirred for 1 hour under reflux followed by quenching with NH_4Cl (*sat.*) (200 ml) and overnight stirring at room temperature. After evaporation of the ammonia diethylether (500 ml) was added and the organic phase was separated, washed with water (100ml), 2 M NaOH (*aq.*) (2 x 200 ml), water (2 x 100 ml), dried (K_2CO_3) and concentrated. The crude product was recrystallized from petroleum ether (Bp. 30-50 °C) yielding compound **80** (53.40 g, 97%) as a white powder, mp 50-51 °C; (Found: C, 74.4; H, 9.6. Cal. for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3%); δ_H(250 MHz; $CDCl_3$, TMS) 6.54 (2 H, d, J_{meta}2.2), 6.30 (1 H, t, J_{meta}2.2), 3.80 (6 H, s, $OC\mathit{H}_3$), 1.30 (9 H, s, $C(C\mathit{H}_3)_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 160.5, 153.9, 104.1, 96.8, 55.2, 35.0, 31.3; *m/z* 194 (M^+, 50%), 179 (M^+ - CH_3, 100).

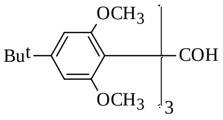
*81 2-Bromo-5-(*tert*-butyl)-1,3-dimethoxybenzene (**81**)*



81

A solution of Br_2 (58.86 g, 0.368 mol) in CCl_4 (110 ml) was added to compound **80** (71.56 g, 0.368 mol) in CCl_4 (600 ml) during 2 hours at 0 °C. After addition the solution was stirred for 1 hour at 0 °C followed by evaporation to dryness. Recrystallisation from *n*-hexane yielded compound **81** (95.88 g, 95%) as a white powder, mp 119-120 °C; (Found: C, 52.7; H, 6.4. Cal. for $C_{12}H_{17}BrO_2$: C, 52.8; H, 6.3%); δ_H(250 MHz; $CDCl_3$, TMS) 6.60 (2 H, s, Ar*H*), 3.89 (6 H, s, $OC\mathit{H}_3$), 1.33 (9 H, s, $C(C\mathit{H}_3)_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 154.9, 150.5, 100.7, 96.3, 54.65, 33.5, 29.6; *m/z* 272 (M^+, 58%, the isotopic pattern was consistent with isotopic pattern for mono-bromo compounds), 257 (M^+- CH_3, 100), m* 178 (272 → 257).

82 *Tris-(4-(*tert*-butyl)-2,6-dimethoxyphenyl)carbinol (**82**) by lithiation of* **80**



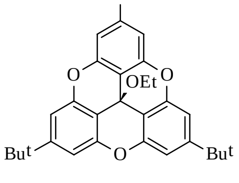
82

A solution of bromobenzene (33.60 g, 0.214 mol) in dry diethylether (100 ml) was added to lithium containing 0.5-1% sodium (3.07 g, 0.439 mol) in dry diethylether (100 ml) under argon. After 4 hours of stirring at room temperature a solution of compound **80** (36.01 g, 0.185 mol) in benzene (270 ml) was added and the reaction mixture was stirred for 72 hours at room temperature. During this period of time the color changed from dark brown to yellow. Diethylcarbonat (7.22 g, 61.16 mmol) in benzene (130 ml) was added dropwise followed by reflux for another 72 hours. The brown mixture was cooled and poured onto ice/water (1 kg) and stirred for 15 min. The organic phase was separated and the aqueous phase was washed with diethylether (100 ml). The combined organic phases were washed with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from *n*-hexane gave compound **82** (18.49 g, 49%) as a white powder, mp 175-180 ^{o}C (dec.); (Found: C, 70.35; H, 8.5. Cal. for $C_{37}H_{52}O_7$: C, 73.0; H, 8.6%; the carbon content was very high which could arise from loses of water during heat); δ_H(250 MHz; $CDCl_3$, TMS) 6.72 (1 H, s, O*H*), 6.49 (6 H, s, Ar*H*), 3.39 (18 H, s, OC*H*$_3$), 1.27 (27 H, s, C(C*H*$_3$)$_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 158.2, 149.2, 125.9, 124.9, 104.2, 56.6, 34.6, 31.3.

*82 Tris(4-(tert-butyl)-2,6-dimethoxyphenyl)methanol (**82**) by lithiation of* **81**

A solution of **81** (4.00 g, 14.64 mmol) in dry THF (50 ml) was cooled to -78 °C under argon and added dropwise 1.5 M *tert*-BuLi in *n*-pentane (19.50 ml, 29.29 mmol, 2 *eqv.*) at a rate keeping the temperature below -60 °C. The intensely yellow solution was stirred for 1 hour at -78 °C followed by dropwise addition of diethylcarbonat (0.58 g, 4.88 mmol) dissolved in dry THF (10 ml) at -78 °C. The reaction mixture was allowed to reach room temperature followed by reflux for 48 hours. The green reaction mixture was cooled to room temperature, quenched by the slow addition of 96% EtOH (15 ml) and washed with diethylether (2 x 100 ml). The organic phase was separated and washed with water (100 ml), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from *n*-hexane gave compound **82** (2.33 g, 79%) as a white powder. The compound was found to be extremely sensitive to acid. Any presence of acid resulted in a color change from colorless to a very intense blue color. The physical constants for the products prepared following the two above procedures were identical.

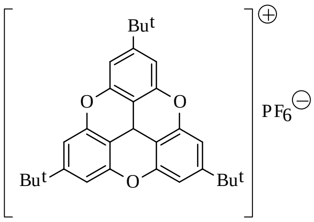
*83 2,6,10-Tri(*tert*-butyl)-12c-ethoxy-4,8,12-trioxa-4,8,12-trihydrodibenzo[*cd,mn*]pyrene (**83**)*



83

A mixture of compound **82** (22.70 g, 37.33 mmol) in water (2.6 L) was treated with *conc.* hydrochloric acid (60 ml) and the blue mixture was refluxed for 4 hours. The reaction mixture was filtered and the filter cake was washed several times with water until the crude off-white xanthon was obtained. This crude product was dried in vacuum (60 °C, 0.8 mmHg) for 3 hours. The dried material was mixed with pyridine hydrochloride (40.24 g, 0.348 mol) and heated to 130 °C for 2 ½ hours. During this period of time the reaction mixture changed color from dark-red to orange/yellow indicating that the reaction had finished. The mixture was cooled, poured into water (500 ml), filtered and the filter-cake was washed several times with water, 2 M HCl (*aq.*) and water again. The filtrate was treated with 25 % NaOH (*aq.*) (*approx.* 150 ml) until basic reaction to litmus and precipitation of a white compound occurred. The white material was collected by filtration and dissolved in 96% EtOH (400 ml) under reflux. Upon cooling the solution product precipitated. This gave compound **83** (13.81 g, 74%) as a white powder, mp > 230 °C (dec.); (Found: C, 79.1; H, 7.7. Cal. for $C_{33}H_{38}O_4$: C, 79.5; H, 7.7%); δ_H(250 MHz; $CDCl_3$, TMS) 7.06 (6 H, s, Ar*H*), 3.13 (2 H, q, $^3J_{AB}$7.0, OCH_2CH_3), 1.35 (27 H, s, $C(CH_3)_3$), 0.92 (3 H, t, $^3J_{AB}$7.0, OCH_2CH_3); δ_C(62.9 MHz; $CDCl_3$, TMS) 154.0, 153.0, 125.9, 108.4, 106.9, 56.9, 35.3, 31.4, 15.3.

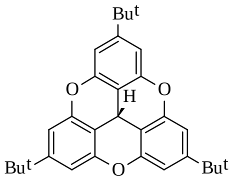
*84 2,6,10-Tri(*tert*-butyl)-4,8,12-trioxa-4,8,12-trihydrodibenzo[*cd,mn*]pyrenium-hexafluorophosphate (**84**)*



84

HPF_6 (*aq.*) (60 w/w-%) (0.95 ml, 1.36 mmol) was added dropwise to a solution of compound **83** (3.00 g, 6.04 mmol) in diethylether (300 ml) at 0 °C. Precipitation of the yellow product took place immediately. The reaction mixture was stirred for an additional 1 hour at 0 °C, filtered, washed with cold diethylether and dried in vacuum giving compound **84** (3.62 g, 100%) as a fine intensely yellow powder, mp >300 °C (dec.); (Found: C, 62.15; H, 5.7; P, 5.3. Cal. for $C_{31}H_{33}F_6O_3P$: C, 62.2; H, 5.6; P, 5.2%); δ_H(250 MHz; $CDCl_3$, TMS) 7.67 (6 H, s, Ar*H*), 1.50 (27 H, s, $C(CH_3)_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 170.2, 153.9, 142.7, 110.5, 104.2, 38.2, 31.4; MALDI-TOF 453 (one peak, $C_{31}H_{33}O_3$-cation).

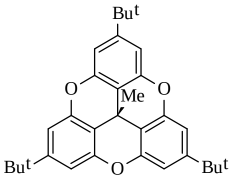
*85 2,6,10-Tri(*tert*-butyl)-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene (**85**)*



85

$NaBH_4$ (0.50 g, 13.20 mmol) was added in one portion to a solution of compound **84** (0.50 g, 0.84 mmol) in DME (50 ml). The reaction mixture changed from yellow to colorless during the additional 1 hour of reflux. The reaction mixture was cooled to room temperature, poured into ice/water (200 g) and diethylether (100 ml) was added. The organic phase was extracted with water (2 x 100 ml), dried (Na_2SO_4) and evaporated to dryness. Recrystallisation from ethylacetate produces very clear crystals suitable for X-ray diffraction. It was also possible to precipitate compound **85** as a white powder by addition of diethylether (*approx.* 10ml) (0.29 g, 76%), mp >300 °C (dec.); (Found: C, 81.8; H, 7.8. Cal. for $C_{31}H_{34}O_3$: C, 81.9; H, 7.5%); δ_H(250 MHz; $CDCl_3$, TMS) 6.94 (6 H, s, Ar*H*), 4.74 (1 H, s, 12c-*H*), 1.32 (27 H, s, $C(CH_3)_3$); δ_C(62.9 MHz; $CDCl_3$, TMS) 152.9, 152.8, 108.6, 106.9, 35.1, 31.4, 20.3.

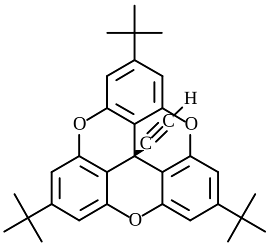
*86 2,6,10-Tri(*tert-*butyl)-12c-methyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene (**86**)*



86

A solution of compound **84** (0.50 g, 0.87 mmol) in dry THF (40 ml) was cooled to -78 °C under argon. CuI (0.33 g, 1.75 mmol) was added. After stirring for 10 min. 1.0 M MeLi (5.2 ml, 5.20 mmol) was added slowly. The reaction mixture changed color from yellow to green. The mixture was stirred for one hour at -78 °C. The reaction mixture adapted an off-white color, which indicated that the reaction had finished. The temperature was allowed to reach room temperature followed by addition of NH_4Cl (*sat.*) (20 ml) to quench excess copper/lithium reagent. The aqueous phase was extracted with $CHCl_3$ (2 x 50 ml) and the combined organic phases were washed with water (2 x 50 ml), dried (Na_2SO_4) and evaporated to give clear oil. This crude product was mixed with boiling acetone (50 ml) and stored in the freezer for 6 hours. After this period of time filtration gave compound **86** (0.21 g, 52%) as white crystals. Recrystallisation from ethylacetate produced clear crystals suitable for X-ray diffraction, mp >290 °C; (Found: C, 82.4; H, 8.0. Cal. for $C_{32}H_{36}O_3$: C, 82.0; H, 7.7%); δ_H(250 MHz; $CDCl_3$, TMS) 6.96 (6 H, s, Ar*H*), 1.57 (3 H, s, C*H₃*), 1.32 (27 H, s, C(C*H₃*)₃); δ_C(62.9 MHz; $CDCl_3$, TMS) 152.33, 152.28, 112.5, 108.5, 35.1, 31.4, 31.2, 23.8.

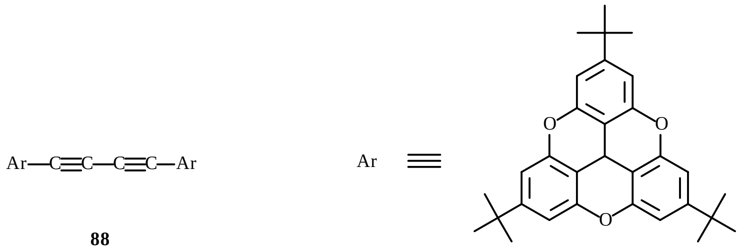
*87 2,6,10-Tri(*tert-*butyl)-12c-acetylene-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene (**87**)*



87

A solution of **84** (1.00 g; 1.67 mmol) in dry THF (50 ml) was added a 11-15% suspension in xylene of sodiumacetylidyne (1.84 g;4.21 mmol) at 0 °C under argon. The solution was heated to reflux for 3 hours during which the yellow color dissappeared. Addition of water (50 ml) quenched the reaction, washed with Et_2O (100 ml), and the organic phase was washed with sat. NaCl (2 x 50 ml), water (2 x 50 ml), dried (Na_2SO_4), filtered and evaporated to dryness. The solid was dissolved in $CHCl_3$ (50 ml), flash chromatographed (SiO_2), evaporated to an off-white compound, which was recrystallized from EtOH giving the product as white powder. Yield: 81% (0.65 g). ^{1}H-NMR: 7.01 (s, 6H); 2.40 (s, 1H); 1.33 (s, 27H). ^{13}C-NMR: 153.6; 152.2; 109.1; 108.6; 108.2; 71.9; 35.3; 31.3; 18.5.

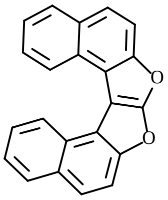
88 *1,4-Bis(2,6,10-Tri(*tert*-butyl)-12c-yl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene)-butadiyn (**88**)*



88

A mixture of **87** (0.50 g; 1.04 mmol), pyridine (15 ml) and CuCl (2.00g; 20.2 mmol) in MeOH (50 ml) was stirred for 2 hours while air was passed though rapidly. Addition of conc. HCl until acid reaction then addition of sat. NaCl (50 ml) took place and washing with Et$_2$O (2 x 50 ml). The combined organic phases were washed with water (2 x 50 ml), dried (Na$_2$SO$_4$), filtered and evaporated to dryness. The solid was dissolved in CHCl$_3$ (50 ml), flash chromatographed (SiO$_2$), evaporated to an off-white compound, which was recrystallized from EtOH giving the product as white powder. Yield: 72 % (0.36 g). ^{1}H-NMR: 6.92 (s, 12H); 1.28 (s, 54H). ^{13}C-NMR: 154.8; 152.7; 109.8; 107.6; 81.8; 68.7; 35.9; 31.8; 30.5

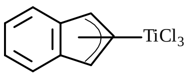
89 *7,8-Dioxa[6]helicene (**89**)*



89

A solution of 7a,14c-dihydro-7,8-dioxa[6]helicene (0.50 g; 1.63 mmol) in 1,2-dichlorobenzene (120 ml) was added DDQ (0.56 g; 2.46 mmol) and refluxed under argon for 48 hours. The reaction mixture was cooled, washed with 10 % NaOH (5 x 100 ml), water (3 x 50 ml), sat. NaHCO$_3$ (50 ml), water (50 ml), dried (Na$_2$SO$_4$) and evaporated to dryness. The solid was dissolved in CHCl$_3$ (50 ml) and column-chromatography (SiO$_2$; CHCl$_3$/hexane 1:4) was performed, collecting the eluent until the red band is reached. Evaporation and recrystallisation from EtOH resulted in slightly yellow needles. Yield: 40 % (0.20 g) mixture of 7,8-dioxa[6]helicene and 5-chloro-7,8-dioxa[6]helicene.

90 *Trichloro(η^5-indenyl)titanium (**90**)*



90

A solution of indene (5.6 g; 48 mmol) in dry THF (25 ml) was added 1.4 M *n*-BuLi (34 ml; 48 mmol) at –78 °C under argon. After the addition the temperature was raised to 0 °C, then cooled again to –78 °C before adding TMS-Cl (6.1 ml; 48 mmol) in one portion allowing the temperature to raise to RT. The solution was evaporated, treated with boiling petroleum ether (100 ml), filtered (removing LiCl), evaporated again, the resulting oil was distillated and the fraction boiling at 128-132 °C/12 mmHg was collected giving the 1-trimethylsilylindene. A solution of 1-trimethylsilylindene (1.90 g; 10 mmol) in CH$_2$Cl$_2$ (50 ml) was added dropwise TiCl$_4$ (1.3 ml; 12 mmol) at 0 °C under argon. The red solution was stirred overnight at RT before evaporation to dryness was performed. The purple crystals was redissolved in boiling CHCl$_3$ (20 ml), filtered using Schlenk-tecnique, the filtrate was cooled to –78 °C and the crystals were collected. ^{1}H-NMR: 7.83 (dd, 2H, J^1= 7.7 Hz, J^2= 2.7 Hz); 7.52 (dd, 2H, J^1= 6.5 Hz, J^2= 3.1 Hz); 7.20 (d, 2H, J=3.4 Hz); 7.12 (t, 1H, J= 3.4 Hz). ^{13}C-NMR: 131.4; 130.4; 127.6; 123.9; 117.6.

Synthesis of polymers

General description of the anionic polymerization of styrene.

A solution of the *Crown ether* (2.63 mmol) in dry *solvent* (20 ml) was added *initiator* (2.63 mmol) under argon. The solution was stirred for 5 min at *the reaction temperature* and added freshly distilled styrene (2.0 ml; 26.3 mmol). The reaction mixture was stirred at *the reaction temperature* for *the reaction time*, added MeOH (5 ml), evaporated to dryness, dissolved in $CHCl_3$ (150 ml) and added MeOH (700 ml). The polymer was collected by filtration and dried in vacuum.

Table ***Error! Unknown switch argument.****. The collected data used in the anionic polymerization of styrene.*

Experiment NR.	**Crown ether**	**Initiator**	**Solvent**	**Reaction Time / min**	**Reaction Temperature / °C**	**Yield / %**
PS1	None	Bu^tLi	Cyclohexane	30	40-50	78
PS2	None	*n*-BuLi	Cyclohexane	30	40-50	46
PS3	None	*n*-BuLi	Toluene	10	Ambient	25
PS4	None	*n*-BuLi	Toluene	10	40-50	66
PS5	**3**	*n*-BuLi	Cyclohexane	30	40-50	30
PS6	**3**	*n*-BuLi	Cyclohexane	30	-78	None
PS7	12-Crown-4	*n*-BuLi	Toluene	10	-78	53
PS8	12-Crown-4	*n*-BuLi	Toluene	10	Ambient	93
PS9[*]	12-Crown-4	*n*-BuLi	Toluene	10	Ambient	86
PS10	18-Crown-6	*n*-BuLi	Cyclohexane	5	Ambient	90
PS11	18-Crown-6	*n*-BuLi	Toluene	10	-78	91
PS12[*]	18-Crown-6	*n*-BuLi	Toluene	10	Ambient	92
PS13	Benzo-12-Crown-4	*n*-BuLi	Toluene	Overnight	Ambient	None
PS14	Dicyclohexano-18-Crown-6	*n*-BuLi	Toluene	10	-78	90
PS15	Dicyclohexano-18-Crown-6	*n*-BuLi	Toluene	10	Ambient	59
PS16	Benzo-18-Crown-6	*n*-BuLi	Toluene	10	Ambient	None
PS17	4'-Methylbenzo-18-Crown-6	*n*-BuLi	Toluene	Overnight	Ambient	None

Preparation of ***PS18****,* ***PS19****,* ***PS20*** *and* ***PS21*** *using* **90** *and* **76** *as catalysts together with MAO.*

In a flame-dried three necked bottle (250 ml) was placed freshly distilled styrene (10.0 ml; 88 mmol) and dry toluene (100 ml), this solution was flushed with argon for 10 min. Then addition of MAO (10 ml; 10 wt-% in toluene; d= 0.875 g/ml; 8.75 g; 0.875 g; 15.10 mmol) took place and the solution was stirred 10 min at 60 °C. The catalyst was added **90** or **76** (5 μmol) (Al/Ti= 3018). The reaction mixture was quenched after 20 min by pouring it into HCl/EtOH (10 %; 200 ml). The mixture was filtered, washed with methanol (50 ml) and dried in vacuum. The polymers were obtained in 13-31 % yield.

---

[*] In this experiment the living character of the polymerization was seen by first consuming one equivalent styrene followed by the addition of another equivalent styrene. The reaction time indicated is the reaction time between and after the second addition.

Appendix

Appendix 1. *Crystallographic data of the 5,17-bis(1-fluorenyl)-tetrapropoxycalix[4]arenes* ***15*** *and* ***77****.*

Appendix 2. *Crystallographic data of the 2,6,10-tri-tert-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[cd,mn]pyrenes* ***85*** *and* ***86****..*

Appendix 3. *Crystallographic data of the 7,8-dioxa[6]helicene (***89***) and 5-chloro-7,8-dioxa[6]helicene (***3D***).*

Appendix 4. *Lithium-ion induced conformational change of 5,17-Bis(9-fluorenyl)-25,26,27,28-tetrapropoxy calix[4]arene resulting in an egg shaped dimeric clathrate. Accepted by Tetrahedron Letters.*

Appendix 5. *Synthesis, structure and properties of various molecules based on the 4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[cd,mn]pyrene system with an evaluation of the effect differing molecular substitution patterns has on the space group symmetry. J. Chem. Soc., Perkin Trans 2, 1997, 2219.*

Appendix 6. *The geometry and structural properties of the 4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[cd,mn]pyrene system in the cationic state. Structures of a planar organic cation with various monovalent and divalent anions. Acta. Cryst., 1999,* ***B55****, 410.*

Appendix 7. *Arrested handedness and disordered stacking in crystals of the pre-helical molecule 7,8-dioxa[6]helicene. Cryst. Eng. Comm., 1999, 6*

Appendix 8. *Preparation and properties of 7,8-Dioxa[6]helicenes and 7a,14c-dihydro-7,8-dioxa[6]helicenes. Submitted to J. Org. Chem.*

Crystallographic data of the 5,17-bis(1-fluorenyl)-tetrapropoxycalix[4]arenes ***15*** *and* ***77****.*

Compound	**15**	**77**
Formula	$C_{66}H_{64}O_4$	$C_{84}H_{88}Cl_5LiO_5Zr$
formula wt	921.17	1452.95
crystal system	Monoclinic	Triclinic
space group	P2/c	P1
Z	4	2
a, Å	24.944(5)	13.832(3)
b, Å	10.351(2)	17.564(4)
c, Å	19.888(4)	18.546(4)
α, º	90	70.71(3)
β, º	91.90(3)	72.37(3)
γ, º	90	71.23(3)
V, Å^3	5132.2(18)	3928.1(14)
ρ, g cm^3	1.192	1.228
crystal dimensions, mm	1.12 x 0.30 x 0.30	0.60 x 0.20 x 0.10
type of radiation	Mo-Kα	Mo-Kα
μ, cm^{-1}	0.072	0.359
T, K	120(2)	120(2)
number of reflections	53378	41636
unique reflections (with I	8494	12285
R_{int}	0.0308	0.0880
R(F), $R_w(F^2)$ all data	0.0438, 0.1284	0.1131, 0.3609

Crystallographic data of the 2,6,10-tri-tert-butyl-4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[cd,mn]pyrenes ***85*** *and* ***86****.*

Compound	**85**	**86**
Formula	$C_{31}H_{34}O_3$	$C_{32}H_{36}O_3$
formula wt	454.6	468.6
crystal system	cubic	orthorhombic
space group	I-43d	Pna2_1
Z	16	4
a, Å	21.692(3)	12.578(3)
b, Å	21.692(3)	12.305(3)
c, Å	21.692(3)	17.314(4)
α, ^{o}	90	90
β, ^{o}	90	90
γ, ^{o}	90	90
V, Å^3	10206.7(20)	2679.9(9)
ρ, g cm^3	1.183	1.161
crystal dimensions, mm	0.35 x 0.30 x	0.35 x 0.10 x
type of radiation	**Mo-Kα**	Mo-Kα
μ, cm^{-1}	0.074	0.073
T, K	293(2)	293(2)
number of reflections	32456	26728
unique reflections (with I	1736	2822
R_{int}	0.0509	0.0873
R(F), Rw(F^2) all data	0.0565, 0.1284	0.0714, 0.1635

*Crystallographic data of the 7,8-dioxa[6]helicene (**89**) and 5-chloro-7,8-dioxa[6]helicene (**3D**).*

Compound	**89**	**3D**
formula	$C_{22}H_{12}O_2$	$C_{22}H_{11}O_2Cl$
formula wt	308.32	342.76
crystal system	Monoclinic	Orthorhombic
space group	C*c* (no. 9)	$Pna2_1$
Z	32	4
***a*, Å**	17.4168(3)	16.496(3)
***b*, Å**	46.5871(6)	15.565(3)
***c*, Å**	14.7689(2)	5.9747(12)
α, º	90	90
β, º	105.190(1)	90
γ, º	90	90
V, Å^3	11564.8(3)	1534.1(5)
ρ, g cm^3		1.484
crystal dimensions, mm		0.38 x 0.15 x 0.075
type of radiation	0.7100 (sychrotron)	Mo-Kα
μ, cm^{-1}		0.261
***T*, K**	100(2)	120(2)
number of reflections	58024	15861
unique reflections (with I > 2σ)	24638	2437
R_{int}	0.0731	0.0550
R*(F)*, $R_w(F^2)$ *all data*	0.1004	0.0393, 0.0942

Appendix 4

Appendix 5

Appendix 6

Preparation and properties of 7,8-Dioxa[6]helicenes and 7a,14c-dihydro-7,8-dioxa[6]helicenes.

Jørgen Eskildsen, Frederik C. Krebs[1], André Faldt, Peter Sommer-Larsen and Klaus Bechgaard*

Department of Condensed Matter Physics and Chemistry, Risø National Laboratory, DK-4000 Roskilde, Denmark.

Abstract: The preparation of several new 7,8-Dioxa[6]helicenes by oxidation of 7a,14c-dihydro-7,8-dioxa[6]helicenes is reported. Determination of the X-ray structure of (cis)-7a,14c-dihydro-3,12-dibromo-7,8-dioxa[6]helicenes, confirms the cis conformation of the 7a,14c hydrogens and a chiral geometry, which was also elucidated by computational methods, which also adressed the pyroelectric properties allowed by the space group symmetery. Deuteration of the sterically crowded 1,14 positions of 7,8-Dioxa[6]helicene influenced the crystal structure of in a subtle way, by not allowing the characteristic “superstructure” of the undeuterated compound.

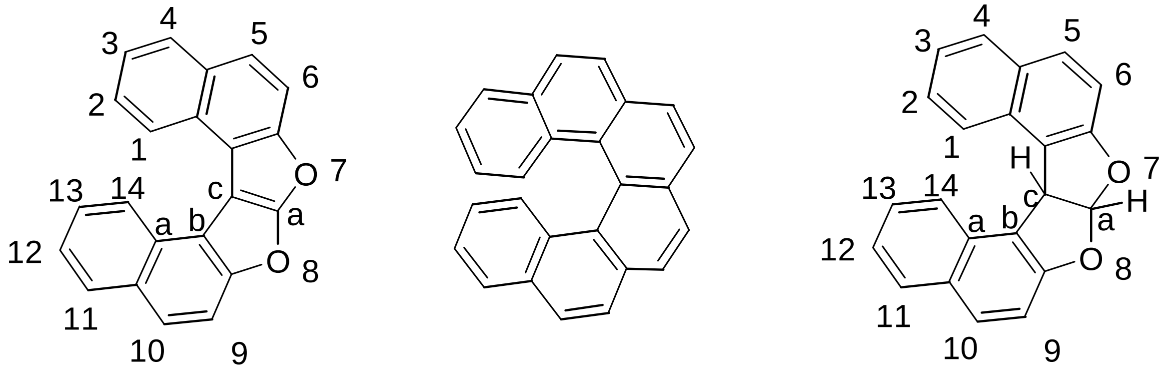
Introduction:

7,8-Dioxa[6]helicene **1**[2] is a six ring heterohelicene and structural models indicate that the presence of the two furane rings gives rise to a low isomerisation barrier between two helical enantiomers relative to the parent benzeniod [6]helicene **2**. We have prepared compound **1** and reported the rather complex crystal structure[3]. Indeed we found marginal helicity of compound **1** as indicated by a low inner pitch[4] of about 0.13 nM for individual enantiomers in the solid state structure, and in accordance with this finding we were unable to isolate the enantiomers due to rapid interconversion in solution. The sulfur analogue of compound **1**, 7,8-Dithia[6]helicene, had previously been prepared by a completely different route, but no structural information was given[5].

Compound **1** was obtained by oxidation of 7a,14c-dihydro-7,8-dioxa[6]helicene **3** which was prepared by a regioselective double condensation[6] of glyoxal with 2-naphthol under acidic conditions.

The condensation of glyoxal with 2-naphtholes to obtain several derivatives of 7*a*,14c-dihydro-7,8-dioxa[6]helicenes and their precursors under acidic and basic conditions has been thoroughly investigated by T. Kito and co-workers[7,8,9] and previous authors[10].

We have combined their methods with a more reproducible version of the oxidative process found by us and report the synthesis of new 7,8-Dioxa[6]helicenes **1** and 7a,14c-dihydro-7,8-dioxa[6]helicenes **3**.

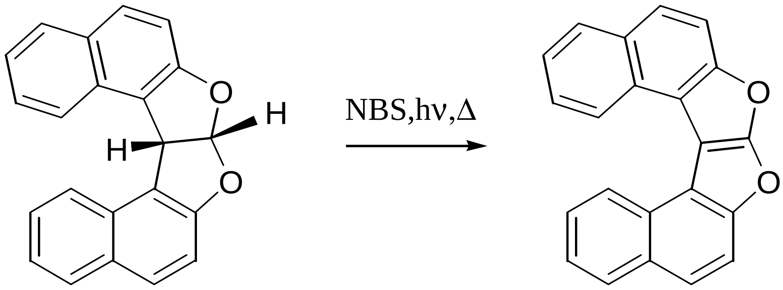


1 **2** **3**

Figure 1. Structure and numbering of **1-3**

We have obtained single crystals of several materials and solved their structure. Also we prepared 1,14 mono-and dideuterated 7,8-Dioxa[6]helicene in order to investigate further the effect of sterical hindrance on the helicity of compound **1**.

An important finding of the structure determinations was that the protons in the bridge positions, ie the 7a,14c positions of 3,12-Dibromo-7a,14c -dihydro-7,8-dioxa[6]helicenes (**3b**) are in a *cis* conformation. We have thus confirmed experimentally the interpretation of NMR spectra and implications from theoretical calculations for such compounds[9,10].



3 **1**

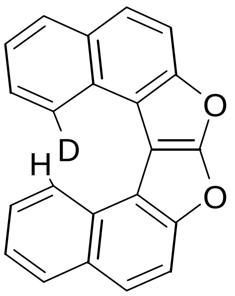
Figure 2. Preparation of **1** from **3**

Results and discussion

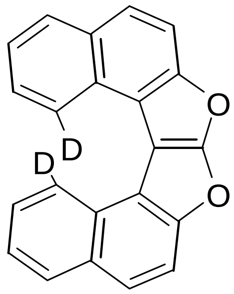
Synthesis

The new 7,8-Dioxa[6]helicenes are obtained by dehydrogenation of 7a,14c-dihydro-7,8-dioxa[6]helicenes (See figure 2). We originally obtained compound **1** in very low yield together with the unexpected compound ,**1d**, by treating compound **3** with DDQ; then obtained reasonable yields by treating compound **3** with NBS in partial sunlight, but finally settled on the more reproducible procedure of using NBS and UV radiation. The reaction most likely proceeds by Wohl-Ziegler radical bromination of the “benzylic” 14c position in compound **3** and derivatives, followed by E_1 elimination of hydrogenbromide. We anticipate an E_1 type elimination because our X ray investigation of compound **3b** has shown that the hydrogens of the 7a and 14c positions are in a cis geometry (see below). Our attempts to dehydrogenate the difluorinated compound **3e** by this method failed either due to lack of solubility or reactivity.

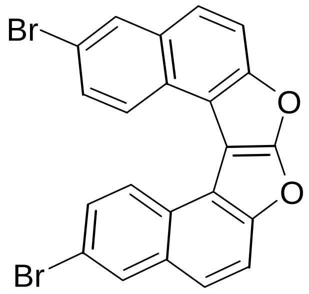
The reason for preparing the deuterated compounds **D-1** and **$D_2$1** and attempting to dehydrogenate the 1,14-di fluoro compound **3e** arose from an interest in investigating the effect on the helicity of **1,** when introducing a small structural perturbation by the substitution of hydrogen with deterium or fluorine atoms in the 1 and 14 positions of the “inner rim” of the helix.



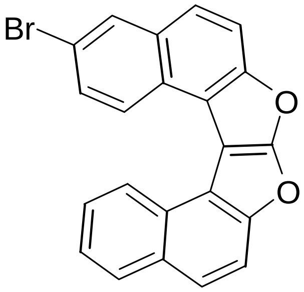
D-1



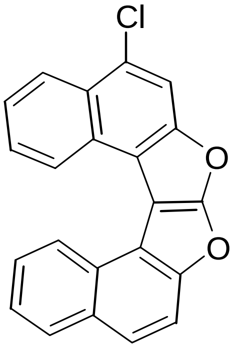
D_2-1



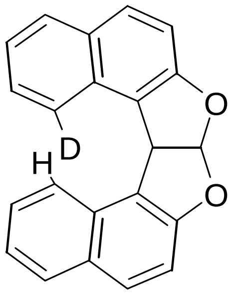
1b



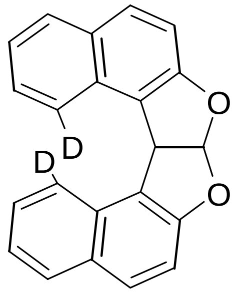
1c



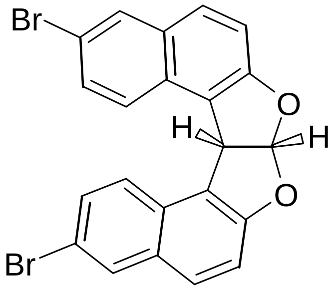
1d



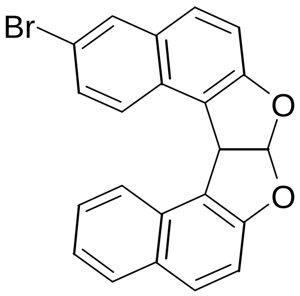
D-3



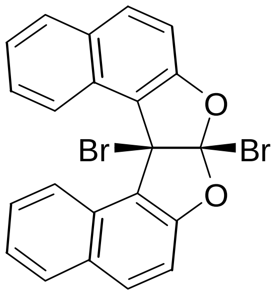
D_2-3



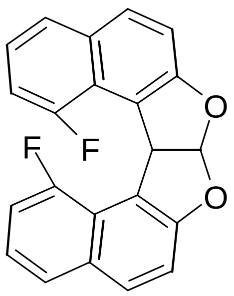
3b



3c



3d

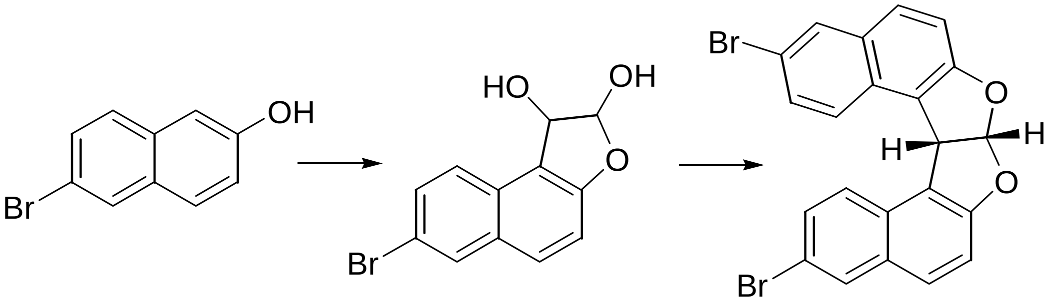


3e

Figure 3. Structures of the 7,8 Di oxa[6]helicenes and dihydro-precursors

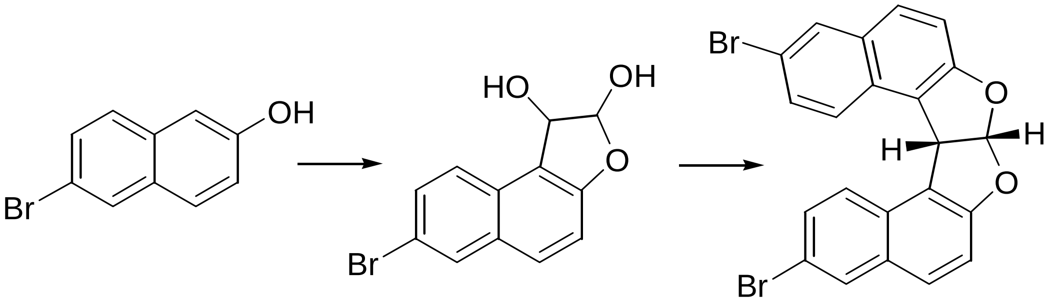
Unexpectedly, after carrying out the UV irradiation of compound **3** for prolonged time with an excess of NBS, the cis 7a,13c dibrominated compound, **3d** was isolated in 21% yield. The cis geometry was established by solving the X-ray structure.

A standard procedure for obtaining symmetrical compounds as compounds **3**,**3b**,**D_2-3** and **3e**, has been to treat the appropriate 2-naphthol with acid in a suitable solvent[6,10]. This procedure did not work when attempting to prepare compound **3b** which was however obtained by combining an initial base catalyzed condensation[9] of glyoxal with 6-bromo-2-naphthol **4** to yield a mixture of 7-Bromo-1,2-dihydronaphtho[2,3-*b*]furan-1,2-diol **5b** and compound **4**. This crude mixture on treatment with acid (See Figure 4) gave the desired compound **3b**.



4 **5b** **3b**

Figure 4. Preparation of **3b**



4 **5b** **3b**

Figure 5. Preparation of **3b**

Similarly when preparing the unsymmetrical compounds **3c** and **D-3** (see Figure 5) we used initial condensation of 2-naphthol with glyoxal to prepare compound **5**[9]. Compound **5** was purified by repeated recrystallizations to deplete remaining 2-naphthol that could contaminate the unsymmetrical compounds. When pure compound **5** was treated with the appropriate 2-naphthols **9** and **4** and acid, the unsymmetrical compounds **3c** and **D-3** were obtained.

8-fluoro-2-naphthol **6**[11] was prepared from 7-methoxy-1-naphtylamin,hydrochloride **10**, and 8-Deutero-2-naphthol **9** was prepared by a series of standard reactions from 7-methoxy-α-tetralone (see Figure 6).

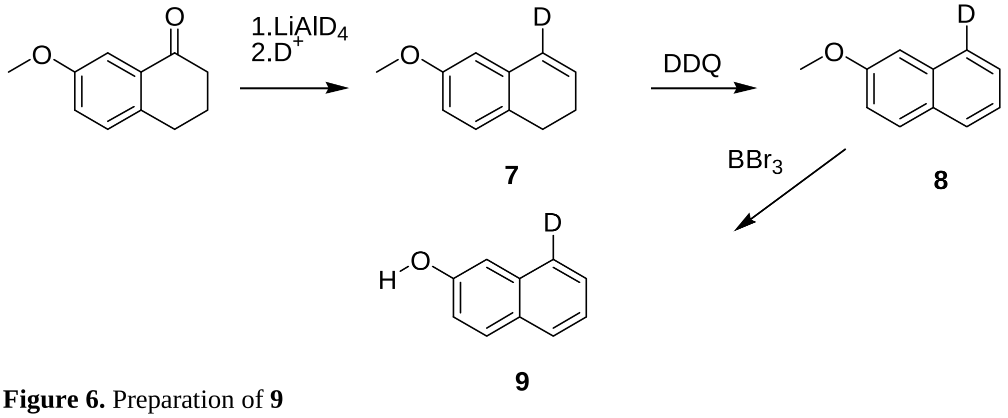


Figure 6. Preparation of **9**

Structural and computational results of *cis*-Dihydro-helicenes. 3

As mentioned in the introductory part the 7a,14c-dihydro-7,8-dioxa[6]helicenes **3** were expected to posses a mirror plane passing through the molecule as supported by NMR in solution and molecular calculations[9,10].As seen in Figure 7 we experimentally confirmed the cis conformation of the hydrogens in the 7a,14c positions of compound **3b**.

On solving the crystal structure of **3b** at temperatures of both 120K and 373K, it however became apparent that the molecule was helical in nature in the solid state at both temperatures as shown in Figure 7. (See also Table 1). We then reinvestigated the calculated structures of **3** and **3b** by computational methods (see experimental section for details). Molecular mechanics optimizations show the structure of the isolated (gas phase) molecule **3** to posses chirality. Contrary to that finding, semi-empirical PM3 calculations show the minimum geometry to posses a mirror plane (C_S -symmetry). *Ab-initio* calculations using local density approximation again find the chiral state to be lowest in energy, but virtually no energy difference exists between the molecule in the chiral conformation and in the C_S-symmetric conformation. Both the PM3 and the *ab-initio* calculations have been performed on structures forced to be either chiral or of C_S-symmetry.

The potential surface for interconversion between the two enatiomers of the chiral conformation of compound **3** was calculated with molecular mechanics. The energy minimum occurs for the two enatiomers of the chiral conformation, whereas the transition state adopts the C_S -symmetric conformation. The interconversion barrier is less than 3 kcal·mol^{-1}.In conclusion, either the molecule does not posses chirality in the gas phase or in solution at reasonable temperatures or the interconversion between the two enantiomers is very fast.

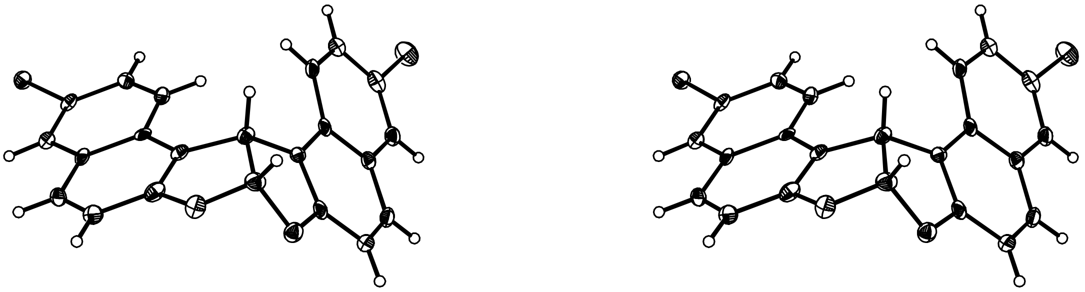


Figure 7

The potential surface for interconvertion between enantiomers for **3b** is similar to that of **3**,but is more relevant for comparison with the actual crystal structure found for compound **3b**. The potential surface is calculated by varying the two dihedral angles defined in Figure 8. The structure is minimized with the two dihedrals fixed to given values. All other bond lengths, bond angles and dihedrals are free.

The minimized energies are plotted against the two dihedrals in Figure 9.

The potential barrier is 2.5 kcal/mol. In the X-ray structure, ϕ_1 and ϕ_2 takes the values 66.6^O and –88.5^O. The fully optimised structure corresponding to the enantiomer minimum shows values of 62.8^O and –96.6^O. When the molecule is optimised in the crystal structure (PNA21) the angles yield 65.5^O and –93.8^O.

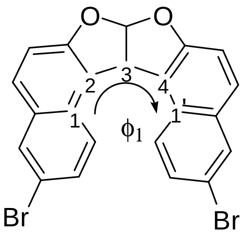


Figure 8

Definition of dihedrals ϕ_1 *and* ϕ_2 *describing the interconversion of the two enantiomers. The dihedral* ϕ_1 *(atom 1-2-3-4) is driven between values of* 65^O *to* 100^O *. The dihedral* ϕ_2 *is obtained through a reflection of* ϕ_1 *(atom 1'-4-3-2) and is driven from* -100^O *to* -65^O

Because the space group of compound **3b** allows pyroelectric behaviour it was of interest to calculate the dipole moment. The dipole moment was calculated for the isolated molecule in the conformation found in the crystal structure. The dipole moment is approximately 2 D. The precise values calculated with LDA and HF are given in Table 2, as well as the component of the dipole vector along the crystal axis. In order to take crystal field effects into account we calculated the electron density in the unit cell using periodic boundary conditions in DMOL[15]. As the program is not capable of handling space group symmetries, the unit cell was reduced in symmetry (P1) and contained four molecules

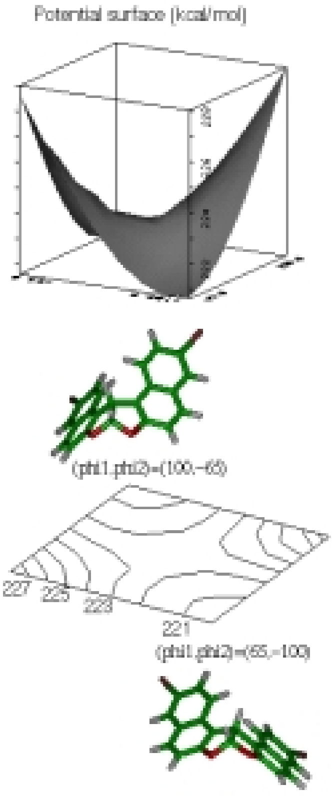


Figure 9 Potential surface for interconversion between enantiomeric forms of ***3b*** *The potential energy is plotted as a function of two dihedral angles, which defines the conformational path between the two enantiomers. The lower curve is a contour map of the potential surface shown in the upper curve. The energy is given in kcal·mol*$^{-1}$ *on both curves. The dihedral angles corresponding to the conformations of the two enantiomeric forms are located in the corners of the contour map. The corresponding conformations are depicted in the figure.*

The dipole moment of interest is the dipole moment corresponding to a unit cell build from full molecules. In order to calculate this dipole moment, the charge was partitioned on the atoms using Mulliken population analysis[16] and the dipole moment was calculated from the atomic charges and positions of the four molecules. A Hirshfeld analysis[17] of the charge density did not yield atomic charges that were transferable from the isolated molecule to the crystal structure. Mulliken charges on the other hand were of course changed when going from the gas phase molecule to the crystal phase molecules, but not dramatically. Table 1 contains the dipole moments calculated from the Mulliken charges for the gas phase molecule and for the unit cell of four molecules. Although the dipole moment for the gas phase molecule calculated from Mulliken charges is overestimated by some twenty percent, the Z-component of the unit cell dipole moment compares roughly with 4 times the Z-components calculated with LDA or HF as expected for four molecules. So we conclude that crystal effects are small and that the value for the Z-component of the dipole moment in the crystal structure is 6 D.

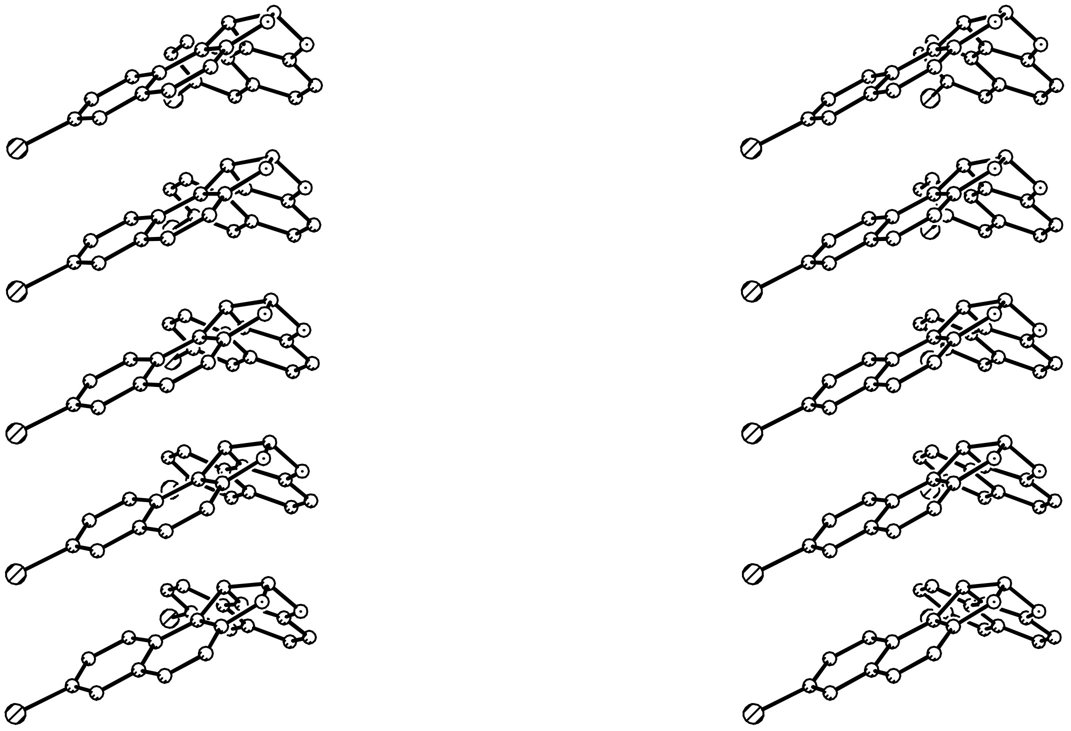


Figure 10

The V-shaped/hat-shaped molecules of compound **3b** pack on top of each other and give rise to stacks in the crystal as shown in figure 10. The stacks all point in the same direction thus giving rise to a polarity in the crystal as permitted by the space group symmetry. This type of crystal packing results in the total vector sum of all molecular dipoles to be non-zero and thus gives rise to a permanent dielectric polarization and subsequent pyroelectric properties (see Figure 11).

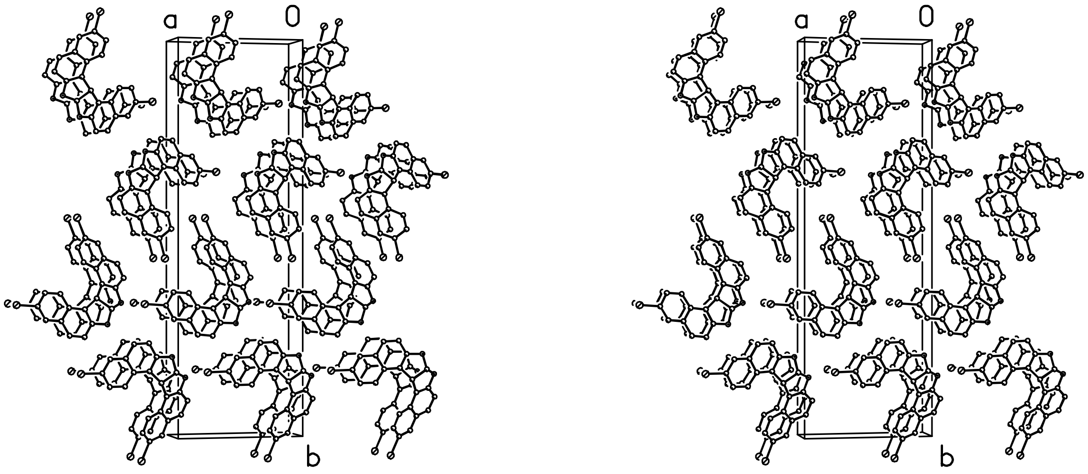


Figure 11

Molecular materials with a general hat-shape like **3b** and with similar packing behaviour (stacking) has been observed and described earlier[17,18]. In one case complete alignment of dipoles gave rise to the maximum possible polarisation[17] whereas in other cases some cancellation or near cancellation of molecular dipoles were observed[18]. In the case of compound **3b** some cancellation is observed and the resulting polarisation in the material is thus not as large as what could have been obtained had all the molecular dipoles been aligned. A calculation of the molecular dipole moment allowed us to estimate the polarization in the material using,

$$P = \frac{Z}{V(T)}\begin{pmatrix}\mu_x\\ \mu_y\\ \mu_z\end{pmatrix} = \frac{Z\mu_z}{V(T)}$$

Where P is the polarization in C m^{-2}, V(T) is the unit cell volume, Z is the number of dipoles in the unit cell and $\boldsymbol{\mu}$ is the dipole moment vector in this crystallographic point group only the component along the polar axis is needed in the equation as the two other components cancel by symmetry. Further dipole enhancement effect of the molecule in the crystal versus the molecule in solution or vacuum is neglected as described in the litterature[19,20]. The calculated molecular dipole moment had a value of about 2D and could be described as a vector in the orthorhombic crystal co-ordinates. Using a simple formula for the polarization as the vectorial sum the polarization could be worked out as 1,2 $\cdot$10 $^{-2}$ C/m^2. Thus 75% lower than the maximum obtainable polarization with this molecule. Unit cell parameters were available for the two temperatures at which the structures were solved and further unit cell parameters were determined for temperatures in-between as shown in Figure 12. Assuming linear thermal expansion in the temperature interval covered in this study the pyroelectric coefficient could be calculated as the temperature derivative of the polarization using the linear expression for the thermal expansion.

$$p_3(T) = \frac{dP(T)}{dT} = \frac{d}{dT}\left(\frac{Z\mu_z}{aT+b}\right) = -\frac{Z\mu_z}{aT^2 + 2bT + \frac{b^2}{a}}$$

The pyroelectric coefficient was calculated to be –1,3 $\cdot 10^{-6}$ C m^{-2} k^{-1} and compares quite well with other organic pyroelectrics. The experimental determination of the pyroelectric coefficient was abandoned due to the extremely thin needle shape morphology of crystals of **3b**. The isomer of **3b**, compound **3d** was also found to exhibit the slight helical conformation as shown in Figure 13. (See also Table 1). The molecules do however not stack in the crystal and crystallize in a centro-symmetric space group. The reason for the lack of stacking is probably the steric demands of the bromine atoms.

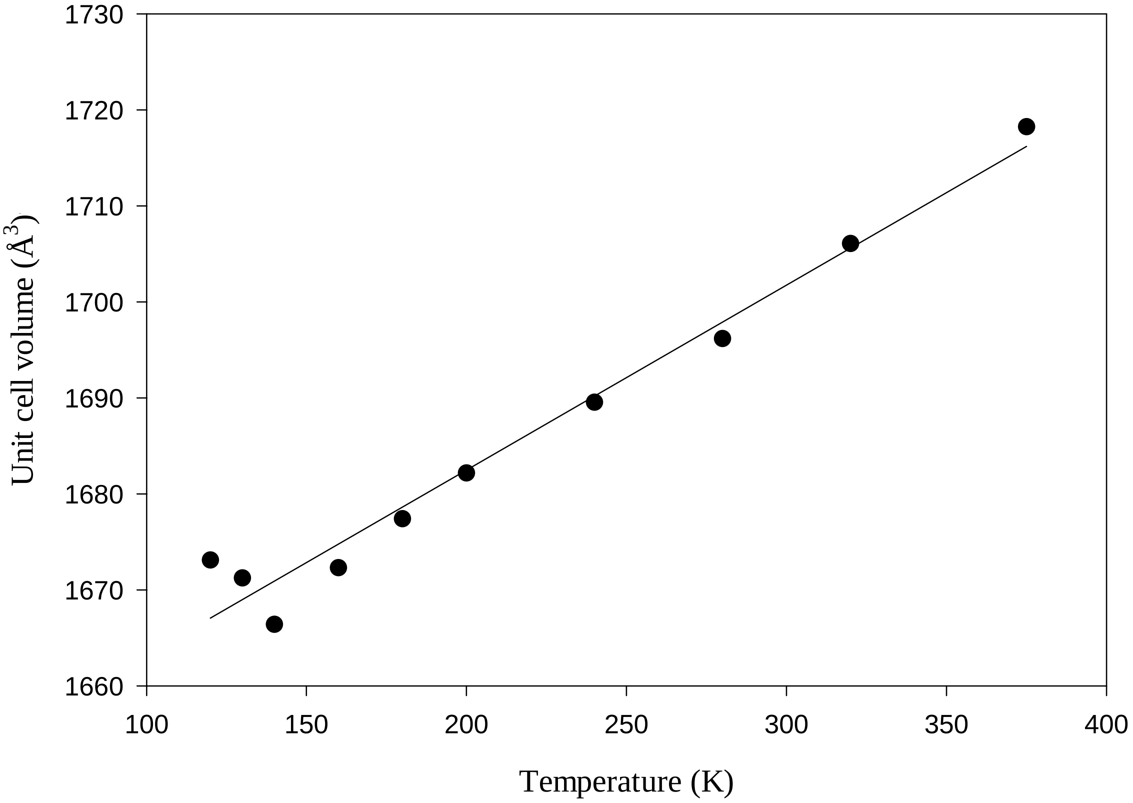


Figure 12 ***The unit cell volume as a function of temperature. The straight line represents linear thermal expansion and can be described as y = aT + b, a = 0.192721 K^{-1}, b = 1643.91.***

Figure 13

Structure of the helicenes 1

The structure of compound **1** was reported previously [3]. Compound 1 stack in homochiral triads of R or S molecules with the triads separated by disordered molecules. The monochlorinated product **1d** was obtained as a by-product from the initial DDQ dehydrogenation of **3** when attempting to prepare **1**. Compound **1d** is the only other helicene of this series that we have succeeded in solving the crystal structure of and the result is quite significant in the discussion of the parent helicene that exhibits very unusual structural properties[3]. While the parent helicene exhibit varying pitch of the helixes in the crystal and a disordered structure with eight different molecules in the asymmetric unit, compound **1d** is perfectly ordered (Figure 14 and Table 3). Both compounds crystallize in non-centro symmetric space groups. While enantiomeric excess and a subsequent permanent dielectric polarization in the parent compound **1** is but a possibility[3], the crystals of **1d** has a definite permanent dielectric polarization and in principle pyroelectric properties.

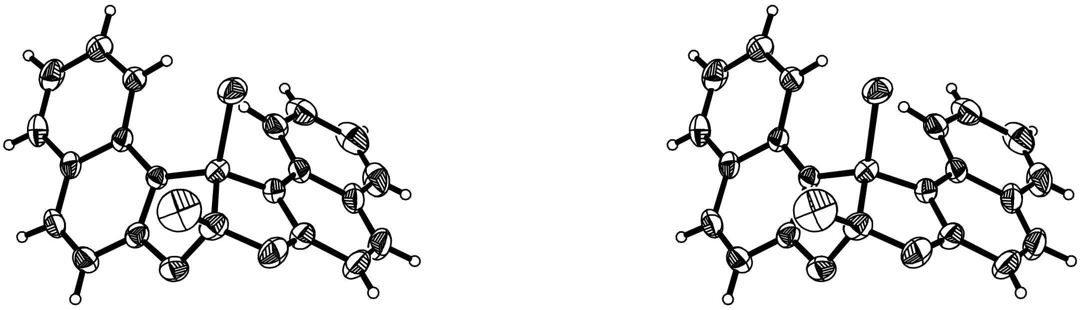


Figure 14

The fact that the helicenes are in dynamic equilibrium in solution and that the structures determined by us show a different degree of helicity in the solid state led us to attempt an investigation of the induction of helicity by substitution in the 1,14 positions. We chose groups exhibiting only subtle differences in steric demand when compared to hydrogen, and prepared the mono- and dideuterated compounds **D-1** and **D$_2$-1.**

When attempting to collect data on **D$_2$-1** a much smaller unit cell than for compound **1** was obtained and also the powder diffractograms of **1** and **D$_2$-1** showed distinct differences as seen in Figure 15. When data were collected in the mentioned smaller unit cell, and the structure was solved it was difficult to obtain a good model. The best model was an extremely disordered model with both *R* and *S* molecules superimposed on each other and placed on a center of symmetry thus suggesting the average of the structure observed for **1**. Attempts were made at both 120K and at 295K with the same structural result being obtained for both temperatures albeit with differences in crystallographic detail (number of observed reflections, cell parameters etc.).

The calculated powder diffractograms based on the “superstructure” of **1** and of the disordered model for **D_2-1** corresponded well with the observed as seen in Figure 13. A comparison of Weissenberg photographs of **1** and **D_2-1** showed that while the superstructure reflections are very strong for parent helicene they were extremely weak for **D_2-1** and only observed after a long exposure time. Their actual presence however indicated that **D_2-1** should exhibit the same superstructural properties as **1** but with a smaller degree of correlation.

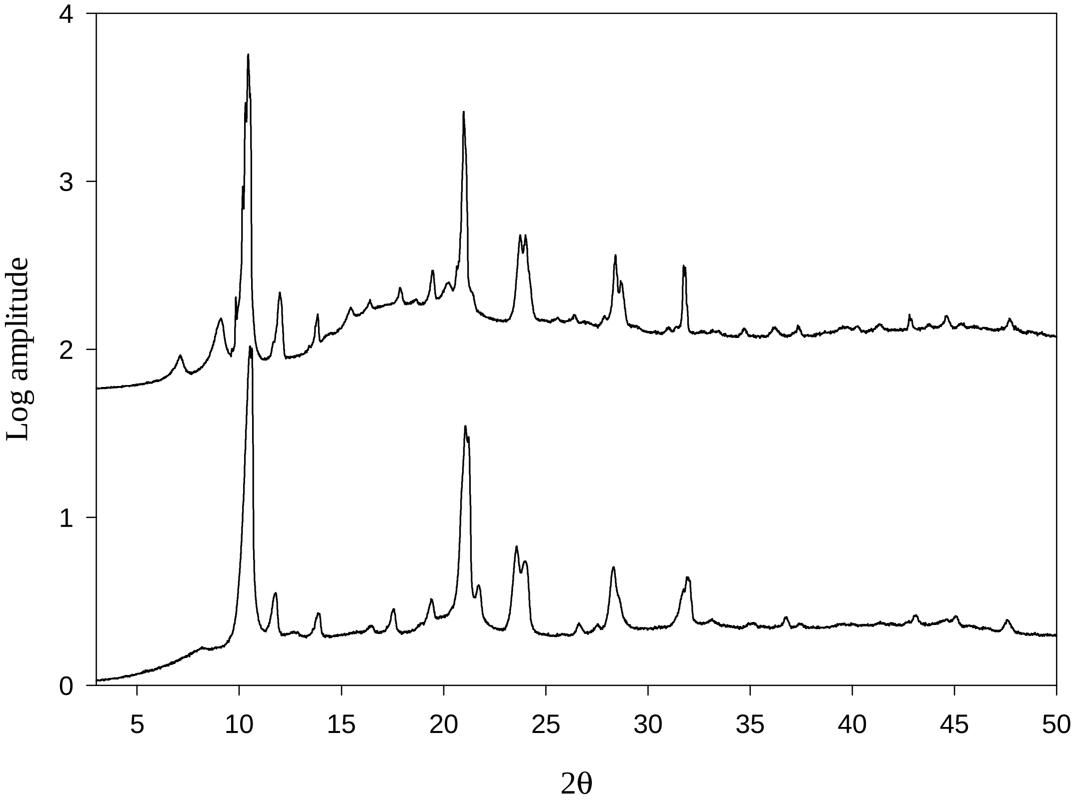


Figure 15 ***Observed powder diffractograms for** 1 **(above) and** D_2-1 **(below, similar to** 1 **obtained from** CCl_4**).***

We finally realized that even compound **1** itself could also be made to exhibit the disordered behavior of the deuterated analogues if recrystalliszed from CCl_4. The appearance of the superstructure of compound **1** is thus ascribed to a thermal annealing effect that is only observed upon slow cooling from toluene or by sublimation in a sealed tube followed by slow cooling, but not by recrystallization from CCl_4. In contrast the deuterated compounds failed to give crystals with developed “superstructure” even under annealing conditions.

Attempts to prepare 1,14-difluoro-7,8-dioxa[6]helicene for further investigation of the steric effect on the helicity of the series failed and only the precursor dihydrohelicene **3e** was obtained.

Conclusions:

The stucture determination and computational results of dihydrohelicenes **3** confirms a cis conformation of the hydrogens in the 7a,14c positions and a frozen chiral conformation of the molecule **3b** in the solid state.

Substitution of hydrogen with deuterium in the sterically hindered 1,14 position of helicene **1** does lead to increased disorder, and the deuterated compounds fail to adapt the subtle “superstructure” of compound **1**.

Finally harsh synthetic conditions when attempting to dehydrogenate compounds **3** to compounds **1** leads to the unexpected halogenated compounds **1d** and **3d**.

Experimental section

Calculational methods:

Potential surface calculation and energy minimization was done using molecular mechanics implemented in the Discover® program with the CFF91 forcefield.[21] Semi-empirical calculations were used to optimize specific molecular geometries for the **3** molecule[21]. The PM3 Hamiltonian[22] was used. *Ab-initio* calculations using the local density approximation (LDA) were used to optimize specific molecular geometries for the **3**molecule and to calculate the dipole moment for the **3b** molecule. The generalized gradient approximation of Perdew and Wang was used[15]. *Ab-initio* calculations using the Hartree-Fock approximation (HF) were used to calculate the dipole moment for the **3b** molecule.[21]

Crystallographic methods

Single crystal data. General crystallographic details can be found in tables 1 and 2. Crystals of **1d**, **3b**, **3d** and **D_2-1** and were mounted on glass capillaries using Epoxy glue. Data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. Absorption corrections were made for compounds**1d**, **3b**, **3d** and **D_2-1** using SADABS[23]. Direct methods for the structure solution and full-matrix least-squares refinements were used for all compounds. For all compounds, hydrogen atoms were included in calculated positions. The Programs used were SMART, SAINT and SHELXTL from Siemens[24,25]. All structures were checked for overlooked symmetry using MISSYM and for voids in PLATON[26].

***Powder data*. Powder diffractograms were collected for compounds** 1 **and** D_2-1 **on a Phillips PW 1820 powder diffractometer.**

Synthesis

7,8-Dioxa[6]helicene 1,

IUPAC name **Naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan**

A 150 mL flask equipped with a Teflon-coated stirring bar, a reflux condenser and a 9W Pen-Ray® UV lamp protected by a quartz tube was charged with 7a,14c-Dihydro-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan, **3**[6] (1.88 g, 6.06 mmol) and 100 mL CCl_4. (The 100 mL CCl_4 was run through Al_2O_3,basic, act. and purged with Ar for 10 min prior to addition of the substrate to deplete the oxygen in the mixture). Heating of the mixture with a heat gun resulted in almost total dissolution of the subtrate. NBS (1.54 g, 8.65 mmol) was added and the mixture was irradiated while bubbling Ar through the mixture and occasionally heating with a heat gun. After 2 to 4 h no more HBr was evolved. The slurry was cooled and the solvent was evaporated in vacuum. The isolated moist solid was treated with a hot mixture of water (80 mL) and toluene (100 mL) under vigorous stirring. Evaporation of the organic phase yielded tan colored crystals which after recrystallization from $CHCl_3$ gave **1**[3] (0.65 g, 35 %), 244-246 °C. ^{1}H-NMR (300 K, $CDCl_3$): 7.60 (t, *J* = 7.5 Hz, 2H), 7.74-7.81 (m, 6H), 8.04 (d, *J* = 8.1 Hz, 2H), 9.09 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR (300 K, $CDCl_3$): 98.61, 113.35, 119.88, 124.73, 125.16, 126.09, 126.51, 127.90, 129.64, 131.75, 152.56, 164.76. MS (GC-MS): 308 (28), 280 (24), 250 (100), 224 (25).

1-Deutero-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan D-1 and

1,14 Dideutero-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan D_2-1

Compounds **D-3** and **D_2-3** were dehydrogenated as described for compound **1** in similar yield. ^{1}H-NMR and MS (GC-MS) had revealed no H/D exchange during the preparation of the deuterated precursors to **D-1** and **D_2-1**. **D-1**: 245-246 °C. ^{1}H-NMR (300 K, $CDCl_3$): 7.60 (t, *J* = 7.5 Hz, 2H), 7.74-7.80 (m, 6H), 8.05 (d, *J* = 8.2 Hz, 2H), 9.08 (d, *J* = 8.4 Hz, 1H). MS (GC-MS): 309 (80), 281

(29), 251 (61), 125 (100). **D_2-1**: 244-246 °C. ^{1}H-NMR (300 K, $CDCl_3$): 7.58 (t, *J* = 7.5 Hz, 2H), 7.74-7.79 (m, 6 H), 8.04 (d, *J* = 8.2 Hz, 2H). MS (GC-MS): 310 (100), 282 (28), 252 (65), 126 (70).

3,12-Dibromo-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan 1b.

Compound **3b** (2.24 g, 4.78 mmol) was suspended in CCl_4 (80 mL), NBS (1.12 g, 6.30 mmol) and irradiated for 5 h. The mixture was evaporated to dryness and stirred with a hot mixture of water (100 mL) and toluene (100 mL). The phases were separated, and the aqueous phase was extracted with another portion of hot toluene (100 mL). The combined organic phases where washed with hot water (50 mL) and evaporated to dryness. After recrystallization from $CHCl_3$ (*ca.* 600 mL) compound **1b** was obtained as long, thin, white needles; (0.47 g, 21 %), 260-264 °C subl.;. ^{1}H-NMR (348 K, C_6D_6): 7.34 (d, *J* = 9.1 Hzm 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.73 (dd, *J* = 8.9 Hz, 2.0 Hz, 2H), 8.07 (d, *J* = 2.0 Hz, 2H), 8.73 (d, *J* = 9.0 Hz, 2H). ^{13}C-NMR spectra were not obtained due to solubility problems.MS (GC-MS): 466 (10, diBr pattern), 385 (6), 278 (17), 250 (60), 125 (100).

3-Bromo-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan 1c.

Compound **1c** was obtained as described for **1b** from **3c** (1.91 g, 4.91 mmol) in CCl_4 (80 mL) and NBS (1.10 g, 6.20 mmol). The crude product was recrystallized from toluene (0.50 g, 26 %). Short, white, thin needles; 234-235 °C. ^{1}H-NMR (313 K, $CDCl_3$): 7.58 (br t, *J* = 7.5 Hz, 1H), 7.69-7.82 (m, 6H), 8.03 (br d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 1.9 Hz, 1H), 8.88-8.93 (2x d, *J* = 9.0 Hz, *J* = 8.3 Hz, 2H). MS (GC-MS): 388 + 386 (11), 250 (43), 125 (100).

5-Chloro-naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan 1d .

Compound **1d** was obtained in very low yield by boiling equimolar amounts of compound **3** and DDQ in 1,2 dichlorobenzene for 48 h. The product obtained was a mixture of compounds **1** and **1d** . Preparative HPLC on reverse phase nucleosil (C18, 5μ) gave a very low yield (1-2 %) of **1d** ., whose structure was finally determined by solving the crystal structure. ^{1}H-NMR (313 K, $CDCl_3$) 7.1 (s, 1H), 7.61 (t, *J* = 8.4 Hz, 1H), 7.68-7.86 (m, 5H), 7.94 (s,1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 9.00 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H).

1-Deutero-7a,14c- dihydronaphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan D-3

Pure compound **5**[9] (recrystallized from $CHCl_3$) (1.80 g, 8.17 mmol) and 8-D-2-naphthol **8** (1.00 g, 6.89 mmol) were dissolved in DME (15 mL). Methanesulfonic acid (4 mL) was added to the solution during 30 min. After stirring for additional 1h water was added (40 mL) and the mixture was filtered. The crystals obtained where thoroughly washed with water and MeOH yielding white crystals of **D-3** (1.52 g, 71 %). ^{1}H-NMR (300 K, CD_2Cl_2): 5.61 (d, *J* = 6.0 Hz, 1H), 7.12 (d, *J* = 6.0 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.50-7.56 (m, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.83 (dd, *J* = 8.3 Hz *J* = 1.1 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 1H) MS (GC-MS): 311 (100), 282 (53), 253 (32), 126 (34).

*1,14-Dideutero-7a,14c- Dihydronaphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan D_2-3*

D_2-3 was prepared from pure 8-D-2-naphthol 9 (no 8-H-2-naphthol had been detected by GC-MS) according to literature procedures for the preparation of 3 from 2-naphthol[6]. The yield after recrystallization from acetone was 56 %. ^{1}H-NMR (300 K, CD_2Cl_2): 5.67 (d, J = 6.0 Hz, 1H), 7.17 (d, J = 6.0 Hz, 1H), 7.27 (d, J = 8.8 Hz, 2H), 7.36-7.42 (m, 2H), 7.58 (d, J = 6.4 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.88 (dd, J = 8.2 Hz J = 1.2 Hz, 2H). MS (GC-MS): 312 (100), 283 (48), 254 (29), 127(48).

Cis-7a,14c-dihydro-3,12-dibromo -naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan, 3b and intermediate **7-Bromo-1,2 dihydronaphtho[2,3-*b*]furan-1,2-diol 5b**

A 250 mL round-bottom flask was fitted with a Teflon coated stirring bar and charged with KOH (2.69 g, 0.048 mol) dissolved in water (100 mL). After purging the mixture with Ar for 15 min. 6-bromo-2-naphthol **4** (10.48 g, 0.047 mol) was dissolved by heating the flask under vigorous stirring and the solution was transferred to a dropping funnel.

Another 250 mL round-bottom flask was fitted with a Teflon coated stirring bar and 40 % aqueous glyoxal solution (31 mL). The naphtholate solution was added dropwise during 45 min under vigorous stirring and the mixture left overnight. The mixture was filtered and the collected light tan crystals where washed thoroughly with water. Some toluene was added and evaporation of toluene and water by using a rotary evaporator yielded a *ca.* 1:1 mixture containing only 6-bromo-2-naphthol **4** and 7-Bromo-1,2-dihydronaphtho[2,3-*b*]furan-1,2-diol **5b** (11.08 g). The ratio was estimated *via* the GC-MS total ion chromatogram.

A 250 mL round-bottom flask was equipped with a Teflon coated stirring bar. The mixture of from above was dissolved in DME (200 mL) and conc. H_2SO_4 acid (15 mL) was added dropwise under vigorous stirring causing white needles to precipitate from the solution. The mixture was left overnight.

The mixture was filtered, and the collected white needles where thoroughly washed with water, methanol and ether and dried in a vacuum oven yielding cis-7a,14c-dihydro-3,12-dibromo - naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan **3b** (6.44 g, 59 %) as white needles showing little solubility in common organic solvents and sublimation on heating. ^{1}H-NMR (372 K, DMSO-*d*6): 5.94 (d, *J* = 5.1 Hz, 1H), 7.32-7.36 (m, 3H), 7.68 (dd, *J* = 9.1, 1.6 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 8.16 (d, 1.6 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H). Recording of ^{13}C-NMR spectra not possible due to insolubility in common NMR-solvents. MS (GC-MS): 468 (13, diBr pattern), 439 (3), 359 (6), 279 (18), 250 (53), 139 (92), 125 (100).

3-Bromo-7a,14c-dihydronaphtho[2,1-*b*]naphtho[1’,2’:4,5]furo[3,2-*d*]furan

3c

To a solution of compound **5**[9] (4,79 g, 0,0217 mol) and **4** (4,81 g, 0,0216 mol) in DCM (200 mL) was added 8 mL borontriflouride etherate at room temperature under Ar. After stirring for 30 min, methanol was added (20 mL) and the solution was heated to reflux temperature. The mixture was filtered while hot and the filtrate placed in a freezer to precipitate **3b**. The crystals were filtered and washed with cold DCM. Yield 4,40 g (52 %); 236-240 °C . ^{1}H-NMR (300 K, CD_2Cl_2): 5.49 (d, *J* = 5.6 Hz, 1H), 7.02 (d, *J* = 5.4 Hz, 1H), 7.11-7.17 (m, 2H), 7.23-7.29 (m, 1H), 7.42-7.60 (m, 3H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.89 (br s, 1H), 8.08-8.13 (m, 2H). MS (GC-MS): 388 (11, mono Br pattern), 252 (25), 139 (100)

1,14-Difluoro-7a,14c-dihydronaphtho[2,1-*b*]naphtho[1’,2’:4,5]furo[3,2-*d*]furan

3e

To a solution of **6**[11] (1.41 g, 8,70 mol) and aqueous glyoxal 40% (0.50 mL, 4.36 mmol) in acetic acid(21 mL) was added conc. sulfuric acid (2.8 mL) during 25 min. The solution was stirred at room temperature for an additional 35 min and diluted to a total volume of 100 mL with water to complete precipitation. The mixture was filtered, and the crystals were thoroughly washed with 2M NaOH(aq), H_2O and methanol and dried. (0.70 g, 47 %) off-white crystals. 196-200 °C. ^{1}H-NMR (300 K, CD_2Cl_2): 5.87 (d, *J* = 5.3 Hz, 1H), 7.00 (d, *J* = 5.2 Hz, 1H), 7.03-7.13 (m, 2H), 7.20-7.28 (m, 4H), 7.58 (d, *J* = 7.8, 2H), 7.77 (d, *J* = 8.8 Hz, 2H). ^{13}C-NMR (300 K, CD_2Cl_2): (H, C

HETCORE) 52.87, 111.50 (d, J = 10 Hz), 113.45, 116.09, 122.86, 123.54 (d, J = 4 Hz), 124.92, 131.08, 132.75 (d, J = 3 Hz), 157.56, (156.43 + 160.79) (d, J = 275 Hz). MS (GC-MS): 346 (100), 317 (65), 288 (30).

7a,14c- Dibromonaphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan 3d

Carrying out the dehydrogenation of compound **3** for prolonged time (approx. 5 h) and with a 50 % molar excess of NBS, yielded the dibrominated compound, **3d**, in 21 % yield after recrystallization from $CHCl_3$. Compound **3d** has a GC-MS spectrum identical to compound **1** but was finally identified as compound **3d** by solving the X-ray structure. 190-195 °C subl., decomp. ^{1}H-NMR (300 K, $CDCl_3$): 7.24 (d, J = 8.9 Hz, 2H), 7.47 (t, s.o., 2H), 7.68 (t, s.o., 2H), 7.88 (d, J = 8.6 Hz, 4H), 9.02 (d, J = 8.6 Hz, 2H).

8-D-5,6-dihydro-2-methoxynaphthalen 7

To a solution of $LiAlD_4$ (1.58 g, 0.038 mol) in dry ether (100 mL) was added a solution of 7-methoxy-α-tetralone (16.52 g, 0.094 mol) in dry ether (100 mL) slowly to maintain gentle reflux. After stirring for 3h, D_2O (8 mL) was added dropwise (caution!) followed a mixture of D_2SO_4 and D_2O (4 + 8 mL) to dissolve salts formed. The mixture was separated and the aqueous phase was extracted with ether. The combined organic phases where washed with D_2O and evaporated to dryness using a rotary evaporator. This crude alcohol was dissolved in dry toluene (300 mL) and added a few crystals of *p*-toluenesulfonic acid. A Dean-Stark apparatus was mounted on the flask and by refluxing the mixture 1.7 mL of D_2O was separated. After cooling to room temperature the toluene phase was washed with D_2O (10 mL) and evaporated to dryness yielding **7**[12] (14.84 g, near quantitative yield). The crude product was used directly in the next step. ^{1}H-NMR (300 K, $CDCl_3$): 2.30 (m, 2H), 2.72 (t, J = 8.1 Hz, 2H), 3.77 (s, 3H), 6.02 (t, J = 3.92, 1H), 6.59 (d, J = 2.5 Hz, 1H), 6.65 (dd, J = 8.1 Hz J = 2.6 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H). MS (GC-MS): 161 (100), 145 (48), 130 (36), 116 (59).

8-D-2-methoxy-naphthalene 8

To a solution of compound **7** (9.31 g, 0.058 mol) in benzene (200 mL) at room temperature was added DDQ (13.15 g, 0.058 mol) in small portions. The mixture was stirred for 1.5 h and filtered. The benzene solution was treated with a 1M NaOH aqueous solution of 0.6 M $Na_2S_2O_4$ until the organic phase no longer was dark. The mixture was separated and the organic phase washed with brine, dried over $MgSO_4$ and evaporated to dryness using a rotary evaporator. This yielded compound **8**[12] (9.17 g, 99.7 %) as tan colored crystals. ^1H-NMR (300 K, $CDCl_3$): 3.93 (s, 3H), 7.13-7.17 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.42-7.45 (m, 1H), 7.72-7.78 (m, 2H). MS (GC-MS): 159 (70), 129 (12), 116 (100) *no peak at m/z = 158 corresponding to 2-methoxynaphthalene was detected*.

8-D-2-naphthol 9

Compound **8** was demethylated with BBr_3 in CH_2Cl_2 according to literature procedures to give compound **9**[12] (80 %) after recrystallization from H_2O. ^1H-NMR (300 K, $CDCl_3$): 5.1 (br, s, approx. 1H), 7.07-7.15 (m, 2H), 7.25-7.35 (t s.o., 1H), 7.41-7.44 (d s.o., 1H), 7.73-7.78 (m, 2H). MS (GC-MS): 145 (100) 116 (64), 90 (8) *no peak at m/z = 144 corresponding to 2-naphthol was detected*.

7-methoxy-1-naphthylamin,hydrochloride 10

Compound **10** was prepared by Semmler-Wolff aromatization. 7-methoxy-α-tetralone-oxime[13] (8.22 g, 0.043 mol) was dissolved in a mixture of HOAc (60 mL) and Ac_2O (20 mL) and stirred for 10 min. HCl(g) was bubbled through the solution for 20 min after wich the mixture was refluxed for 5h and evaporated to dryness using a rotary evaporator. The crude dark oil containing mostly 7-methoxy-1-naphtylamineacetamide was refluxed overnight in a mixture of EtOH (90 mL) and conc. hydrochloric acid (25 mL). Most of the EtOH is removed using a rotary evaporator. The crude brown crystals were isolated by filtration and recrystallized from boiling water containing a small amount of HCl. After drying compound **10**[11] was obtained as white crystals (2.31 g, 26 % from the oxime).

References and notes

(1) Also at Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark.

(2) In the text we use the simple names 7,8-Dioxa[6]helicenes and 7a,14c-dihydro-7,8-dioxa[6]helicenes for the compounds of type **1** and **3**. In the experimental section correct IUPAC names are used throughout

(3) Krebs, F.C.; Faldt, A.; Thorup, N.; Bechgaard, K.; *Cryst. Eng. Com.*, submitted.

(4) The pitch corresponds to in the increment of the helix per turn, see: Navaza, J.; Tscoucaris G.; le Bas G.; de Rango C. *Bull. Soc. Chim. Belg.*, **1979**, *88*, 863.

(5) Dopper, J. H.; Oudman, D.; Wynberg, H. *J. Amer. Chem. Soc.* **1973**, 95, 3692.

(6) Dischendorfer O. *Monatsh.*, **1940**, *73*, 45.

(7) Kito, T.; Yoshinaga, K.; Yamaye, M.; Mizobe, H. *J. Org. Chem.* **1991**, *56*, 3336.

(8) Fan, X.; Yamaye, M.; Kosugi, Y.; Okazaki, H.; Mizobe, H.; Yanai., T.; Kito, T. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2001.

(9). Fan, X.; Yanai, T.; Okazaki, H.; Yamaye, M.; Mizobe, H.; Kosugi, Y.; Kito, T. *J. Org. Chem.* **1995**, *60*, 5407.

(10) Coxworth, E. C. M. *Can. J. Chem.* **1967**, *45*, 1777.

(11) Sheikh, Y. M.; Ekwuribe, N.; Dhawan, B.; Witiak, D. T. *J. Org. Chem.* **1982** *47* 4341.

(12) Guidugli, F. H.; Kavka, J.; Garibay, M. E.; Santillan, R. L.; Joseph-Nathan, P. *Org. Mass. Spectrom.*, **1987**, *22*, 479.

(13) Booker-Milburn, K. I.; Dunkin, I. R.; Kelly, F. C.; Khalaf, A. I.; Learmonth, D. A.; Proctor, G. R.; Scopes, D. I. C. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 3261.

(14) Perdew, J.P.; Wang, Y. *Phys Rev* **1992**, *B45*, 13244. Functional keword in DMOL: gga(P91)
(15) Mulliken, R.S. *J. Chem. Phys.* **1955**, *23*, 1833.
(16) Hirshfeld, F.L. *Theor. Chim. Acta B*,**1977**, *44*, 129.

(17) Krebs, F.C.; Larsen, P.S.; Jacobsen, C.S.; Boutton, C. and Thorup, N. *J. Amer. Chem. Soc.* **1997**, 95, 1208

(18) Faldt, A.; Krebs, F.C. and Thorup N. *J. Chem. Soc., Perkin Trans. 1I*, **1997**, 2219.

(19) Spackman, M.A. *Chem. Rev.***1992**, 92, *1769.*

(20) Howard, S.T.; Hursthouse, M.B.; Lehmann, C.W. and Frampton, C.S. *J.Chem. Phys.* **1992**, 97, *5616.*

(21) Computational results obtained using software programs from Molecular Simulations Inc. Molecular mechanics calculations were done with the *Discover*® program, using the CFF91 forcefield. Semi-empirical calculations were done using the *MOPAC* program. *Ab-initio* calculations using the local density approximation were done with the *DMOL*[22] program. *Ab-initio* calculations using the Hartree-Fock approximation were done with the *Turbomole* program. Split-valence basis set (svp) was used with effective core-potentials (ECP). Graphical displays were printed out from the *InsightII*® molecular modeling interface.
(22)Stewart, J.J.P. *J. Comp. Chem.* **1998**, *10*, 221.

(23) Empirical absorption program (SADABS) written by George Sheldrick for the Siemens SMART platform.

(24) Sheldrick, G. M. (1995) *SHELXTL95*. Siemens Analytical X-ray Instruments Inc., Madison Wisconsin, USA.

(25) Siemens (1995). *SMART* and *SAINT*. *Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison Wisconsin, USA.

(26) Spek, A. L. *Acta Cryst*. **1990**, *A46*, C-31.

Bibliographic Data Sheet **Risø-R-1148(EN)**

Title and authors

Synthesis and structure of functional organic molecules: Calix[4]arenes, Trioxatriangulenes and Helicenes, Ph.D. Thesis by André Faldt

ISBN	ISSN
87-550-2627-3, 87-550-2628-1 (Internet)	**0106-2840**

Department or group	Date
Condensed Matter Physics and Chemistry Department	February 2000

Groups own reg. number(s)	Project/contract No(s)

Pages	Tables	Illustrations	References
200	7	78	136

Abstract (max. 2000 characters)

This Ph.D. thesis describes the synthesis and structure of a series of organic and metalorganic molecules. The idea of the project was to combine the supramolecular properties of calix[4]arenes with the catalytic properties of a metallocene. This was attempted by substitution at the *upper rim* of the calix[4]arene with a metallocene. It proved however not possible to combine these two moieties. It was possible to substitute the *upper rim* of calix[4]arene with two fluorenyl moieties and it was found by X-ray crystallography that the formation of a pentachloro zirconate tetrahydrofuran complex was obtained instead of the expected calix[4]arene metallocene. By NMR and MALDI-TOF analysis it was proven that the transition metal tetrahalides are strong enough as Lewis acids to endorse the cleavage of one or more of the propoxy groups present at the *lower rim* of the calix[4]arene. The anionic polymerization of styrene was investigated as a function of addition of crown-ethers and tetrapropoxy-calix[4]arene and it was found the addition of crown-ethers strongly increased the reaction rate in the polymerization. In addition work is presented regarding the synthesis of 2,6,10-tris(*tert*-butyl)trioxatriangulene derivatised at the 12c-position and the synthesis of 7,8-dioxa[6]helicene together with structural discussions originating from the X-ray structures.

Descriptors

Synthesis, calix[4]arenes, metallocenes, structure, X-ray, synchrotron, properties, Ziegler-Natta, atactic, isotactic, syndiotactic, polystyrene, anionic polymerization, tris(tert-butyl)trioxatriangulene, 7,8-dioxa[6]helicene

Available on request from Information Service Department, Risø National Laboratory,
(Afdelingen for Informationsservice, Forskningscenter Risø), P.O.Box 49, DK-4000 Roskilde, Denmark.
Telephone +45 4677 4004, Telefax +45 4677 4013