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Spécialité : Chimie organique

Thème

Study and synthesis of poly 2-8-14-20 tetra(dimethyl),5-11-17-23 tetracarboxy calix[4]arene 25-26-27-28 tetrol, using homogenous catalys (HCl) and heterogenous catalys (saidite H$^+$).

Soutenu le : 21 /09/2020 devant le jury composé de :

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قَدْ خُلِقَ هذا العَالمُ على مَبْدأ التَبادُلْ، فَكُل
امْرَئٍ يُكَافَأُ على كُل ذَرةِ خَيرٍ يَفعلهَا، ويُعَاقبُ
على كُل ذَرةِ شر يَفْعَلهَا
"شمس التبريزي"

شُكرًا لكُل شَخْصٍ قَابَلنَا بِوَجْهٍ بَشُوشْ
وكَلِمةٍ طَيبَةٍ في رِحْلةِ بَحْثِنَا هَذِهْ......

بسم الله الرحمن الرحيم

والصلاة و السلام على أشرف المرسلين

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Dedications

To my very dear **parents;** who have always been there for me, Their unconditional love, support and encouragement have been a great help.

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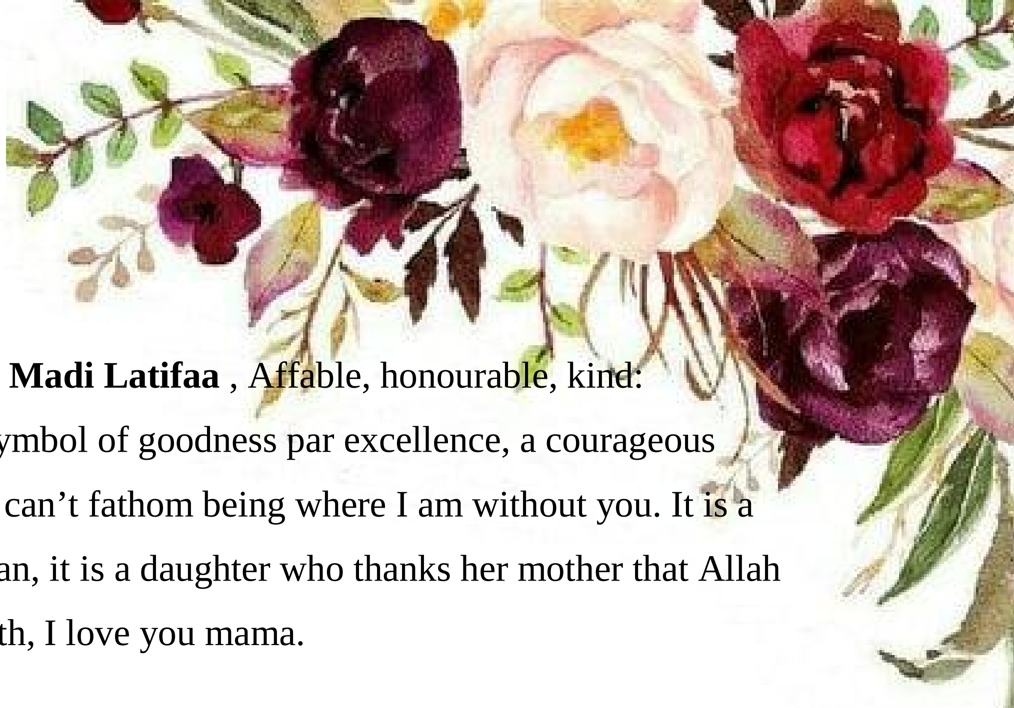
I dedicate this work and give special thanks to my close friend and work partner **keddani ikram** , for all the good times and for her Sharing Hard Times.

To all of them, I offer my thanks, respect and gratitude.

Miss Malek kheira

Dedications



To my dearest mother **Madi Latifaa** , Affable, honourable, kind:
You represent for me the symbol of goodness par excellence, a courageous proud and strong mother, I can't fathom being where I am without you. It is a woman who thanks a woman, it is a daughter who thanks her mother that Allah grants you long life in health, I love you mama.

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ABBREVIATION LIST:

DP: The degree of polymerization
e.g : for example
p: para
tert: tertio
syn: same side
anti: opposite side
endo: reserved for the isomer which has its substituent closest to the heaviest branch.
exo: reserved for the isomer which has its substituent farthest from the heaviest branch.
mp: melting point
h:hour
vivo: phenomenon observed in the organism
ISSC: international social science council
NPs: nanoparticules
f-element :f-element of periodic table
SPCCEs: screen printed calixarene electrodes
IR: infrared (infrared light)
^{1}**H NMR:** proton nuclear magnetic resonance
NMR: Nuclear magnetic resonance
p.p.m: parts per million
p-HBA: para hydroxybenzoic acid
p-HBA/F: poly-para hydroxybenzoic acid/Formaldehyde
p-HBA/A: poly-para hydroxybenzoic acid/Acetone
polymer p-HBA/F: poly-5_11_17_23 tetracarboxy calix[4]arene 25_26_27_28 tetrol/ Formaldehyde
polymer p-HBA/A: poly-2_8_14_20 tetra(dimethyl),5_11_17_23 tetracarboxy calix[4]arene 25_26_27_28 tetro/ Acetone

Macromolecular science is one of the most interesting fields, only in the 1920s H.Stdinger proposed the notion of the macromolecule the economic importance of polymer materials led to an explosion of research in this field, both theoretical and experimental, from the late 1930s onwards. Indeed, macromolecular compounds play a very important role in all areas of life.[1]

Artificial macromolecules, which result from the chemical modification of natural macromolecules, as well as synthetic artificial macromolecules, created from simple molecules, usually called polymers. Polymers are made up of a large number of fundamental units, called monomers. The latter are organic, inorganic artificial or synthetic molecules whose nucleus is essentially made up of a carbon atom (or silicon in the case of silicone polymers)[2]. In case of the macromolecules formed of n phenolic units (n varies from 4 to 20) linked together by methylene bridges in ortho position with respect to the hydroxyl group. They have a hydrophilic cavity at the hydroxyl groups and another hydrophobic cavity between the benzene rings. [3]

Which is called this macromolecule The macrocycles (the Calixarenes) the high chemical and thermal stability of calixarenes allows a wide range of conditions and uses and applications in several fields either in chemistry or biology pharmacology and the most interesting is in the field of the environment and this is the focus of our research The purpose of this study is to highlight and develop new pathways for calixerene.

This work consists of three chapters, the first chapter divided into three main sections:

- The first part is devoted to a presentation of the generalities about polymers (history properties and their reactions).

---

[1] T.W.G.Solomons: organic chemistry; sixth edition, 1996, j. Wiley & sons Inc, P: 855-856

[2] Hamadi Fouzia thèse présenté pour l'obtention du titre magister, spécialité chimie des matériaux O.E.B 2003.

[3] Mohamed Habib Noamane, Synthése et coordination de derives calixaréne de thicalixaréne en conformation 1, 3-alternée, spécialité sciences chimiques, 2013

- In second part we present the calixarenes (history, nomenclature, properties) then the Homogénous and hetérogouns catalysis.
- Final par we present the calixarene in green chemistry.
- The second chapter we talk about analysis techniques and experimental part which included a study of synthesis and synthesis of a oligomer calixaren (results and discussion).

I. POLYMERES

I.1 Historic:

Polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of plastics, rubber, adhesives, fibers coatings.[1]

Polymeres have existed in natural from life began and those as DNA; RNA proteins and polysaccharides; play crucial roles in plant and animal life[2].

Only much later did polymer science come to academic life, Perhaps because of its origins polymer science tends to be more inter disciplinary than most sciences combining chemistry chemical engineering, materials and other fields as well. They are all around us in everyday us in rubber, in plastics, in resins and in adhesives and adhesive tapes[3].

Some of the synthetic polymers were actually discovered during the nineteenth century, but it was not until the late “1930s” that the manufacture and use of such materials really began in earnest. There were several reasons:

The first one was the need in the inter-war years to find replacements for natural materials such as rubber, which were in short supply.

The second reason was that there was by then an understanding of the nature of these materials[4] .

In next " Table I. 1 " we have selected a few important dates that have marked the progress of an area in many of them corresponding to the discovery of new materials followed by their development.

[1, 3] L .H.sperling . introduction to physical science .wiley. interscience;2005 ;page 1

[2] R . J . yong . p .A .lovell , Intrtoduction to polymer , 2and Ed ; 2000 , page 9.

[4] Bower.D.I-An introduction to polymer physics-CUP;2002; page 2;3

Table I. 1: The most important stations in the history of the polymer[5]

1838	A. PAYEN succeeded in extracting from wood a compound of formula ($C_6H_{10}O_5$) in which it gives the name cellulose.
1844	C. GOODYEAR develops the vulcanization of natural rubber.
1846	C. SCHONBEIN obtains nitrocellulose, the first "artificial" polymer by action of a sulfo-nutric mixture on cellulose.
1866	M.BERTHLOT discovers that "styrene", heated at 200°C for a period of a few hours, turns into a resinous polymer.
1883	H. de CHARDONNET obtains "an artificial silk" by fellage of annitrocellulose-based collodion.
1907	A. HAFMANN produces the first synthetic rubbers by polymerization of conjugated dienes.
1910	L. BAEKELAND develops the first industrial process for the production of conjugated dienes. Of a synthetic polymer, the formophenolic polymers are producedunder the name "Bakelia".
1919	H.Staudurger introduces the notion of macromolecule then realizes the polymerization of many ethylenic monomers. It can be considered as the father of macromolecular science.
1925	T.SVEDBERG proves the existence of macromolecules in measuring their molar mass by ultracentrifugation.
1928	K.MEYER and H.MARK relate the chemical structure to the structure crystallographic polymerization.
1933	E.FAWCETT and R.GIBSON engineers from ICI (United Kingdom) carry out the Radical polymerization of ethylene under high pressure.
1938	W.CAROTHERS (of the Nemours bridge) and his team prepare the first synthetic polyamides known as "nylon".
1942	P.FLORY and M.HUGGINS propose a theory of solutions. Macromoleculars.

---

[5] -J. M. Lehm, « Chimie et physico-chimie des polymères », SNEL S.A France, 2001, p:1- 7.

1943	O.BAYER synthesizes the first polyurethanes.
1947	T.ALFREY and C.PRICE propos R discovers the polymerization of ethylene under low pressure.
1954	G.NATTA obtains and identifies isotactic polypropene.
1955	M.WILLIAMS, R.LANDEL and J.FERRY propose a relationship between time and the environment. chain relaxations and glass transition temperatures.
1956	M.SZWARC establishes the principles of "living" polymerizations from work on the anionic polymerization of styrene.
1957	A.KELLER obtains and characterizes the first single crystals. Macromoleculars.
1959	J.MOORE develops steric exclusion chromatography.
1960	Discovery of thermoplastic elastomers and discovery of the corresponding morphologies.
1974	Development of aromatic polyamides by the Bridge Farm of Nemours.
1980	W.KAMINSKY and H.SINN discover the effect of aluminoxanes, the metallocene-initiated polymerization of olefins.
1982	A team from Du pont de Nemours led by O.WEBSTER discovers the group transfer polymerization of acrylic monomers and gives the time to a multitude of research studies on the control of polymerization of these monomers.
1982	T.OTSU introduces the concept of control of radical polymerizations, this concept will be applied by ERJZZARDO and D.SOLOMON (1985) then by M.GEORGE (1992) to the controlled polymerization of styrene.
1986	D.TOMALLIA carries out the synthesis of the first dendrimers.
1992	D.TIRREL synthesizes the first perfectly iso-molecular polymer by genius engineering.
1994	M.SAWAMOTO and K.MATYJA SZEWESKJ bridge polymerization controlled by atony transfer.
2000	After more than twenty years of work on conductive polymers intrinsic, H.SHIRASKAWA. AJ. HEEGER A.G.MCDIARMID are awarded the Nobel Prize in Chemistry. the theory of copolymerization in chain.

I.2 Introduction:

the term polymeris used to mean a particular class of macromolecules consisting at least to a first approximation, of a set of regularly repeated chemical units (monomer) of the same type or possibly of a very limited number of different types (usually only two), joined end to end or sometimes in more complicated ways to form a chain molecule [6]

The macromolecular structures thus defined have molecular dimension (characterized by their molar masses), much high than those of molecules simple it results for the polymer resulting from the new properties usable

The number of monomer units constituting a polymer chain is called the degree of polymerization (DP); it is directly proportional to the molecular weight of the polymer the assembly within a chain macromolecular of a small number of monomer units is called a sequence and the first terms in the sequence series are designated by diad triad tetrad…[7]

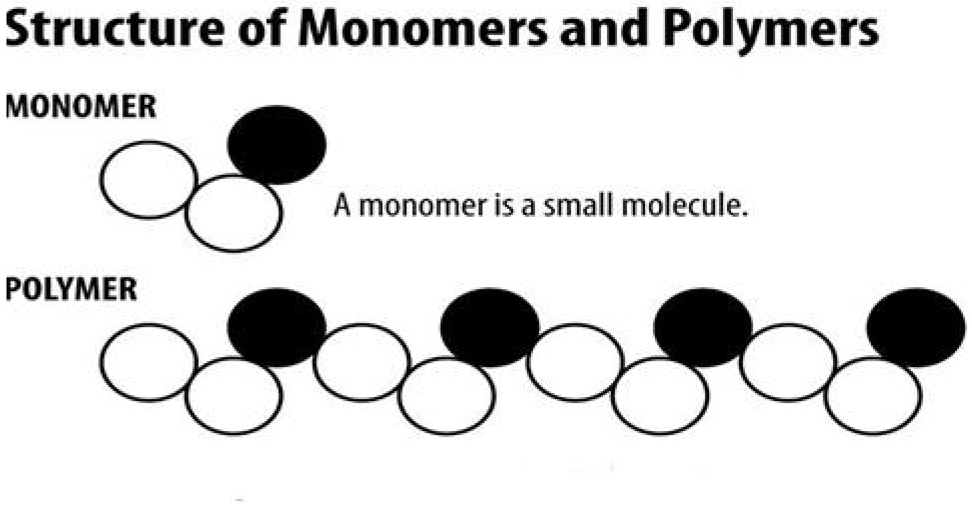

Figure I. 1: structure show the different between monomer and polymer[8]

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[6] -Bower D.I. - An Introduction to Polymer Physics-CUP (2002) ; page 8

[7] -Michel Fontille ; Yves Gnanou ;Chimie et physico-chimie des polymères ; 1er Edition ;2002 page 4

[8] Anonymous : https://www.quora.com/Whats-the-difference-between-a-monomer-and-a-polymer

I.3 Classification Of Polymers: [9]

There are several ways to classify polymers according to the properties retained for to characterize them, we indicate below the most common classifications.

I.3.1 Depending On The Chemical Nature*:*

I.3.1.1 Mineral polymers:

Are made up of chains containing a single body...such as diamond, graphite and phosphorus and sulfur or by chains containing several hetero atoms such as: silicates poly phosphoric acids and chlorides from poly phosphonitriles

I.3.1.2 Organic polymers:

It's the richest class, they're almost the most all commonly used polymers. Organic polymers of are: poly olefins, polyvinyl, polydienes; polyamides, polyesters and poly phenols and poly acrylics.

I.3.1.3 Mixed polymers:

Are endowed with interesting properties including good thermal resistance (300-350 C°).The heteroatom can be either in the main chain or in the side patterns.

I.3.2 According to the chain structure:

I.3.2.1 Linear and one-dimensional polymers:

Chaining in one direction of space.

I.3.2.2 Two-dimensional polymers:

Chain extending in two directions space **EX:** Graphite.

I.3.2.3 Three-dimensional polymers:

It is possible to transform molecules linear molecules into 3D molecules by bridging. These are three-dimensional networks, They represent about 30% of industrial polymers.

---

[9] M.Madkour, « Polymères, synthèse macromoléculaire », Tome1, Office des publications universitaires O.P.U Alger, 1982, page 2- 61

I.3.3 According to their origin:[10]

I.3.3.1 Natural polymers:

Existing in the state in nature as they are very numerous, it is common to subdivide them according to their plant, animal or mineral origin.

I.3.3.2 Artificial (or regenerated) polymers:

Although the basic constituent is of natural origin they are the result of a chemical transformation of the functions carried by the monomer units

EX: "cellulosic derivatives "whose basic molecule is cellulose

I.3.3.3 Synthetic polymers:

The monomer molecules that make it possible to obtain them. Do not exist in nature however it can be noted that the structures made by synthesis are often close to those of natural polymers.

I.3.4 According to thermal behavior:[11]

I.3.4.1 Thermoplastic:

Subjected to a moderate temperature rise, polymers become soft but without changing the chemical bonds.

I.3.4.2 Thermosetting:

High temperatures cause bridging reactions and irreversible cross-linking that lead to rigid three-dimensional networks

I.3.4.3 Thermo elastics:

The current objective is the development of polymers capable of retaining elasticity at moderately elevated temperatures to the thermal limitation, which is the weak point of the current elastic bands, is overcome

---

[10] C.Oudet, « Polymères, structures et propriétés, Introduction », Masson, Paris, 1994, p :1-3.

[11] ه.باين ، هاندركسن .ج ، د كرلم ..هاتموتد "الكيمياء العضوية "دار ماكجيروهيل للنشر , الرياض ،1983

I.3.4.4 Elastomers:[12]

An elastomer is a linear or branched polymer transformed by vulcanization into a network three-dimensional weakly cross-linked infusible and insoluble. elastomers differ from thermosetting materials by their elasticity property rubber i.e the ability to undergo very large reversible deformations under

I.4 Polymerization reaction:

Polymerization reactions are classified according to the properties of the polymers obtained from thermoplastic and thermosetting materials. However, there is a additional classification according to the type of chemical reaction that occurs, namely addition or condensation

I.5 Addition Polymerization (Chain):

In chain growth polymerization, the catalyst that initiates the reaction causes the formation of an active site, to which a molecule of monomer and so on The monomer reacts quickly, always by the same addition to the chain getting longer. The process is interrupted by a termination reaction[13]

I.6 Condensation Polymerization:

Polycondensation occurs by interaction of one or more compounds with removal of a simple body such as water, ammonia ... etc. Important examples of this type of polymerization include nylons (polyamides), poly esters...[14]

---

[12] ,[14] D. C. Miles et J. H. Briston, ' Technologie des polymères ', Dunod, Paris, 1968.

[13] -H. Coria, ' Introduction à la chimie organique ', Inter edition, Paris, 1987.

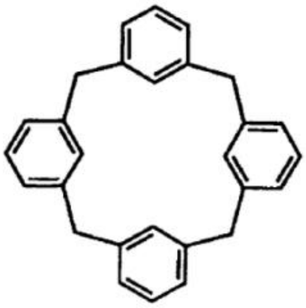
II. CYCLIC POLYMERS (CALIXARENES):

II.1 Introduction:

The world of organic chemistry is populated by several million compounds distributed among hundreds of families. Some of these families have commanded the attention of chemists for many decades and have reached a venerable patrician status. Many others are more recently arrived and have yet to establish their place in th hierarchy of chemical importance. Among the latter is the family of compounds called the calixarenes[15].

Calixarenes, a family of vase-like cyclic macrocycles, have been under development in the research laboratories for just over 50 years, with the first paper on calixarenes having appeared in 1944[16].

Calixarenes acquired their name because of the resemblance of the shape of one of the conformers of the smallest member of their family to a type of Greek vase called a calix crater "**Figure I. 1**" The name was initially chosen to apply specifically to the phenol-derived cyclic oligomers, but it has subsequently taken on a more generic aspect and is now applied to a wide variety of structurally related types of compounds. The calixarenes were first discussed in comprehensive fashion in 1989 in the first volume of Monographs in Supramolecular Chemistry.[15]



[1_4] metacyclophane

Calix crater

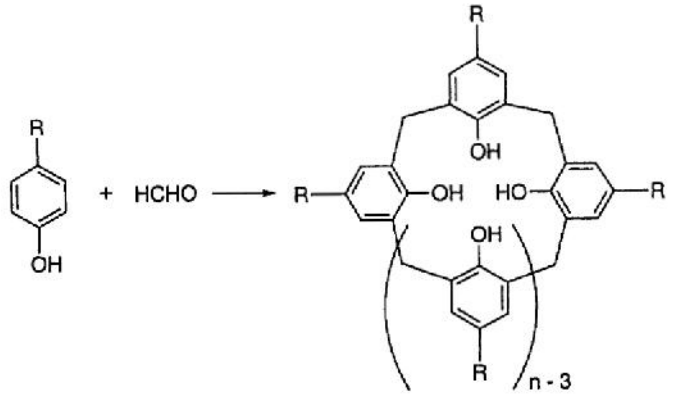
Figure I. 2: [14] Metacyclophane and Clix crater

---

[15] C.David Gutsche .calixarenes revisited. .1998. p1

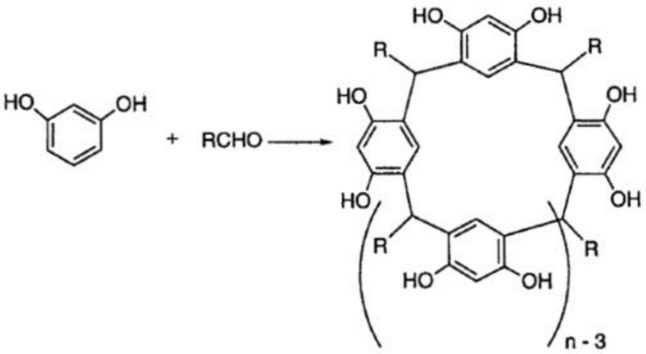
[16] Y.K. Agrawal, S. Kunji and S.K. Menon.analytical applications of calixarenes.vol. 17. No. 2,1998 p69-124

The calixarene family can be subdivided into two major branches, the phenolderived cyclooligomers **(1)** and the resorcinol-derived cyclooligomers **(2),** as shown in the present monograph.[17]



Phenol-derivedCalixarenes

(1)



Resorcinol
derivedCalixarenes

(2)

Figure I. 3: two major branches of clixarenes

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[17] C.David Gutsche .calixarenes revisited. 1998. p2

II.2 Historic:

The path of scientific research is seldom straight, often taking twists and turns quite unexpected at the outset of an odyssey. Such is the case with phenol formaldehyde chemistry, which began over a century ago in the laboratories of Adolph von Baeyer. It has developed in ways that could not have been foreseen by this eminent scientist but which would certainly provide him with amusement and delight were he still alive to enjoy the passing scene of twenty-first century chemistry.[18]

II.2.1 Adolph Von Baeyer:

Adolph Von Baeyer carried out reactions with phenols and aldehydes in 1872[19] Using formaldehyde synthesized as described above, Baeyer showed that it reacts with phenol in a fashion similar to that of the larger aldehydes to produce a resinous material. However, he was unable to isolate pure substances from any of these reactions and, therefore, could not obtain elemental analyses which might have allowed him to propose possible structures. In retrospect we can appreciate how formidable a problem he faced, for even today with our impressive array of analytical techniques the structure of the phenol-formaldehyde product is not known in complete detail. However, Baeyer did manage to provide some structural insights by proposing a dimesitylmethane structure for the more tractable product obtained from mesitylene and formaldehyde. So, even though he was unsuccessful in characterizing the phenol-formaldehyde product, Baeyer had, nevertheless, given birth to phenol-formaldehyde chemistry.[20]

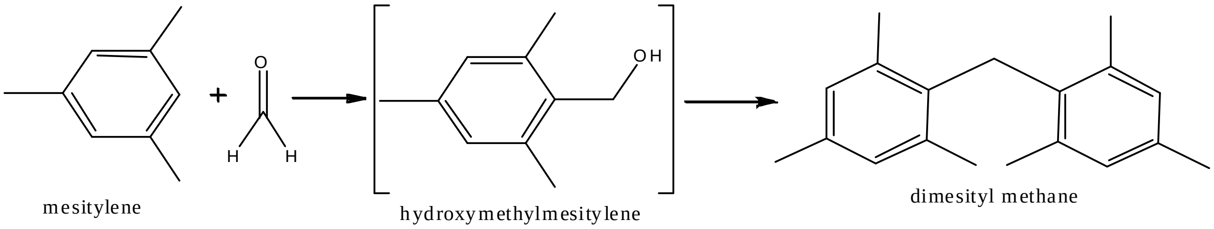

Figure I. 4: structure proposed of the phenol-formaldehyde product

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[18] C. David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p1

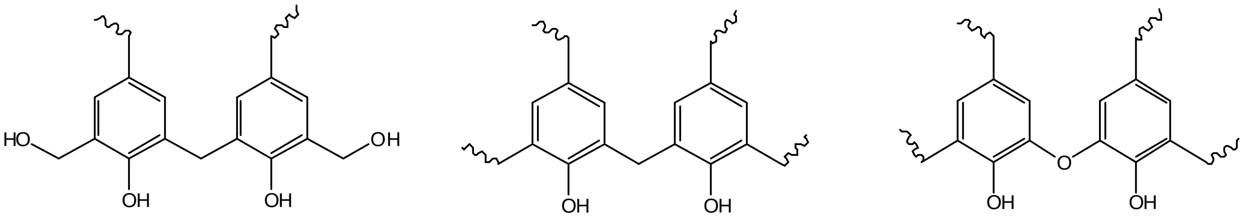
[19] J. Vicens And V.Bohmer. Calixarenes: A Versatile Class Of Macro Cycliccompounds.1st Eddition .1991.P3

[20] C. David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p3

II.2.2 Leo Baekland:

A recent immigrant to the United States from Belgium, discovered that heating Baeyer’s resinous tar turned it into a hard brittle solid. He patented his process in 1908, eponymously named its product “Bakelite”, and went on to establish the first plastics industry in the world. [21]

The progress that has been made and the problems that remain unresolved are recounted in a variety of books and articles. As had already been realized by Baeyer in 1872, however, it is CH_2 and CH_2OCH_2 groups that are the most likely linkages between pairs of aromatic rings in a formaldehyde-phenol condensation product. Thus the dominant structural diaryl moieties in a typical resin are those shown in Plate resoles, novolaks and dibenzyl ethers.[22]



Resoles novalaks dibenzylethers

Figure I. 5: structures of resoles, novalaks, dibenzylethers

II.2.3 Alois Zinke:

In 1942 Alois Zinke and his coworker Erich Ziegler decided to ‘‘simplify’’ the problem by looking not at phenol itself but at p-substituted phenols in the condensation reaction with formaldehyde. Whereas phenol reacts at both the ortho- and para- positions to form a highly cross-linked polymer in which almost all of the phenolic units are attached to three other phenolic residue

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[21] Jacques Vicens.Calixarenes in the Nanoworld.2007 p2

[22] C. David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p5

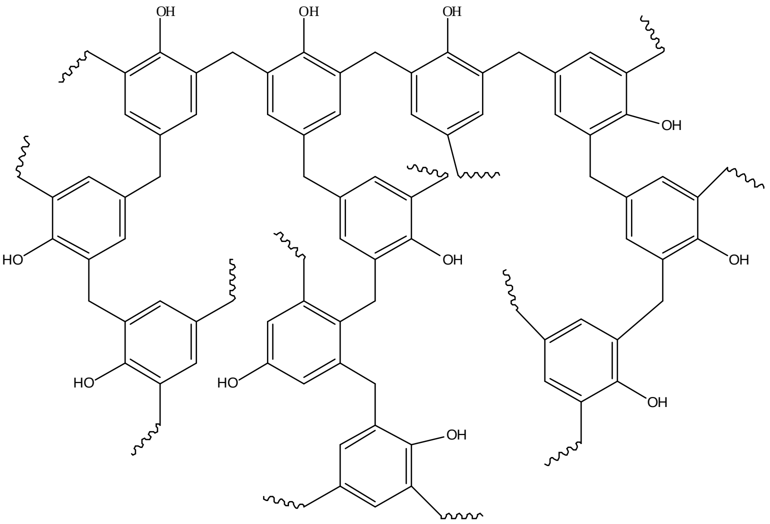

Figure I. 6: phenol reacted at ortho- and para- positions

a para-substituted phenol can react only at the two ortho- positions, thereby reducing the cross-linking possibilities.[23]

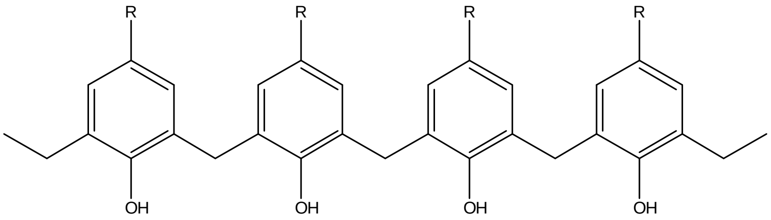

Figure I. 7: p- substituted phenol reacted at the two ortho- positions

II.2.4 Joseph Niederl:

By 1944, however, the idea of a cyclic structure had sprung to the minds of several investigators and was ‘‘in the air’, so to speak Joseph Niederl and his coworker Heinz Vogel. At New York University, for example, had proposed a cyclic tetrameric structure for compounds obtained by the acid-catalyzed treatment

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[23] David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p6

of aldehydes and resorcinol, so it was a propitious time for the Austrian workers to propose the cyclic tetrameric structure for the base-induced product.[24]

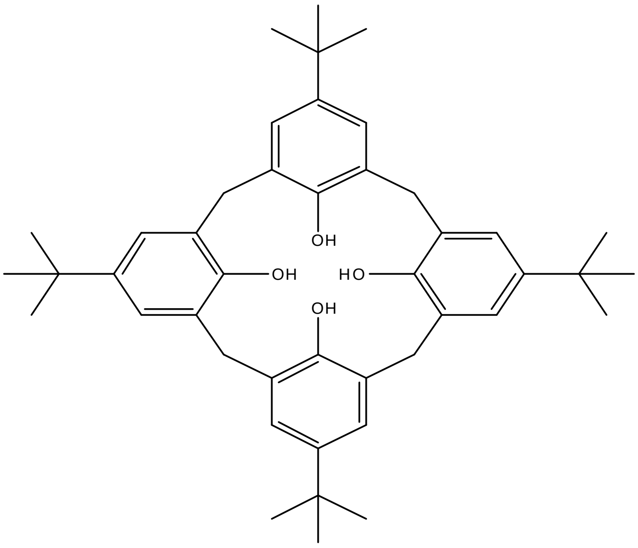

Figure I. 8: structure of cyclic tetrameric

II.2.5 Hayes And Hunter:

A step-wise synthesis of a cyclic tetramer by Hayes and Hunter in 1950s subsequently demonstrated that such a structure was feasible,while Comforth's crystallographic studies subsequently indicated that the compounds produced by Zinke were clearly cyclic compounds (although the assertion that only the cyclic tetramer was produced was not correct)[25]

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[24] David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p7.

[25] Philip Osbome Brown .Synthesis And Characterization Of Calixarene-Based Supramolecular Frameworks.A Thesis Submitted In Partial Fulfillment Of The Requirements For The Degree Of Doctor Of Philosophy.Department Of Chemistry.Carleton University.2006.P .7

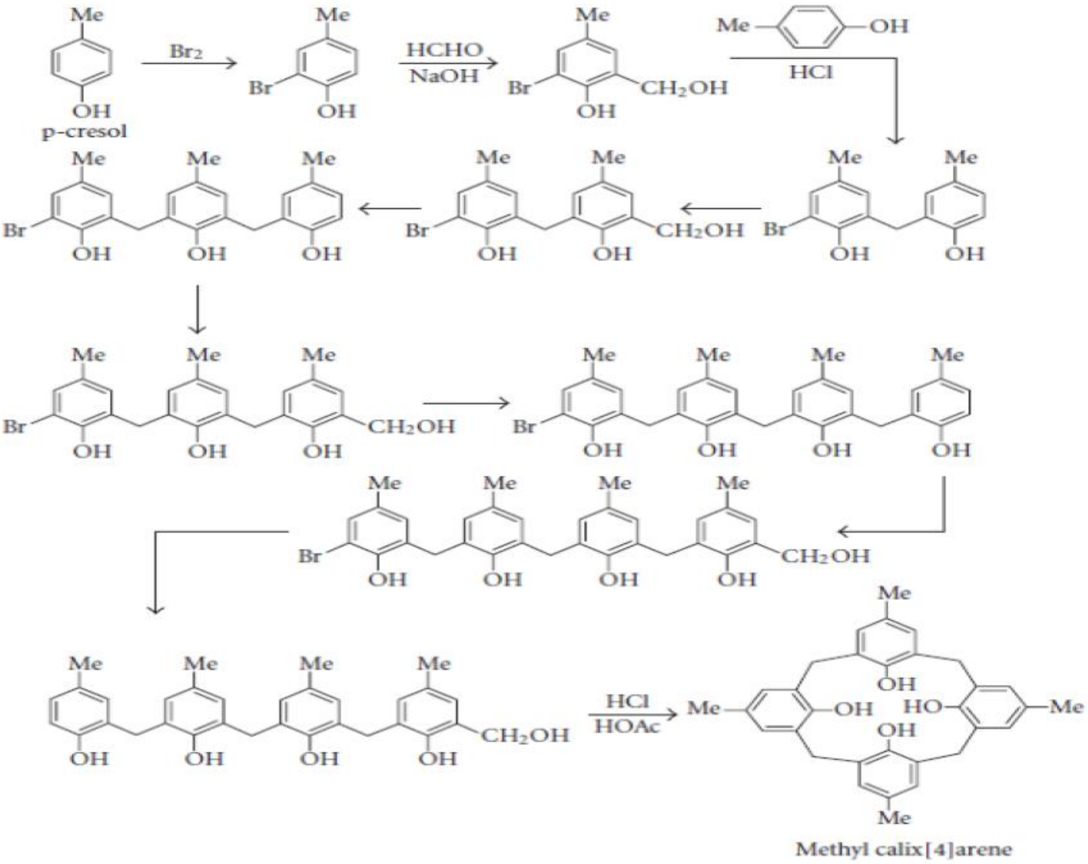

Figure I. 9: Ten-step synthesis of methylcalix[4]arene by Hayes and Hunter.[26]

Hayes and Hunter concluded that their synthesis showed that ‘‘cyclic structures may be produced under suitable environmental conditions in the hardening process of phenol-formaldehyde resins’’, thereby confirming ‘‘that the analogous novolaks which Zinke and his collaborators claimed to have obtained by heating resoles such as 2,6-bis-hydroxymethyl-4-tert-butylphenol are, at least, sterically possible’’.[27]

II.2.6 Gutsche:

In 1970s Gutsche and coworkers reinterpreted the Zinke results and developed methods for synthesizing each of the three major cyclic oligomers comprising the original Zinke mixture in good and reproducible yields. It is the easy single-step accessibility of these materials, for which the name “calixarenes” was coined

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[26] P. Jose and S. Menon.Lower-RimSubstituted Calixarenes and Their Applications.Volume 2007, Article ID 65815 doi:10.1155/2007/65815.2007.p1-16

[27] David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p12

C. Gutsche used the term "calixarenes" with the prefix "calix" referring to the Latin word for vase and the suffix "arene" indicating the presence of the aromatic nuclei of the molecule. His work paved the way for a new era of supramolecular chemistry.

A number of areas now comprise calixarene chemistry including, inter alia cation, anion, and molecule complexation, ion transport phenomena, enzyme model building, and the construction of sensors for a wide variety of applications.[28]

II.3 Nomenclature And Representation:

Gutsche coined the name "calix[4]arenes", which derives from Latin "calix" (Greek xuki^) meaning vase, pointing out the presence of a cup-like structure in these macrocycles when they assume the conformation in which all four aryl groups are oriented in the same direction. This conformation is called *cone* and is usually observed in the solid state.The name was extended to larger macrocyclic compounds. A bracketed number between calix and arene specifies the size of the macrocycle and the name of the p-substituen is added to indicate from which phenol the calixarene is derived. The cyclic tetramer obtained from *p-tert*butylphenol, for example, is named p-tert-butylcalix[4]arene. Since the number of compounds has proliferated during the years, it seemed more appropriate to apply the term "calixarene" to the basic macrocyclic structures devoid of substituents. According to this nomenclature the p-tert-butylcalix[4]arene (A) is named 5,11,17,23-tetra-ten-butylcalix[4]arene-25,26,27,28-tetrol. Authors prefer to use the more systematic name in the experimental part of their papers and the short one in the text. Two major classes of calixarenes are known, the phenol-derived cyclooligomers (B) and the resorcinol-derived cyclooligomes (C) which are also named (generating sometime confusion) resorcinarenes, resorcarenes, resorcin[4]arenes, calixresorc[4]arenes, depending on the personal preference of the authors. Apart from the nomenclature there are two main differences between the two classes:of calixarenes, the first one is related to the synthesis and the second one to the orientation of the OH groups with respect to the macrocyclic ring. In fact, the calix[n]arenes are usually obtained *via* the base-

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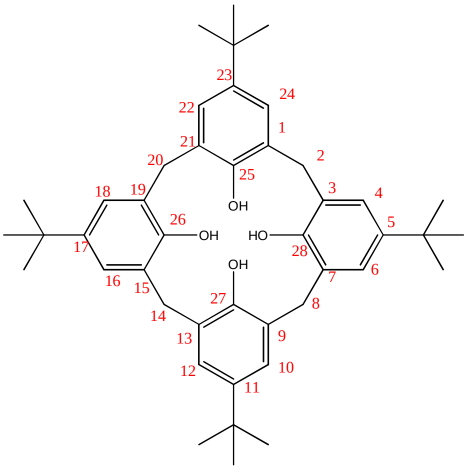
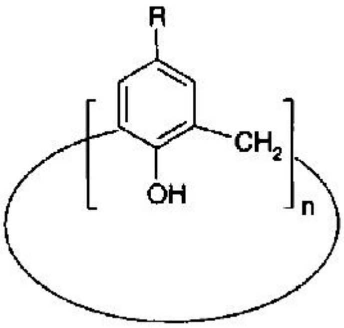
[28] Zouhair Asfari,Volker Bӧhmer,Jack Harrowfield and Jacques Vicens.Calixarenes 2001. .2001. p1

catalysed condensation of p-alkylphenols and formaldehyde and their OH groups are directed towards the interior of the macrocyclic ring *(endo-OH* calixarenes) whereas the calixresorc[4]arenes are prepared through the acid catalysed condensation of resorcinol and aldehydes and are exo-OH calixarenes, since these groups are oriented away from the annulus. *endo-OH* calixarenes also used as receptors or as building blocks are calixarenene-related compounds, the most important being the homooxacalixarenes (D), which can be obtained both by one step and by fragment condensation synthesis. Two regions can be distinguished in calixarenes (E), the phenolic OH groups region and the para position of the aromatic rings, which are called respectively the "lower rim" and the "upper rim" of the calix. In calix[4]arenes, adjacent nuclei have been named "proximal" or (1,2) whereas the opposite ones are in "distal" or "diametrical" (1,3) positions.[29]



(A)



(B)

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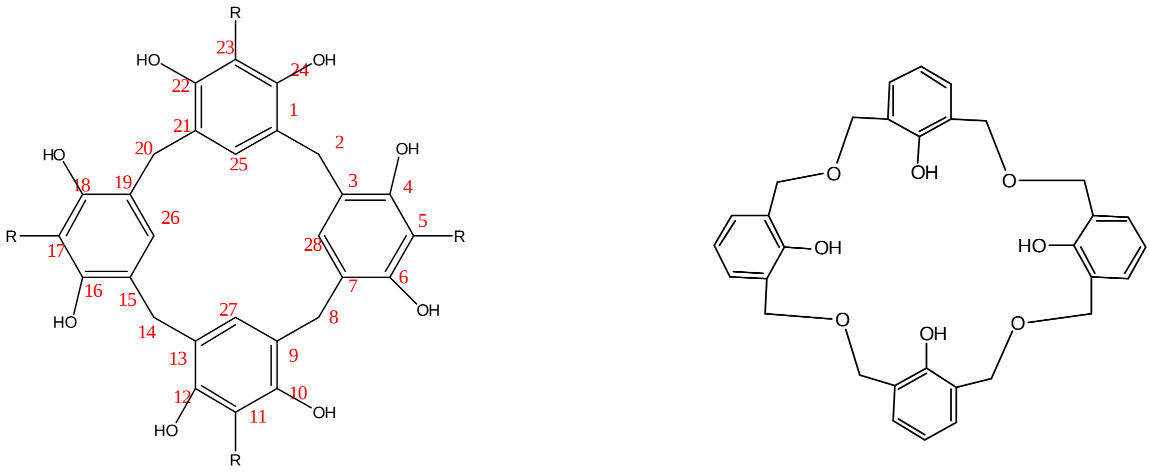
[29] Luigi Mandolini .Rocco Ungaro .Calixarenes In Action. .2000.p3



(C) (D)

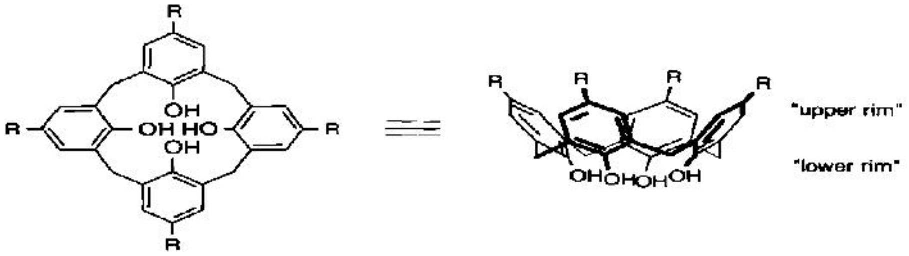


Figure I. 10: different examples of calixarene structures

II.4 Conformational Properties: [30]

The 1H NMR spectra of unmodified calix[4]arenes show a pair of doublets at low temperature and a singlet at high temperature for the bridging methylenes. This behaviour has been interpreted as due to the interconversion between two mirror image conformations “**Figure I.11**”, which is slow (on the NMR time scale) at low temperature and fast at higher temperature. A Nuclear Over hauser Effect investigation has allowed to establish, that the low temperature spectra correspond to the *cone* conformation and that the low field doublet is due to the axial proton H. whereas the high field doublet is attributed to the equatorial proton H.

Tetramethoxy and tetraethoxycalix[4]arenes are also conformationally mobile but the introduction at the lower rim of calix[4]arenes of alkyl group bulkier than ethyl blocks the ring inversion process thus producing compounds with different stereochemistrydepending on the orientation of each aryl group which can project upward ("u") or downward (d) relative to an average plane defined by the methylene bridges. The four different possible conformations (figure1.8) have been named by Gutsche as cone (u,u,u,u), partial cone (u,u,u,d), 1,3-alternate (u,d,u,d) and 1,2-alternate (u,u,d,d).

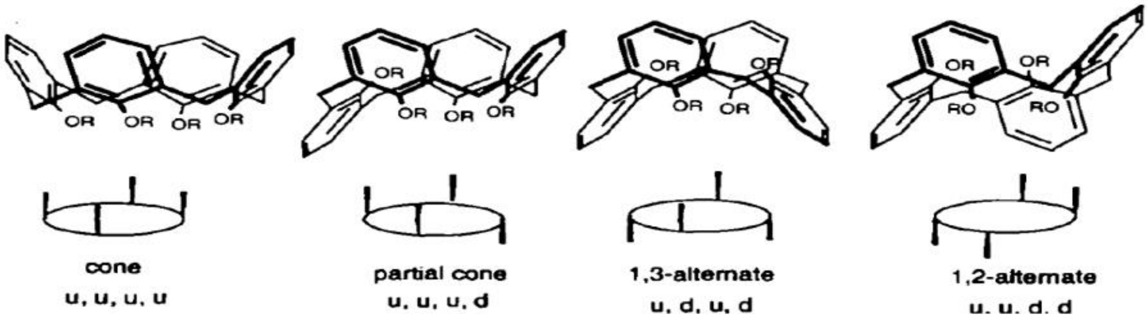


Figure I. 12: Conformations of calix[4]arene derivatives

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[30] Luigi Mandolini .Rocco Ungaro .Calixarenes In Action. .2000.p6

They can be easily identified through their 1H and 13C NMR spectra. Particularly useful are the 1H and 13C NMR patterns of the bridging methylene groups which are different for three out of four conformations “**Figure I. 13**”. The less common 1,2-*alternate* conformation shows a similar pattern to the *partial cone,* although the two conformations can be distinguished in the aromatic part of the spectrum.

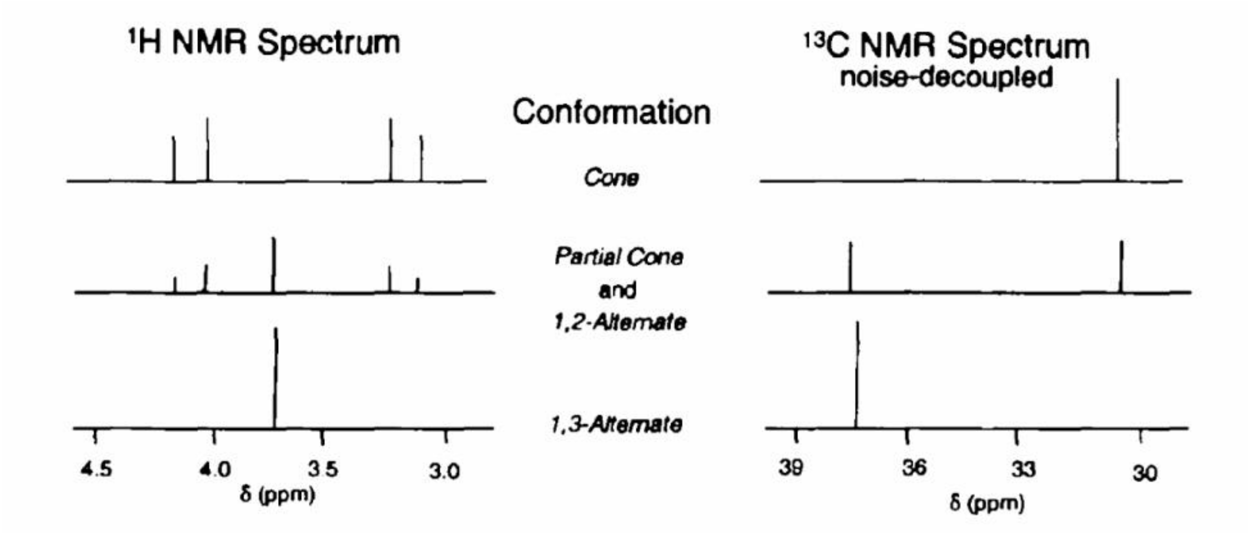

Figure I. 14: Patterns of the signals expected in the 1H and 13C NMR spectra of the four

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II.5 Synthesis Of Calixarenes:

II.5.1 Single Step Synthesis Of Calixarenes:

II.5.1.1 Base-Induced Procedures:[31]

Zinke's procedure for the base-induced condensation of p-substituted phenols and formaldehyde has been shown by Cornforth, Gutsche and others to yield mixtures of products which mayor may not contain the cyclic tetramer.A procedure developed by the chemists at the Petrolite Corporation that was originally thought to produce the cyclic tetramer has been shown to actually form the cyclic octamer.

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[31] J. vicens. Calixarenes: A Versatile Class Of Macro Cyclic Compounds. 1st eddition .1991 p6

One of the most useful results of Gutsche's reinvestigation of the Zinke, Cornforth and Petrolite procedures was the development of a method for making the cyclic hexamer in excellent yield, this work showing that by proper choice of reaction conditions p-tert-butylphenol can be transformed to the cyclic tetramer, cyclic hexamer, or cyclic octamer as the major product.

In what we will refer to as the *“Modified Zinke”* Cornforth Procedure' a mixture containing p-tert-butylphenol, 37% formaldehyde solution, and an amount of NaOH corresponding to 0.045 equivalents with respect to the phenol is heated for 2 hat 110-120°C to produce a resinous mass called the 'precursor'. The precursor is then heated in diphenyl ether for 2 h, the reaction mixture is cooled and treated with ethyl acetate and a copious precipitate is removed by filtration. Recrystallization from toluene produces p-tertbutylcalix[4]arene as glistening, white rhombs with mp 342-344 °C. we will refer to as the 'Modified Petro Ute Procedure' a mixture containing p-tert-butylphenol, 37% formaldehyde solution and an amount of KOH corresponding to 0.34 equivalent with respect to the phenol is heated for 2 h, and a 'precursor' is obtained as in the Modified Zinke-Cornforth Procedure. In the second phase, however, xylene rather than diphenyl ether is used as the reaction solvent, with the result that the product is almost pure *p-tert*butylcalix[6]arene , obtainable in yields as high as 85% as a white powder with mp 380-381 °C after recrystallization from chloroform-acetone.In what we will refer to as the "Standard Petrolite Procedure” a slurry prepared from p-tert-butylphenol, paraformaldehyde and an amount of NaOH corresponding to 0.03 equivalents with respect to the phenol in xylene is stirred and refluxed for 4 h. The cooled solution is filtered and the copious precipitate is recrystallized from chloroform to afford p-tert-butylcalix[8]arene in 65 % yield as glistening crystals which quickly lose their solvent of crystallization and transform to a white powder with mp 411-412°C.

II.5.1.2 One-Step, Acid-Catalyzed Synthesis Of Calixarenes:

II.5.1.2.1 Phenol-Derived Calixarenes:

Although the base-induced reaction of p-tert-butylphenol with formaldehyde remains the method of choice for synthesizing the major and minor calixarenes, acid-catalysis under appropriate conditions, also yields a product consisting of cyclic rather than linear oligomers, with the large cyclic oligomers present in relatively larger amounts than in the base-induced product. [32]

Several studies were carried out to optimize the acid catalyzed synthesis to produce large calixarenes by varying the acid catalysts, the solvent, the reaction times, reactant ratios and concentrations. The highest yields of large calixarenes were produced with a high concentration of para-tertbutylphenol, s-trioxane, and p-toluenesulphonic acid in chloroform. These conditions resulted in a very high yield of large calixarenes with the smallest in size being calix[7]arene and ranging to give macrocycles as large as calix[20]arene.[33]

II.5.1.2.2 Resorcinol-Derived Calixarenes:

Subsequent to the work of Niederl in the 1940s, considerable attention has been given to these resorcinol-derived calixarenes, and their structures have been conclusively proved. Högberg in particular studied them in detail and devised a procedure that was adapted to largescale operation by Cram and coworkers for the preparation of calix[4]resorcarenes.Niederl-Högberg Procedure (Synthesis of C-methylcalix[4]resorcarene).A solution of resorcinol and acetaldehyde in aqueous ethanol is maintained at 80 ^{o}C for 16 hrs.

The cooled mixture is filtered to give70% of a light yellow product that is pure enough for subsequent use.For each particular aldehyde, however, the optimization of the conditions must be worked out. Lewis acids ($AlCl_3$, $SnCl_4$, BF_3) in ether are also effective catalysts.In keeping with the current emphasis on environmentally benign operations, a solvent-free, high-yield procedure has been reported in which

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[32] C. David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p35

[33] Christian Martinez.Synthesis And Conformational Properties Of Hexamethyl Triazacalix[6]Arenes.A Thesis Of Master Of Science. Faculty Of The Department Of Chemistry
California State University, Sacramento2019.p20

resorcinol and benzaldehyde derivatives are mixed with a catalytic amount of solid acid at ambient temperature.[34]

II.5.2 Multi-Step Synthesis Of Calixarenes:

II.5.2.1 Non-Convergent Stepwise Syntheses:[35]

The non-convergent stepwise synthesis is long, tedious and often has low overall yields. Recognizing these deficiencies, several research groups have devised a convergent pathway that reduces the total number of steps and greatly improves the synthetic utility of the stepwise procedure. Calixarenes formed by convergent synthesis involve using well defined fragments. These fragments are commonly synthesized in a stepwise manner and primarily in a 3 + 1 approach or 2 + 2 manner to give calixarenes, This stepwise synthesis can be skillfully exploited for the construction of polysubstituted, dissymmetric, asymmetric and bridged calixarenes,. The choice between the “3 + 1” and “2 + 2” methods often depends on the relative ease of construction of the component parts.

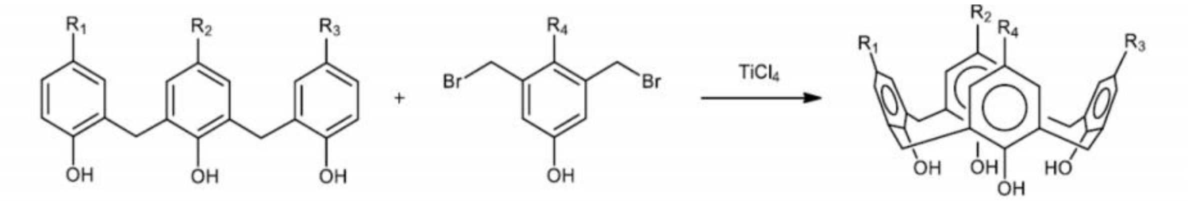

Figure I. 15: Convergent 3 + 1 Stepwise synthesis

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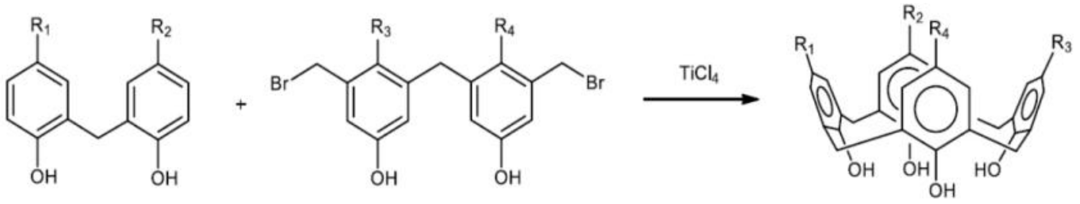

Figure I. 16: Convergent 2 + 2 Stepwise synthesis

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[34] C. David Gutsche.Calixarenes An Introduction.2nd Edition.2008.p35

[35] Hristian Martinez.Synthesis And Conformational Properties Ofhexamethyl Triazacalix[6]Arenes.A Thesis Ofmaster Of Science. Faculty Of The Department Of Chemistry California State University, Sacramento2019.P22

II.6 Homogeneous Catalysis And Heterogeneous Catalysis Used In Synthesis Of Calixarenes:

II.6.1 Homogeneous Catalysis:

Homogeneous catalysts have been well researched, since their catalytic centres can be relatively easily defined and understood, but difficulties in separation and catalyst regeneration have prevented their wider use. These challenges are the focus of much current research.

The most widely used homogeneous catalysts are simple acids and bases. Such catalysts are inexpensive enough that they can be neutralized, easily separated from organic materials, and disposed of. This, of course, is not a good example of green chemistry.[36]

II.6.2 Calixarene Formation Reaction In Basic Media:

C. Gutsche et al. have worked for many years to better understand the mechanismsof calixarene formation and to optimize their synthesis. Their systematic study of the influence of experimental conditions on the distribution of the calixarenes formed allowed to show that the temperature and the base concentration used are the most important parameters for the important. The influence of the alkaline counterion has also been studied using bases of the type **LiOH, KOH, RbOH** and **CsOH**.[37]

II.6.3 Calixarene Formation Reaction In Acidic Medium:

Acid-catalyzed calixarene synthesis using **Lewis acids**, such as **SnCl4** or **TiCl4** or **Brönsted**, have also been described. C. Gutsche et al. also studied the condensation of resorcinols and aldehydes by the acid route, leading to the formation of calixresorcarcenes [37]

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[36] Anonyme:https://www.globalspec.com/reference/63165/203279/4-3-homogeneous-catalysis

[37] Marie Clément.Calixarènes pour la synthèse radiolytique de nanoparticules métalliques.these de doctort en Chimiethéorique et/ou physique. Université Paris-Saclay, 2017 p25

II.6.4 Heterogeneous Catalysts:

Heterogeneous catalysis is a type of catalysis in which the catalyst occupies a different phase from the reactants and products. This may refer to the physical phase solid liquid or gas but also to immiscible fluids.[38]

There is a whole spectrum of heterogeneous catalysts, but the most common types consist of an inorganic or polymeric support, which may be inert or have acid or basic unctionality.[39]

- In our work we have used activated clay as a heterogeneous catalyst.

Acid activation is a common chemical modification of clays, usually bentonite with a hot solution of a mineral acid (typically HCl or H_2SO_4), and it is used for both scientific and industrial purposes. The aim is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity. The product consists partly of the remains of the starting mineral and partly of an amorphous, porous protonate and hydrated silica phase with a three-dimensional cross-linked framework. Illites containing non-swelling interlayer spaces dissolve more slowly than smectites but the chemical composition of the layers has a greater effect on the process thanswellability. The dissolution rate of organo clays decreases with the size of organic cations.

Acid activation modifies principal clay properties and thus also their industrial applications. The extent of clay mineral dissolution is derived by many methods, such as chemical analysis, IR or NMR spectroscopy, X-ray diffraction, thermal analysis and microscopic investigation and titration [40]

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[38] Anonyme: https://www.nature.com/subjects/heterogeneous-catalysis

[39] Anonyme: https://www.globalspec.com/reference/63164/203279/4-2-heterogeneous-catalysts

[40] Developments in Clay Science , Chapter 10.1 , Acid Activation of Clay Minerals , Volume 5, 2013, Pages 385-409

II.7 Genetality On The Clay:

Several centuries before our era, the Chinese used certain clays for the decoloration of fatty oils. M.-C. Alexanian, Doctor of Physical Sciences, who reveals this factadds that the Egyptians the Greeks, and then the Romans were well aware of their degreasing and bleaching properties Sometimes there will be an apparent similarity in the action of clay and certain medicines such asantiseptics.

This similarity is only apparent because there is a difference fundamental between the action of clay and antiseptics chemicals. An explanation seems to be possible for the role played by the agile metabolism. Indeed, according to a NASA clay would have played an important role, at the appearance of the life on earth by contributing to the concentration of amino acids, constituent elements of proteins.

Containing metals, clays attract nucleoproteins .whose assembly forms the deoxyribonucleic acid chains (D.N.A.). It is therefore likely that clay canint ervening the process of transformation and assimilation of nutrients, thus in the maintenance phenomena of life and defense against aggression and aging.[41] **.**

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[41] Raymond Dextreit- l'argile qui guérit-mémento de médecine naturelle.2019

II.7.1 Introduction:

Clay is a natural soil. It is more precisely an earthy rock with a very fine texture,waterproof when dry, plastic when wet[42]; is a sedimentary rock, largely composed of specific minerals, more or less hydrated aluminium silicates in general with a laminated structure (phyllosilicates) or fibrous structure (sepiolite and palygorskite) hich explains their absorption qualities and theirplasticity [43]

A true gift of natur, clay is essentially composed of alumina silicates. Hydrated in which are embedded mineral elements that give it its colour.

These elements present in reduced quantities are oxides of alumina, titaniu calcium,of magnesium, poassium and sodium

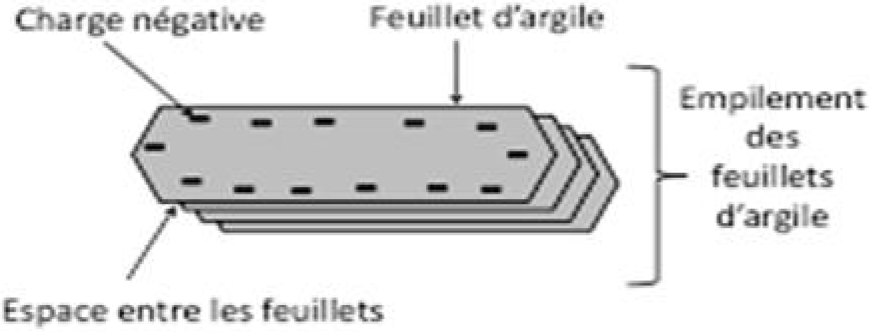

Figure I. 17: structure of clay showing the stacking clay sheets[44]

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[42] P. Komadel, D. Schmidt, J. Madejova, B. Ciel, Appl. Clay Sci.5- 113, 1990.

[43] Caillère S., Henin S. et Rautureau M., "Minéralogie des argiles : Classification et nomenclature (Tome 2)", Ed. Masson p 9, 107 et 114, Paris, 1982.

[44] Anonymous : https://fr.slideshare.net/EPTCL/connaitre-et-faire-vivre-le-sol

II.7.2 Classification:

The clay classified into three main families according to the thickness of the sheets (0.7nm) or (1nm) or (1.4 nm) , which correspond to a number of tetrahedral oxide layers(Si) and octahedrons (Al , Ni , Mg , Fe2+ , Fe3+ ; Mn , Na , K ….)

The gap between sheets may contain water as follows than ions. This results in variations in the distance between sheets, and thus macroscopic dimensional variations clay when it hydrates (dilation) or dries out (contraction) which can cause cracks to form.[45]. Clay minerals are divided into several types large families this present in the following schema:

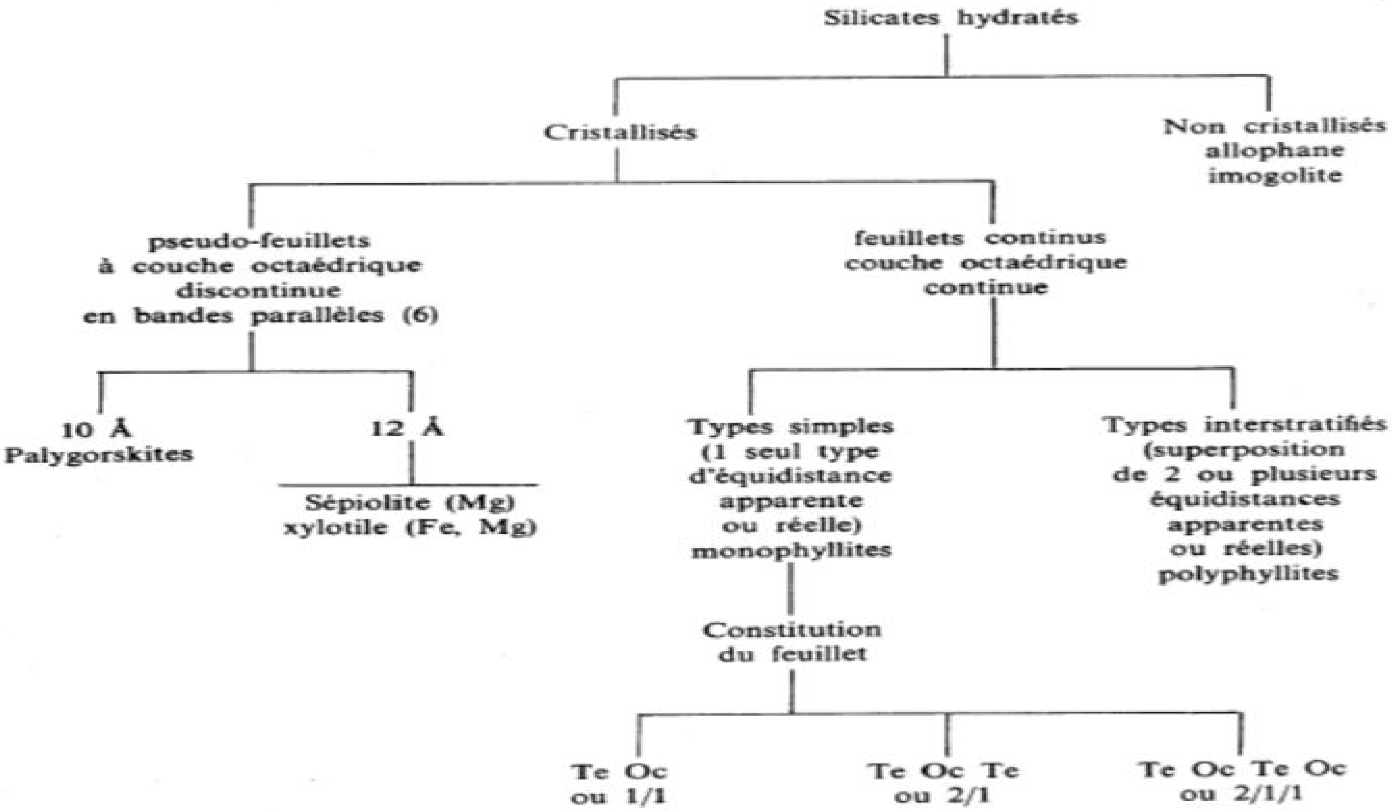

Figure I. 18: General classification of clays according to Millot[46]

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[45] anonyme : https://www.doc-developpement-durable.org/file/Agriculture/articles Wikipedia/Argile_Wikipedia-Fr.pdf

[46] Thèse pour le Diplôme d'État de Docteur en Pharmacie ; L'ARGILE, son utilisation A L'officine ; Hernot François ; Soutenue Publiquement Le 6 Juin 2016 ; Page 39

- The clays are differentiated by their type of combination tetrahedral and octahedral stacking sheets, the cation of the octahedral layer, the charge of the clay and the type of inter-foliar equipment

II.7.3 Clay Of Saida:

The formation of the Saida Clay in the Takhemaret region is revealing news lithostratigraphic, biostratigraphic and sedimentological data. In terms of lithostratigraphic, this formation is subdivided into three units:
lower clay-rich, carbonate-clay, upper clay-rich.

Discovered ammonite levels allow biostratigraphic correlations; with others with tethysian affinity, the results obtained are very promising the identification of the Saidite clay reveals its nature on tronite which remains belonging to the smectite.

This nontronite nature is due to the high iron content;use of this natural local iron-rich source to replace commercial products[47]

These nontronite which constitutes the clay of Saida called "Saidite" are dioctahedral montmorillonite clays in which there is a complete substitution of iron in the octahedral position (Sherma et al., 1962). Another study by (Goodman et al., 1976) showed a weak substitution of Si and Al in the tetrahedral sites by $Fe3+$ ions.

The following “**Table I. 2**” shows the chemical compounds of the ben adouane saida clay (which we used in this research)

Table I. 2: Chemical composition of clay from Ben Adouane Saïda (bn) by XRF[48].

Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	P.A.F	∑ %	SiO_2/Al_2O_3	SiO_2/Fe_2O_3
Wt.% (SA1)	40.36	13.58	10.76	01.70	22.36	01.19	16.05	106	02.97	03.75

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[47] La Formation des Argiles de Saïda (Jurassique supérieur) dans le domaine tlemcenien oriental (Takhemaret, Algérie) : données bio stratigraphique ichnologiques et sédimentologiques ;Genève;décembre ; 2015 page 37-40

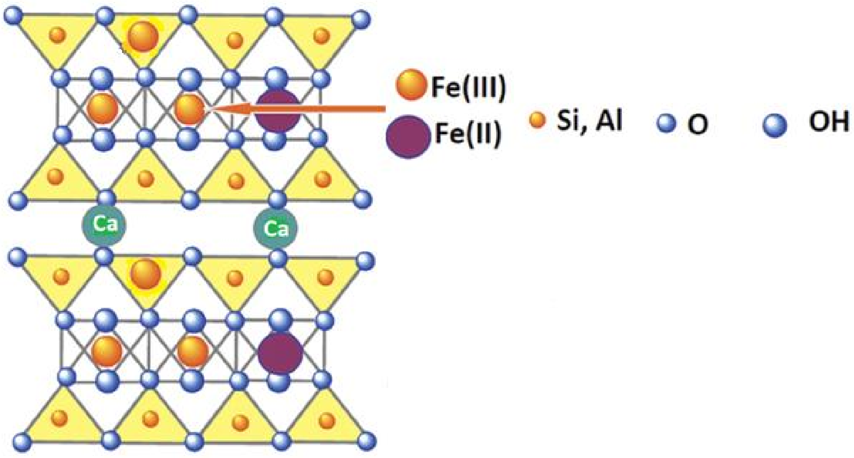

Figure I. 19: Schematic representation the structure of a Nontronite[48]

III. Calixarene In Green Chemistry:

The purpose of chemistry green, also named chemistry for sustainable development or eco-compatible chemistry or sustainable chemistry, is to prevent pollution by designing products and chemical processes that allow for reduce or eliminate at source the use and synthesis of substances dangerous. In 1998, Anastas and Warner proposed twelve principles for putting into practice green chemistry, a modern chemistry that respects the environment. the environment. All these principles aim to reduce discharges, the quan-of material used, in particular non-renewable resources the energy expenditure as well as risks and dangers.

To be truly green, chemistry must fully satisfy the twelve principles. If only one is satisfied, we can be very far from green chemistry.[49]

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[48] Rozenson, I., Heller-Kallai, L., 1977. Mossbauer Spectra Of Dioctahedral Smectites. Clays And Clay Minerals 25, 94-101

[49] Jacques Augé et Marie-Christine Scherrmann.Chimie verte Concepts et applications.2016. p4

III.1.1 The 12 Principles Of Green Chemistry:

- waste: design chemical syntheses to prevent waste, leaving no waste to treat or clean up.

- Design safer chemicals and products: design chemical products to be fully effective, yet have little or no toxicity.

- Design less hazardous chemical syntheses: design syntheses to use and generate substances with little or no toxicity to humans and the environment.

- Use renewable feedstock: use raw materials and feedstock that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

- Use catalysts, not stoichiometric reagents: minimize waste by using catalytic reactions. Catalysts are used in small amounts and carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

- Avoid chemical derivatives: avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

- Maximize atom economy: design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any wasted atoms.

- Maximize atom economy: design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any wasted atoms.

- Use safer solvents and reaction conditions: avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals. If a solvent is necessary, water is a good medium as well as certain eco-friendly solvents that do not contribute to smog formation or destroy the ozone.

- Increase energy efficiency: run chemical reactions at ambient temperature and pressure whenever possible.

- Design chemicals and products to degrade after use; design chemical products to break down into innocuous substances after use so that they do not accumulate in the environment.

- Analyze in real time to prevent pollution: include inprocess real-time monitoring and control during syntheses to minimize or eliminate the formation of by-products.

- Minimize the potential for accidents; design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fire, and release to the environment[50]

III.2 The Synthesis Of Calixarenes In Green Chemistry:

The synthesis of calixarenes can be conventionally done by heating at high temperature for a few hours and using various solvents in large quantities. The greener synthesis can be done with microwave-assisted synthesis and the solvent-free method where both of these methods can reduce reaction time, energy use, solvent, and waste with a higher percentage yield than that from the conventional synthesis method

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[50] Marc A. Dube,Somaieh Salehpour Applying the Principles of Green Chemistry to Polymer Production Technologymacromolecular journalsVolume8, Issue1DOI: 10.1002/mren.2013001032014p7–28.

making the synthesis of cyclic oligomer calixarenes and their derivatives more environmentally friendly.[51]

Worldwide demand for environmentally friendly chemical processes and products requires the development of novel and cost-effective approaches to pollution prevention. One of the most attractive concepts in chemistry for sustainability is Green Chemistry, which is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and applications of chemical products. Although some of the principles seem to be common sensetheir combined use as a designer framework frequently requires the redesign of chemical products or processes. It should be noted that the rapid development of Green Chemistry is due to the recognition that environmentally friendly products and processes will be economical on a long term.[52]

III.3 Toxicity Of The Calixarenes:

Until 2000, little systematic research had been carried out on the toxicity of the calixarenes either at the cellular level or in vivo. A brief report in a review by Gutsche in 1985 stated that the calixarenes had shown no activity in the Ames test. In the abstracts of ISSC 2000, Perret et al. noted that certain calix[4]arene phosphonate derivatives showed no effects on the cell growth of human fibroblasts . In the same abstract the authors noted that giant vesicles based on amphiphilic phosphonato-calix[4]arene derivatives could coalesce with the cell membranes of human fibroblasts without causing cell death. More recently, Shahgaldian et al. have reported that solid lipid nanoparticles based on amphipihilic calix[4]arene derivatives show zero haemolytic effects at concentrations ranging up to 300 mg/l . Similarly, Da Silva et al. in a recent publication have shown that for a series. So far the calixarenes have shown a remarkable degree of non-toxicity. In view of these properties the calixarenes and their derivatives have a high potential for a wide range of biopharmaceutical applications which are only now beginning to be studied.[53]

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[51] Ratnaningsih Eko Sardjono. Rahmi Rachmawati.Green Synthesis of Oligomer Calixarenes.From the Edited Volume.DOI: 10.5772/67804 .2017.p1-14

[52] Anonymous https://pubs.acs.org/doi/full/10.1021/cr0783784

[53] E.DaSilva, A.N. Lazar, A.W. Coleman..Biopharmaceutical applications of calixarenes..volume14 issue 1.2004p3-20

III.4 Applications Of Calixarenes In Green Chemistry:

Calixarenes are interesting cage macrocycles, widely investigated due to their valuable properties, especially formation of inclusion complexes; these macrocycles are promising for a variety of applications. One should point out the use of calixarenes in the biological field and in design of pharmaceutic agents. Calixarenes form metal nanoparticles, e.g. AuNPs and AgNPs, as well as organic NPs, and serve for construction of sensors; they also may be used as extractants of f-elements. [54]

III.4.1 Calixarenes As Extractant And Sensors:

Many calixarene derivatives have been reported with the introduction of functional groups at the phenolic hydroxy group and at the p-position with respect to the phenolic hydroxy group, substituting the original t-butyl group. Calixarenes and their derivatives are highly versatile scaffolds for the design of three dimenional (3D) cavities, which can selectively form complexes with guest molecules or ions and have been regarded as the third generation of host molecule after crown ethers and cyclodextrins in supermolecular chemistry.[55]

They act as host molecules as they possess cavities. The shape of calixarenes is like a cup or a bucket with a defined upper and lower rim along with a central annulus. Both the upper and lower rims can be tailor made to provide highly preorganized structures. They have the ability to bind to a variety of ions and find applications as ion sensors. The aromatic rings of calixarenes rotate and produce different conformations. These conformations play a critical role in various properties such as the selectivity of the calixarene to complex with a specific species.[56]

Other calixarenes bearing phosphonate group at the lower and upper rim are potential macrocyclic receptors for the extraction of lanthanide or tetravalent cations and for detoxification of radioactive water.[57].

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[54] Malgorzata Deska; Barbara Dondela; Wanda Sliwa.Selected applications of calixarene derivatives. Issue 6,2015p394

[55] ZhiquanShen.Applications of Calixarenes in Polymer Synthesis.Volume261,Issue1,DOI:10.1002/masy.200850110 , 2008,p74-84

[56] Anonymous https://www.alfa.com/en/calixarenes/

[57] E. Da Silva, A.N. Lazar, A.W. Coleman..Biopharmaceutical applications of calixarenes, Journal of Drug Delivery Science and Technology volume14 issue 1,2004, p3-20.

Calixarene bulk modified screen-printed electrodes (SPCCEs) have been designed, fabricated and utilized as one-shot disposable electrochemical sensors.[58]

III.4.2 Calixarene Complexes As Polymerization Catalysts:

Calixarenes have been used as ligands to prepare rare earth calixarene complexes. A series of rare earth calixarene complexes have been synthesized and employed as efficient catalysts for the polymerization of ethylene, styrene butadiene, propylene oxide, styrene oxide, trimethylene carbonate, and 5,5-dimethyl trimethylene carbonate,There are two main applications of calixarenes in polymer synthesis useof metal calixarene complexes as catalysts for polymerization, and star polymers with a calixarene core.[59]

III.4.3 Bioactive Molecules, Medications:

Calixarenes have been widely used for the detection of molecules of pharmaceutical interest. In the organic solvents, the detection of steroids, including cortisone, prenisolone and their derivatives has been investigated by NMR in presence of calixresorcinarenes.[59]

It is well known that the toxicity is a barrier to the discovery and development of potent drug molecules. However, most calixarene derivatives showed low or no toxicity in the animal models Calixarenes have shown antiviral antibacterial antifungal, antitubercular, and anticancer activities.[60]

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[58] Prashanth Shivappa Adarakatti, Christopher W. Foster, Craig E. Banks, Arun Kumar N.S., Pandurangappa Malingappa.: Application to environmental samples. International Journal Devoted toResearch and Developmentof Physical and Chemical Transducers , Volume 267, 1 November 2017, Pages 517-525.

[59] E. Da Silva, A.N. Lazar, A.W. Coleman..Biopharmaceutical applications of calixarenes, Journal of Drug Delivery Science and Technology volume14 issue 1,2004, p3-20.

[60] Satish Balasaheb Nimse and Taisun Kim ,Biological applications of functionalized calixarenes,Chemical Society Reviews, Issue 1, 2013,p 366-386.

I. EXPERIMENTAL TECHNIQUES

I.1 FTIR Spectroscopy:

Infrared spectroscopy is certainly one of the most important analitycal techniques available to today's scientists. Is a technique based on the vibration of the atoms of a molecule an infrared spectrum of commonly obtained by passing infrared radiation thought a sample and determining what fraction of the incident radiation is absorbed at a particular energy .the energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule[1]

Also, each molecule has a characteristic spectrum often referred to as the fingerprint.

A molecule can be identified by comparing its absorption peak to a data bank of spectra.

Figure II. 1: structure show the different between monomer and polymer[2]

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[1] Barbara ,H, Sturat, Infrared spectroscopy : fundamental and application , 2004, page 1- 2

[2] anonymous : http://jean-jacques.auclair.pagesperso-orange.fr/ftirUV/protocole.htm

IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.[3]

- The infrared range between (4000 cm-1 and 400 cm-1) corresponds to the vibration energy range of the molecule.
- In IR the molecular vibrations that absorb radiation classified into the category shown in the following figure (II. 2)

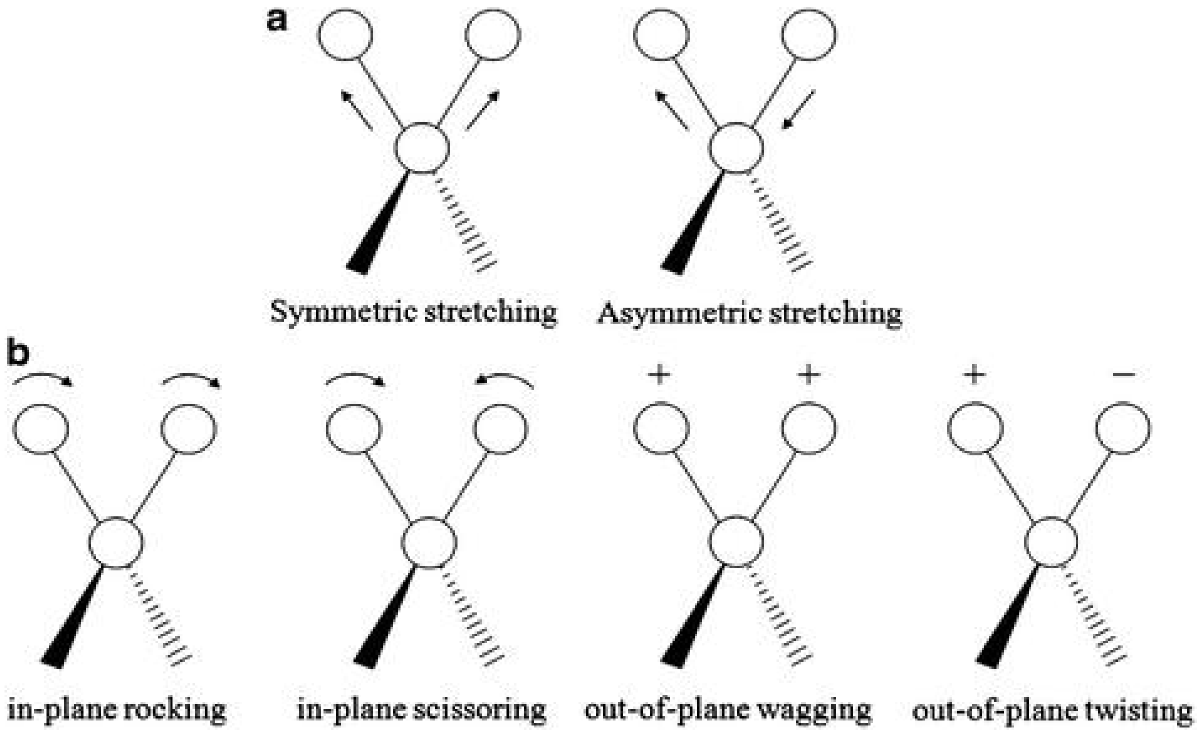

Figure II. 2: molecular vibration modes in IR[4]

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[3] Anonymous:https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared%3A_Theory

[4] M.orgla guerrero.p, Gregos .p , The candian journal of chemical engineering ; v 98 ; page 36 ; 2019

- The characteristic IR absorption bands for a selected group of polymers are summarized. Following Table presents the characteristic IR absorption bands for a selected group of additives.

table II 1: Correlation of chemical structure and FTIR

Type of link	***Wave number (cm-^{1})***	***Band width***	***Absorption intensity***
O-H without hydrogen link	3580- 3650	Thin	Strong
O-H with hydrogen link	3200 – 3300	Large	Strong
O-H of a carboxylic acid	2500 – 3200	Large	Variable
C-H of groups CH_2, CH_3, CH in alkanes, alkenes and aromatic rings	2900 -3100	Variable (multiple bands)	Variable
C=C in an aromatic cycle	1500 – 1600	Thin	Middle
C = 0 of a carboxylic acid	1700 – 1725	Thin	Strong

I.2 The ^{1}H NMR:

"Any motion of a charge particle has an associated magnetic field "

The nucleus of hydrogen atom (proton) as a spinning bar magent because it possesses both electric And magnetic spin .the nucleus of H- atom generate a magnetic field NRM involves the interaction between and oscillating magnetic of electromagnetic radiation and the magnetic energy of H-nucleus when these are placed in an external static magnetic field [5]

- The values of a chemical shift can be explained using some concepts common in organic chemistry, such as inductive or mesomeric effects or certain magnetic anisotropies in space. It should also be noted here that the extent of the domain depends on the type of nucleus being studied

I.2.1 chemical displacement :

The range of chemical displacement of protons extends over less than 15 ppm and most often, as shown in Figures, over just over 10 ppm. As we will see the values of a chemical shift can be explained by means of some concepts usual in organic chemistry, for example inductive or mesomeric effects or some magnetic anisotropies in space.

It should also be noted here that the extent of the domain depends on the type of nucleus being studied.

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[5] - Dr. Vinod Jenna and al ;l Problems and solution in Proton NMR spectroscopy ; page [1] [2];USA 2016

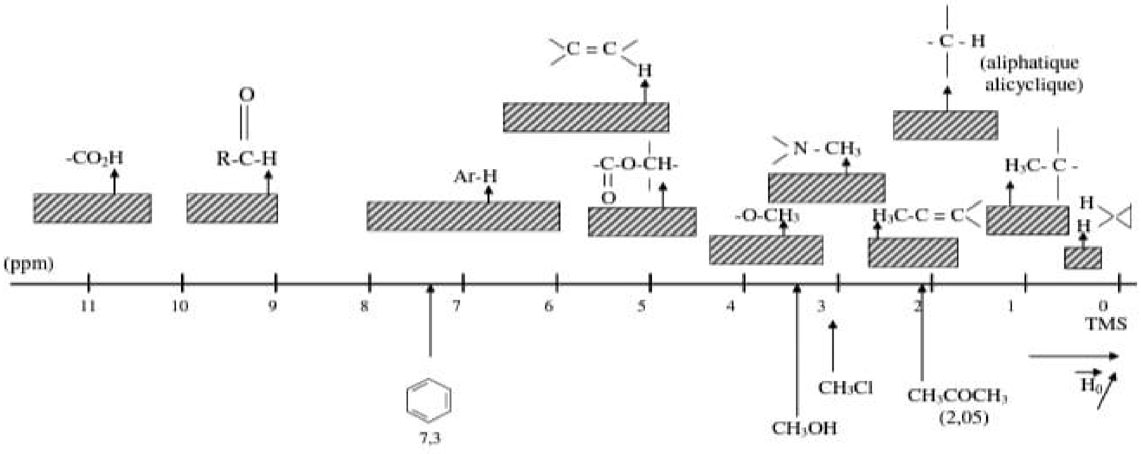

Figure II. 3: representation of some chemical displacements of the proto[6]

I.3 Bench Kofler :

The kofler bench is an offline apparatus for microscopy in that the bench contains a metal strip With temperature gradient ranging from 50°c to 260°c The temperature is controlled by placing a sample at a certain location of the bench and after heating the sample is examined by a light microscopy .[7]

Figure II. 4: apparatus of bench kofler[8]

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[6] - C.J Ducauze and D.N Rutledge ; Chapitre 2 : la spectrometrie RMN ; AgroParisTech ; page 43
[7] Stephen R .Byen and All ; Solid- state properties of pharmaceutical matarials , Ed 2017 , p 144
[8] anonymous : http://culturesciences.chimie.ens.fr/content/utilisation-du-banc-kofler-pour-mesurer-une-temperature-fusion-918

Abstract:

This work is focused on the study of the synthesis of a cyclic polymer p-HBA/F and p-HBA/A, using non-toxic products. This polymer belongs to the family of calixarene which are molecules of interest in biosynthesis. The synthesis of this cyclic polymer is based on the condensation of acetone with para-hydroxy benzoic acid, its last products are non-toxic, and we used an ecological acid catalyst to remain in the principle of green chemistry. This synthesis produces the cyclic polymer we want, which has several uses in various fields, including medical, environmental, because of its properties.

Keys word: cyclic polymer (p-HBA/F and p-HBA/A), condensation, non-toxic green chemistry.

Résume :

Ce travail est axé sur l'étude de la synthèse d'un polymère cyclique p-HBA/F et p-HBA/A, en utilisant des produits non toxiques. Ce polymère appartient à la famille des calixarènes qui sont des molécules d'intérêt dans la biosynthese. La synthèse de ce polymère cyclique est basée sur la condensation de l'acétone avec l'acide para-hydroxybenzoïque, ses derniers produits sont non toxiques, et nous avons utilisé un catalyseur acide écologique pour rester dans le principe de la chimie verte. Cette synthése produit le polymère cyclique que nous voulons.qui a plusieurs utilisations dans divers domaines, notamment médical, environnemental, en raison de ses propriétés.

Mot clé : polymère cyclique (p-HBA/F, p-HBA/A), condensation, non toxique, chimie verte

ملخص :

يتمحور هذا العمل حول دراسة تصنيع بوليمر حلقي , بإستخدام مواد كيميائية غير سامة حيث ينتمي هذا البوليمر إلى عائلة الكالكسارين وهي جزيئات ذات أهمية في عالم التصنيفات الكيميائية في شتى مجالاتها يعتمد تصنيع هذا هذا البوليمر الحلقي على تكثيف الأسيتون بحمض البارا هيدروكسي البنزويك , و الذي يعتبر مادة غير سامة حيث إستخدمنا محفزا بيئيا للبقاء في مبدأ الكيمياء الخضراء , يدخل هذا البوليمر الحلقي المصنع ضمن مجالات إستخدماتية كثيرة ومجلات مختلفة أهمها : الصيدلانية ,الطبية , البيئية .... , لما يمتاز به من خصائص كثيرة

الكلمات الرئيسية: بوليمر **حلقي** ، تكثيف ، غير **سام** ، كيمياء **خضراء**