SYNTHESIS, SOLUTION BEHAVIOUR AND APPLICATIONS OF CALIX[n]ARENES

THESIS SUBMITTED
IN FULFILMENT FOR THE REQUIREMENTS
OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

by

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For my daughter

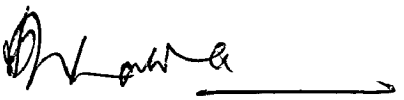
Shaifali

CERTIFICATE

This is to certify that the thesis entitled, ***Synthesis, solution behaviour and applications of calix[n]arenes*** being submitted by **Ms. Meena** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry is a record of bonafide research work carried out by her.

Ms. Meena has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached a requisite standard.

The results embodied in this thesis have not been submitted, in part or in full, to any other university or Institute for the award of any degree or diploma



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ABSTRACT

The thesis titled, "Synthesis, solution behaviour and applications of calix[n]arenes" has been divided into six chapters.

Calix[n]arenes constitute an important class of compounds that can serve as useful building blocks for designing molecular receptors for ionic and molecular recognition. **Chapter I** of the thesis presents an overview of the literature published on calix[n]arenes during the last five years with a special emphasis on their chemical transformations at the upper and the lower rim to provide newer deep cavity, bridged, capped, chromogenic and fluorogenic calixarenes. This chapter also includes their applications and their use as catalysts, metal ion extractants for the treatment of radioactive wastes and in the development of ion selective electrodes.

Chapter II deals with our results on the functionalization of calix[n]arenes at the upper and the lower rim. Alkyl chains have been introduced in the calixarene architecture by esterification and etherification at the lower rim and conformational analyses of the products have been done with the assistance of ^{1}H NMR and ^{13}C NMR spectroscopic methods. Upper rim derivatization of calix[n]arenes has been carried out by the application of Friedal-Crafts alkylation and acylation as well as by Fries rearrangement of calixarene esters. Detailed study of the Fries migration in different solvents and temperatures reveal that the rearrangement proceeds smoothly in benzene and carbon disulphide. Acylation of the solvent has been observed when toluene is used as a solvent in the Fries migration revealing thereby that calix[n]arenes can function as organized media for regioselective acylation of compounds that form host-guest complexes with them. Calixarene ketones obtained from the Fries migration and Friedal-Crafts reaction have been identified by UV, IR and NMR spectral data.

Since calixarenes possess both hydrophobic and hydrophilic functionalities in the same molecule, they can be expected to behave as non-ionic surfactants. One of the pre-requisites for studying molecular recognition by these molecules is to determine whether they can incorporate the guest molecule in their molecular cavities or whether they themselves can aggregate to form topological variants in solution. **Chapter III** deals with our results on dynamic laser light scattering experiments conducted on derivatized calixarenes in solution. It has been observed that the solution behaviour of *p*-tert-butylcalix[4]arene is much different from that of *p*-tert-butylcalix[6]arene and *p*-tert-butylcalix[8]arene. On the other hand, hexakis(hexadecyloxy)calix[6]arene exists as a dimer at 0.5 x 10^{-3} M concentration while hexasulphonated calix[6]arene does not aggregate at concentrations up to 0.5 x 10^{-3} M.

Chapter IV gives the details of experiments conducted on dye-sensitized photooxygenation of amino and hydroxy naphthalenes. It has been observed that photooxygenation of 2-aminonaphthalene results in the formation of 2,6-naphthoquinone. The reaction has also been studied in the absence and presence of different concentrations of *p*-tert-butylcalix[n]arenes (n=4,6,8). The results obtained reveal that *p*-tert-butylcalix[6]arene enhances the rate as well as yield of formation of 2,6-naphthoquinone while *p*-tert-butylcalix[4]arene and *p*-tert-butylcalix[8]arene do not affect the reaction.

Since calixarenes possess a pre-organized cavity and sites for hydrogen bonding and hydrophobic interactions in their molecular architecture, they are expected to serve as excellent hosts for a variety of guest molecules. **Chapter V** describes the experiments conducted on recognition of various quinones with different calixarenes and it has been observed that 2,6-naphthoquinone forms a 1:1 complex with *p*-tert-butylcalix[6]arene while 1,4-benzoquinone forms a 2:1 complex with *p*-tert-butylcalix[4]arene and *p*-tert-

butylcalix[6]arene. The stoichiometry of complexation has been determined by Job's continuous variation plots, UV and NMR titrations. The association constants of molecular complexes formed range from 3.30×10^2 - 7.15×10^2 M^{-1}. On the other hand, 1,4-naphthoquinone, 9,10-anthraquinone, 1,2-dihydroxy-9,10-anthraquinone and 1,2,5,8-tetrahydroxy-9,10-anthraquinone have been observed to show no interaction with *p*-tert-butylcalix[n]arenes (n=4,6,8).

Chapter VI incorporates our results on the syntheses of calix[n]arene oximes and Schiff bases. The products obtained have been identified by UV, IR and NMR spectroscopy. This chapter also describes our preliminary results on complexation behaviour of synthesized calixarene oximes and Schiff bases with transition metal ions [Co(II), Ni(II), Cu(II) and Fe(II)] through UV, IR and NMR spectroscopic methods. It has been observed that calix[n]arene oximes show better complexing ability than calix[n]arene Schiff bases. Calix[4]arene oximes have been observed to form a 1:1 complex with transition metal ions while calix[6] - and calix[8]arene oximes form complexes with transition metal ions in a 1:2 stoichiometry.

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5. Promotion of selectivity through Organized media: Fries rearrangement of calix[n]arene esters, H.M. Chawla and Meena, *Tetrahedron (Communicated)*.
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7. Usual reaction products from fries rearrangement of calixarene esters, H.M. Chawla and Meena, *10th International Symposium on Organic Synthesis*, Bangalore, Dec. 11-16, 1994.

NOTES

1. All the melting points reported in this thesis are uncorrected and were taken on an electric melting point apparatus (Toshniwal, India).
2. UV spectra were taken on Hitachi 330 and Perkin Elmer's (Lambda-3B) spectrophotometers.
3. IR spectra were recorded in KBr discs or chloroform on a [5-DX] Nicolet FT-IR spectrophotometer. The abbreviations such as s,w,m,sh,bs,w-sh and m-sh refers to strong, weak, medium, sharp, broad and strong, weak and sharp, medium and sharp respectively.
4. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-D_6 on Jeol [JNM-FX100] (IIT Delhi) and Varian XL-300 (RSIC, Bombay) FT-NMR spectrometers using TMS as an internal standard and value reported are in δ scale. The abbreviation such as s,bs,d,t,q and m indicate singlet, broad singlet, doublet, triplet, quartet and multiplet respectively.
5. Atomic absorption was determined by Atomic Absorption spectrophotometer AAS 4129, Electronic Corporation of India.
6. Thermal analyses of the compounds was carried out by using simultaneous thermal analyser STA 780 series (Stanton Redcroft, UK).
7. The molecular mass of several calix[n]arenes synthesized was determined by vapour pressure osmometry using vapour pressure osmometer (Knauer, W.Germany).
8. Elemental Analysis was carried on Perkin Elmer's 240C CHN Analyzer.

9. The completion of the reaction and the purity of the synthesized compounds were checked by TLC performed on silica gel (BDH, Bombay) plates using iodine for visualizing the spots.

10. The solvents used were purified and dried before use.

11. Pet. ether refers to the petroleum ether fraction with a boiling point range of 60-80°C.

12. For the sake convenience, the names of calixarenes used in this thesis have been further shortened. For example, 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxycalix[4]arene has been usually referred as *p*-tert-butylcalix[4]arene while 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix[6] arene and 5,11,17,23,29,35,41,47-octa-tert-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene are referred as *p*-tert-butylcalix[6]arene and *p*-tert-butylcalix[8]arene respectively. Similarly names of 25,26,27,28-tetrahydroxy calix[4]arene, 37,38,39,40,41,42-hexahydroxycalix[6]arene and 49,50,51,52,53, 54,55,56-octahydroxycalix[8]arene have been shortened to tetrahydroxycalix[4] arene, hexahydroxycalix[6]arene and octahydroxycalix[8]arene respectively.

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