STUDIES ON SYNTHESIS AND REACTIONS OF CALIX[n]ARENES

By

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Submitted

in fulfilment of the requirement of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology, Delhi

February, 2004

CERTIFICATE

This is to certify that the thesis entitled, "***STUDIES ON SYNTHESIS AND REACTIONS OF CALIX[n]ARENES***", being submitted by Mr. Lukesh Bajaj to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by him.

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

The results contained 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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ACKNOWLEDGEMENTS

It gives me an immense pleasure and great opportunity to express my profound sense of gratitude and indebtedness to Professor and Head H. M. Chawla, for his painstaking guidance, invaluable suggestions and constant encouragement throughout the execution of research work embodied in this thesis. I would also like to thank him for making all facilities available for my research work.

I would also like to thank Dr. R. Varadarajan for his valuable support and guidance.

A mention of my colleagues, whose support egged me on, is a must. Of note among them are Tania and Satish – their help during writing of the thesis was immense. My seniors, Venkatesh, Anuradha and Meenakshi -- who set an example of ability and intelligence before us -- deserve special mention. I would also like to thank my lab mates Vandna, Bindu, Ananya, Sahu, Rahul, Suneel, Anjali, Sarika, Namrata, Arpita and Kamini for their constant help and support. I am also extremely grateful for the help rendered to me by Dr. Ranjana Saxena and Personal Secretary to Prof. Chawla, Ms. Seema Arora.

I thank Department of Biotechnology, Govt. of India and Indian Institute of Technology, Delhi for research fellowships.

Last, but not the least, I would like to take this opportunity to offer my sincere regards to all members of my family for their invaluable support and constant encouragement that made it possible for me to pursue and complete my research work.

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ABSTRACT

The thesis titled, "**STUDIES ON SYNTHESIS AND REACTIONS OF CALIX[n]ARENES**", presents the research work carried out on the synthesis, characterization and applications of some novel calix[n]arene derivatives. The research work has been divided into six chapters.

Calixarenes represent phenolic macrocyclic metacyclophanes that possess a flexible hydrophobic pocket encompassed by hydrophobic and hydrophilic ends (termed upper and lower rim) in their molecular architecture. They can serve as useful building blocks for designing novel derivatives/conjugates that can provide molecular assemblies and aggregates to induce molecular recognition behavior. **Chapter-I** of the thesis presents an overview of the literature published during the past ten years in the field with special emphasis on their synthesis, conformational analysis, organizational behaviour and self-assembly of calixarenes.

Chapter II deals with the synthesis of various chromoionophores and their spectral characterization (IR, NMR, UV and FAB mass spectral analysis). Conformational analyses of the synthesized azocalixarenes have been accomplished by ^{1}H and ^{13}C- NMR spectroscopy. The synthesis of these chromoionophores has been achieved by combining the chromogenity and thiophilicity concepts reported earlier from our laboratory.

Chapter III describes the synthesis of various acyl, bromo and Mannich base derivatives of calix[4]arenes followed by their further functionalization. For instance, the acyl calixarene derivatives have been converted to their respective hydrazones and oximes, the bromo derivatives to their cyano analogues while the Mannich reaction products have been converted to the corresponding (thiophenyl)methyl and cyano methyl derivatives.

The cyano derivatives have also been converted to the corresponding tetrazoles by treatment with sodium azide. The characterization of synthesized compounds has been achieved by IR, UV, NMR and single crystal X-ray diffraction analysis.

Preliminary UV-visible spectral investigations have been conducted to evaluate the recognition characteristics of synthesized chromoionophores towards transition metal ions and results have been described in **Chapter IV**. Some of the synthesized chromoionophores have been found to selectively recognize Hg(II) and Pd(II) ions. The interaction of palladium complex of the 5,11,17,23-tetrakis-(2-hexadecylthiophenylazo)-25,26,27,28-tetrahydroxy calix[4]arene ($2c_3$) with aliphatic amines has also been reported in this chapter.

Chapter V describes an economic procedure for the synthesis of different esters of *p-tert*-butylcalix[n]arenes and development of their analytical profiles through HPLC analyses. While synthesized products obtained have been spectroscopically characterized, their HPLC profiles have been documented in this chapter. Preliminary results on the study of reactions at the methylene bridge of tetramethoxy *p-tert*-butylcalix[4]arene using strong bases like *n*-BuLi or LDA in THF have been incorporated in **Chapter VI.**

NOTES

1. All 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 Perkin Elmer's(Lambda-3B) spectrophotometer.
3. IR spectra were recorded in KBr discs on a [5-DX] Nicolet FT-IR spectrophotometer.
4. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on Bruker Spectrospin-300MHz FT-NMR spectrometers using TMS as internal standard and values reported are on δ scale. The abbreviation such as s, bs, d, t, q, bm and m indicate singlet, broad singlet, doublet, triplet, quartet, broad multiplet and multiplet respectively.
5. FAB-mass spectra of some of the synthesized compounds were recorded on a JEOLSX 103/DA-6000 Mass Spectrometer available at Central Drug Research Institute, Lucknow. *m*-Nitro benzyl alcohol was used as the matrix.
6. Elemental Analysis was carried on Perkin Elmer's 240C-CHN Analyzer.
7. The completion of the reaction and the purity of the synthesized compounds were checked by TLC performed on silica gel coated glass plates using iodine for visualizing the spots.
8. Purification of several of the synthesized compounds was carried out by column chromatography over silica gel (60-120 mesh)obtained from Qualigens Fine Chemicals Limited, Mumbai.
9. All analytical HPLC assays were carried on Waters 2487 instrument with a Dual λ Absorbance Detector. The samples were dissolved in HPLC grade THF.

10. The solvents used were purified and dried before use by procedures described in "Purification of Laboratory Chemicals" by W. L. F. Amarego and D. D. Perrin, *Bath Press and Bath*, Britain.

11. For the sake of convenience, the names of calixarenes used in this thesis have been 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 or even parent calix[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*-calix[6]arene and *p-tert*-butylcalix[8]arene respectively. Similarly names of 25,26,27,28-tetrahydroxycalix[4]arene, 37,38,39,40,41,42-hexahydroxy calix[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 and even further shortened to calix[4]arene, calix[6]arene and calix[8]arene.

12. Abbreviations used in this thesis are:

    THF – Tetrahydrofuran;

    DMF – N,N'-Dimethylformamide;

    $CDCl_3$- Deuterated chloroform;

    CD_3OD- Deuterated methanol;

    D_2O – Deuterated water;

    DMSO-d_6 – Deuterated Dimethyl sulfoxide.

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