

Studies in the Synthesis and Applications of Novel

Calix[n]arene derivatives

By

BINDU SRIVASTAVA

Department of Chemistry

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

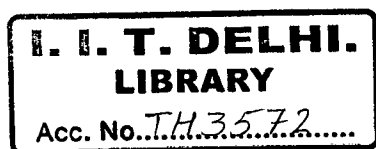
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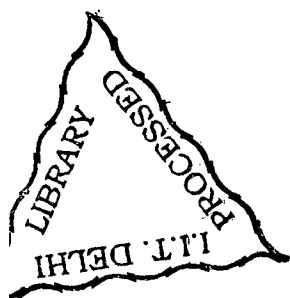
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Synthesis of calix[4]arene propyl



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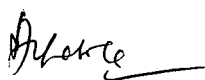
*DEDICATED
TO
MY PARENTS*

CERTIFICATE

This is to certify that the thesis entitled, “**Studies in the synthesis and applications of novel calix[n]arene derivatives**” being submitted by **Ms. Bindu Srivastava** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Ms. Bindu Srivastava has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or in full, to any other University or Institute for the award of any other degree or diploma.



Prof. H. M. Chawla

Department of Chemistry
Indian Institute of Technology, Delhi,
Hauz Khas, New Delhi- 110016



Dr. N. Pant

Department of Chemistry
Indian Institute of Technology, Delhi,
Hauz Khas, New Delhi - 110016

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Today I submit my PhD thesis for evaluation. The accomplishment will not sink in until a few more days, but I feel good about it nonetheless. The thesis dissertation marks the end of a long and eventful journey of over five years whereby I have been accompanied and supported by many people. It is a pleasant aspect that I have now the opportunity to express my gratitude to all of them.

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Bindu

BINDU SRIVASTAVA

ABSTRACT

The thesis titled, “*Studies in the synthesis and applications of novel calix[n]arene derivatives*”, describes the research work carried out to establish novel synthetic protocols for new calix[n]arene derivatives and evaluation of their molecular recognition characteristics through application of spectroscopic and analytical techniques (IR, ^1H NMR, ^{13}C NMR, FAB-MS and X-ray spectroscopy). The accomplished research work has been divided into five chapters.

Chapter I of the thesis focuses on recent advances in self-aggregation of calix[n]arenes and illustrates various interactive mechanisms involved in molecular organization by choosing suitable examples from the literature. **Chapter II** describes the study of *O*-propylation of calix[4]arenes in the presence of different bases and varying reaction conditions to selectively obtain mono-, di-, tri- and tetra-*O*-propylated calix[4]arenes. The effect of various reaction parameters and conformer distribution of products obtained has been rationalized in the light of current concepts of chemistry and supramolecular chemistry. **Chapter III** highlights new methodologies to achieve selective formylation of calix[n]arenes at the upper rim *via ipso*-substitution by using either combination of dichloromethylmethyl ether-titanium tetrachloride or hexamethylenetetramine-trifluoroacetic acid as the formylating reagents. *Ips*o-formylation in the presence of dichloromethylmethylether and TiCl_4 provides a convenient access to monoformylated *p*-*tert*-butylcalix[4]arenes as the only product in good yields which depend on the temperature and reagent concentration. *Ips*o-formylation using hexamethylenetetramine (HMTA) and trifluoroacetic acid (TFA) has been observed to allow the isolation of bisformylated bis(*tert*-butyl)calix[4]arenes in / good yields with unprecedented

regioselectivity. *Ips*o-formylation using HMTA-TFA has also been found to be influenced by the nature of the substituent R (alkyl/ester) on the phenolic units of the calix[4]arene and the reaction is sequential to allow exhaustive formylation on prolonged reaction in the absence of steric barriers. The hard acid character of the formylated calix[4]arenes has been utilized to determine the structural changes and the flexibility of formyl calix[4]arene oxyanions in the presence of Ba^{2+} . Preliminary changes in the absorption and conformation profiles of formylated calix[4]arenes on addition of barium salt and the effect of bulky alkyl chains at the lower rim on interaction with barium ions has been examined in the present work. **Chapter IV** describes the work carried out on the synthesis and characterization of molecular receptors with appended benzothiazolyl or dithiane moieties at the upper rim of calix[4]arene annulus through the condensation of formyl or acetyl calix[4]arene with 2-aminothiophenol or 1,2-ethane dithiol respectively. The synthesized benzothiazolyl calix[4]arenes have been determined to exhibit remarkable selectivity towards Cu^{2+} ion recognition while the dithiane appended calix[4]arenes exhibit selective interaction with Hg^{2+} over other transition metal ions. **Chapter V** of the thesis illustrate our exploration into synthetic routes for designing calix[4]arene derivatives with extended hydrophobic cavities obtained through introduction of olefinic and enone groups at the upper rim of calix[4]arene annulus *via* Wittig and Friedel Craft's acylation reactions respectively. Role of different Lewis acids in Friedel Craft's acylation reaction has been investigated to realize the first examples of mono-, di- and trisubstituted calix[4]arene enones.

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