

**SYNTHESIS AND APPLICATIONS OF
CALIX[4]ARENE AND
TETRATHIACALIX[4]ARENE DERIVATIVES**

By

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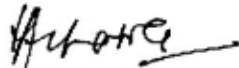
Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled "***SYNTHESIS AND APPLICATIONS OF CALIX[4]ARENE AND TETRATHIACALIX[4]ARENE DERIVATIVES***" being submitted by **Mr. Suneel Pratap Singh** 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.

Suneel Pratap Singh 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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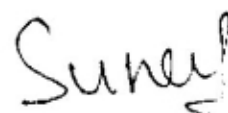
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ABSTRACT

The thesis titled, **SYNTHESIS AND APPLICATIONS OF CALIX[4]ARENE AND TETRATHIACALIX[4]ARENE DERIVATIVES** presents the research work carried out on the synthesis, characterization and applications of some novel calix[n]arene and tetrathiacalix[n]arene derivatives [n=4,6,8]. A number of novel synthetic procedures have been developed and mechanism of the reactions involved have been investigated. The new chemical entities and their conformational geometry has been determined by utilizing various spectroscopic techniques (IR, UV, NMR), single crystal X-Ray and Mass spectral analysis. The accomplished research work has been divided into five different chapters:-

Chapter I of the thesis presents a brief overview of the recent research work published on the conformation, self assemblage and recognition characteristics of calixarene derivatives. The emphasis of this chapter is to explain the salient features of calixarene chemistry relevant to work presented in the thesis and the reference list is not meant to be exhaustive in nature.

Chapter II dwells upon the synthesis of azocalixarenes to understand the role of hydrogen bond assistance in the diazonium coupling reaction of calixarenes and substituted aminopyridines and its role in determining the mechanism the reaction and prediction of the most stable conformation of plausible products. Single crystal structures of some of the synthesized compounds have also been determined to confirm the conclusions drawn from spectroscopic analysis. A study on interaction of some of the synthesized azocalixarenes with various alkali, alkaline and transition metal ions through

UV-VIS spectrometric analysis reveals that some of them are highly selective towards cesium metal ion with enormous potential for future applications

Chapter III deals with the synthesis of calix[4]arene based carboxamide derivatives in diverse conformations, their characterization and reactions with plausible mechanisms involved. The synthesized calix[4]arene carboxamide derivatives have been explored as ionophores for metal ions and as extractants for oxyanions which include chromate and dichromate anions. It is expected that the findings will be useful for development of new molecular receptors for anions.

Chapter IV details the procedures adopted for the synthesis and characterization of new upper rim substituted calix[4]arene based receptors for molecular and ionic recognition. A facile method for regioselective introduction of nitro groups in calix[4]arenes under very mild conditions ($\text{NaNO}_2/\text{aq. HCl}$) has been reported in this chapter. Conformational morphosis of synthesized *p*-nitro-calix[4]arenes derivatives has been examined by variable temperature NMR experiments while X-ray crystallographic analysis of some of the synthesized compounds have been used to explore the formation of molecular complexes with guest molecules and supramolecular arrays of calixarenes. This chapter also describe the synthesis of a series of novel calix[4]arene hydrazone and semicarbazone based neutral receptors for their potential use in anion recognition. The preliminary UV-Visible and ^1H NMR titration experiments revealed that 25,26,27,28-tetrapropoxycalix[4]arene tetra-semicarbazone can recognise H_2PO_4^- through a 1:1 binding-stoichiometry in preference over other anions (Cl^- , Br^- , I^- , HSO_4^- , ClO_4^- and CH_3COO^-).

Chapter V presents the results of studies directed towards understanding of the molecular assemblage and polymorphic modifications of azocalix[4]arenes. In this work, we have achieved a novel conformational morphosis methodology for obtaining different calix[4]arene polymorphs by realigning intermolecular forces through interaction with cesium ion. The study has enabled us to realize the first examples of ‘true’ polymorphs of calix[4]arene derivatives with identical solvent and solvent-substrate ratio. We have also examined the molecular assemblage of another azocalixarene derivatives with the help of spectroscopic techniques (UV-Vis and ^1H NMR spectroscopy) and X-ray crystallography to suggest an intense competition between self assemblage and solvent induced aggregation of calixarenes.

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