STUDIES ON SYNTHESIS AND APPLICATIONS OF SUBSTITUTED CALIXARENES

by

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CERTIFICATE

This is to certify that the thesis entitled ***"Studies on synthesis and applications of substituted calixarenes"*** being submitted by **Mr. Satish Kumar** 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.

Mr. Satish Kumar 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 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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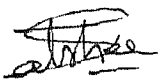

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ABSTRACT

Calixarenes are recently rediscovered well defined macrocyclic cavity containing molecules. They have considerable potential to develop versatile host molecules for recognition of ions and neutral molecules. **Chapter I** of the thesis gives an overview of synthesis, reactions and applications of calixarenes with special emphasis on the findings reported during the past five years.

The thesis titled "***Studies on synthesis and applications of substituted calixarenes***" mainly deals with the recent work carried out in our laboratory on the chemistry of calixarenes particularly on the synthesis of *p*-nitro, *p*-sulphonato, *p*-bromo, *p*-acyl calixarenes through one pot reactions. New one pot methods developed for the synthesis of *p*-nitro, *p*-sulphonato, *p*-bromo, *p*-acyl, and *p*-thiomethylmethyl calixarenes have been described in **Chapter II**. The procedures utilized in the synthesis of these compounds are based upon well established mechanisms of *ipso*-substitution in aromatic compounds. The products have been analyzed by IR, NMR, UV, and X-ray crystallography studies (*p*-nitrocalixarenes derivatives only).

During the present work *ipso*-nitration of *p-tert*-butylcalixarenes has also been examined through Ac_2O/HNO_3, $AcOH/HNO_3$. cerium(IV) ammonium nitrate, $KNO_3/AlCl_3$ and KNO_3/AcOH. It has been observed that although *p*-nitrocalixarenes are obtained in all these cases, HNO_3/AcOH methodology gives the best results in terms of yield and purity of the products. It has been observed that cerium(IV) ammonium nitrate in acetone/acetonitrile can also be used for *ipso*-nitration of calix[n]arenes

The synthesized *p*-nitrocalix[n]arenes were reduced with several reducing agents viz. Sn/HCl, Zn/HCl, $NaBH_4$/ethanol/$CuSO_4$, Fe/HCl, NaSH/Methanol to determine the best conditons for their reduction. *p*-Aminocalixarenes obtained were diazotized and coupled with simple phenols (e.g. phloroglucinol, resorcinol, 2-naphthol) to produce chromogenic calix[n]arenes. In an analogous way, water soluble sulphonated calix[n]arenes were obtained through *ipso*-sulphonation. Likewise *p*-acylated calixarenes were prepared by treatment of acyl chlorides with *p-tert*-butylcalix[n]arene in the presence of $AlCl_3$. These reactions when carried out in dichloromethane and nitrobenzene produced facile routes to different acylated

calixarenes. The products obtained were either *p*-acyl calix[n]arene esters or *p*-acyl calix[n]arenes depending on the reaction conditions.

The *p*-acylation reaction was successful with anisoyl chloride and benzoyl chloride but lower yields were obtained with 4-nitrobenzoyl chloride and 2,2-dimethylpropanoyl chloride. However, the reaction failed with propanoyl chloride and acetyl chloride. Rational explanations for observed findings have been proposed likewise.

Ipso-bromination reactions were carried out with $Br_2/CH_3COOH/Fe/CH_2Cl_2$, NBS/CCl_4 or $CHCl_3$, acetone, ethylmethylketone. It was determined that $Br_2/CH_3COOH/Fe/CH_2Cl_2$ gives *p*-bromosubstituted calix[n]arenes, while NBS/CCl_4 under reflux gives bridge substituted bromo calix[n]arenes.

The *p*-methylthiomethyl ether derivatives of calix[n]arenes were synthesized with calixarenes having free para position and $SOCl_2$/DMSO.

The synthesized calixarenes were examined for their interaction with small organic compounds (e.g., aliphatic amines, aromatic amines, ammonium and alkali metal salts and phenols) and the results have been compiled in **Chapter III**. Likewise cyclic voltammetric studies of *p*-aminocalix[n]arene to examine reversibility and redox potential has been carried out. Interactions of synthesized methylthiomethyl ether with transition metal ions (e.g., Cd^{2+}, Hg^{2+}, Pd^{2+} etc.) by UV-vis spectroscopy has also been incorporated in this chapter. Host-guest complexation in some cases has been examined and established by ^{1}H-NMR, UV-vis and Job's plots.

Chapter IV describes the synthesis and applications of calixarene derivatives, which are covalently linked to modified polyacrylonitrile. The hydrolyses of polyacrylonitrile was carried out by H_2O_2/aq. NH_3, and aqueous sodium hydroxide and the carboxyl group thus generated was converted to polyacroyl chloride, which were condensed with hydroxycalix[n]arenes in the presence of NaH or $AlCl_3$. The modified polymers obtained were characterized by NMR, IR, SEM, TGA and DTA data.

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