ANION RECOGNITION PROPERTIES OF SOME NOVEL IMIDAZOLIUM AND AMIDE-BASED RECEPTORS

by

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DEPARTMENT OF CHEMISTRY

Submitted

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This thesis is dedicated to Maa Sharda

CERTIFICATE

This is to certify that the thesis entitled, **"Anion Recognition Properties of Some Novel Imidazolium And Amide-Based Receptors"**, being submitted by Miss. Anamica Tripathi, to the 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. Miss. Anamica Tripathi has worked under my guidance and supervision and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results embodied in this thesis have not been submitted in part or in full, to any other University or Institute for award of any degree or diploma.

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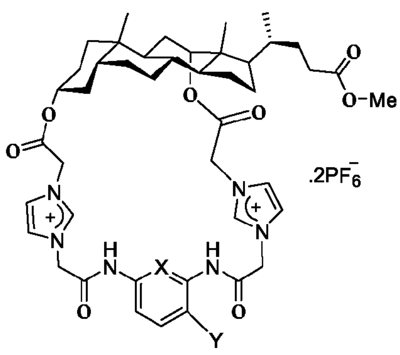
ABSTRACT

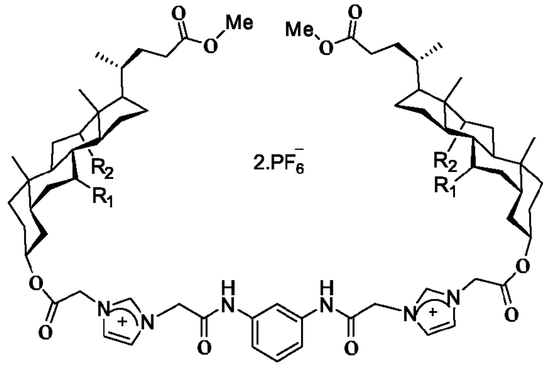
Anions recognition has now become an important area of research. Consequently, various analytical methods are developed for anion recognition. Recently, visual detection methods like color change, gel formation/collapsing and precipitation have attracted much attention for anion recognition. Besides, use of anions as a template to synthesize various mechanically-interlocked molecular architectures such as rotaxanes and catenanes are also gaining research interest due to the presence of such assemblies in biological systems.

The present thesis deals with the synthesis of steroidal and non-steroidal receptors containing imidazolium and amide moieties and studies of their anion recognition properties through gel and precipitate formation. Chiral receptors having amide moieties were also synthesized and their enantioselectivity for chiral guests were determined by gel and precipitate formation and ^{1}H NMR titration. The enantioselectivities of some chiral receptors were determined by colorimetric changes of their silver nanoparticles in the presence of chiral guests. It also focuses on the study of anion-templated pseudorotaxane formation. The thesis has been divided into four chapters.

The first chapter presents a brief literature survey on anion receptors chemistry. The second chapter describes the synthesis and anion binding properties of steroidal and non-steroidal receptors having imidazolium and amide moieties. The following steroidal cyclic (**I-III**) and acyclic receptors (**IV-VI**) having imidazolium and amide moities have been synthesized.



I : X= CH, Y= H
II : X= N, Y= H
III : X= CH, Y= -NO_2

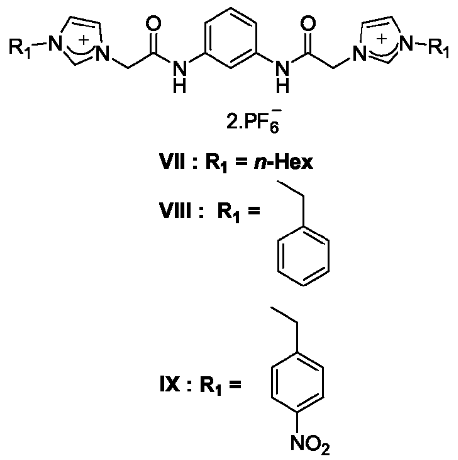


IV : R_1 = H; R_2 = H
V : R_1 = H; R_2 = -OH
VI : R_1 = -OH; R_2 =-OH

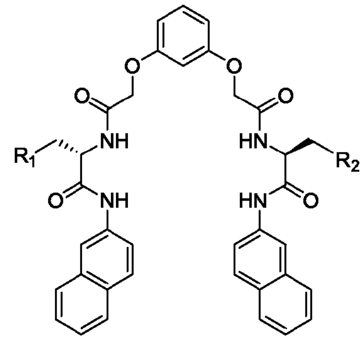
The anion recognition properties of cyclic receptors **(I-III)** with anions were studied and it was found that receptor **I** showed organogel formation in the presence of only HSO_4^- ion, whereas other cyclic receptors **II** and **III** did not show gel formation with any anion. The anion binding properties of the cyclic receptors **(I-III)** by UV-Vis titrations showed that receptors **I** and **III** were highly selective for Cl^- ion, whereas receptor **II** showed higher selectivity for oxoanions (HSO_4^- and $H_2PO_4^-$ ions), especially for HSO_4^- ion (6000 M^{-1}).

The anion recognition properties of acylic receptors **(IV-VI)** were also carried out and it was found that the only receptor **IV** with lithocholic acid framework showed gel formation behavior in the presence of anions HSO_4^- and $H_2PO_4^-$. Further, anion binding studies of these acyclic receptors by ^1H NMR titrations carried out and revealed very low binding affinity for anions.

The anion binding properties of non-steroidal acyclic receptors **(VII-IX)** having amide and imidazolium moieties were also studied. These compounds showed precipitate formation in the presence of $H_2PO_4^-$ ion, selectivity, even in the presence of other anions.



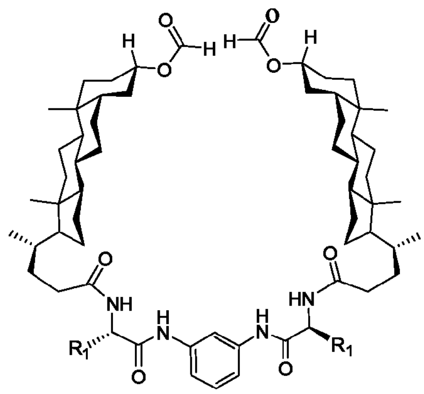
The third chapter deals with the synthesis of chiral receptors **X-XI** and studies of their chiral recognition properties towards anions of α-hydroxy and *N*-tosyl α-amino acids.



X: **R$_1$** = -CH$_2$Ph
XI: **R$_1$** = -CH(CH$_3$)$_2$

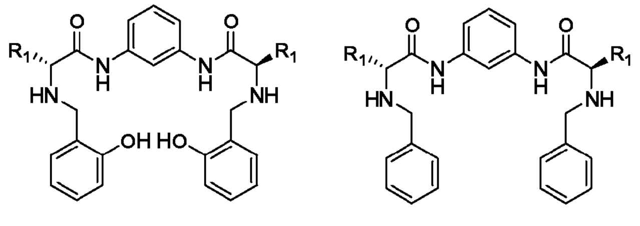
It was found that receptors **X** and **XI** formed a gel and precipitate, respectively, with TBA salt of *R*-mandelic acid, whereas with *S*-mandelate the solutions of both receptors remain clear. Further, these receptors also formed a partial-gel and precipitate, respectively, with TBA salt of *N*-tosyl-D-valine. For other amino acids (TBA salt of *N*-tosyl phenylalanine and alanine), the partial-gel or precipitate formation was observed with both the enantiomers. The enantioselective formation of a gel and precipitate by these receptors **X** and **XI** can be used as a visual method of enantioselective recognition for TBA salts of *R*-mandelic acid and *N*-tosyl-D-valine.

Chiral receptors **XII** and **XIII** having steroidal frameworks were also synthesized and their chiral recognition properties were examined by ^{1}H NMR titrations. These receptors showed enantioselectivity for TBA salt of *N*-tosyl L-phenylalanine and L-valine.



XII: R_1 = $-CH_2Ph$
XIII: R_1 = $-CH(CH_3)_2$

In addition, the chiral anion recognition properties of non-steroidal chiral receptors **XIV** and **XV** having amide, amino and phenolic groups were studied by ^{1}H NMR titrations. These receptors showed enantioselectivity towards enantiomers of TBA salt of *N*-tosyl-D-phenylalanine and D-valine with increased binding affinity. For TBA salts of α-hydroxy acid (mandelic acid and tartaric acid), only receptor **XV** showed enantioselectivity with the anion of D-tartaric acid.



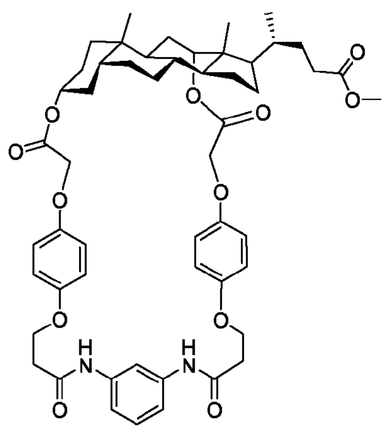
XIV = $-CH_2Ph$
XV = $-CH(CH_3)_2$

XVI = $-CH_2Ph$
XVII = $-CH(CH_3)_2$

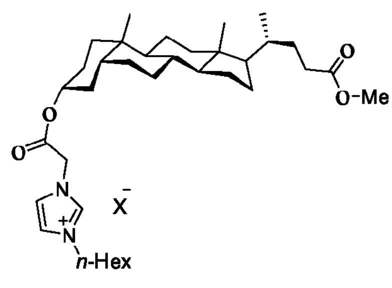
To evaluate the effect of –OH on binding of chiral guest molecules by receptors **XIV** and **XV**, receptors **XVI** and **XVII** with phenyl units were synthesized. The ^{1}H NMR titrations data revealed no binding affinity of receptors **XVI** and **XVII** for chiral anions, presumably due to intramolecular hydrogen-bonding of the amide protons with amino groups.

Recently, metal nanoparticle-based sensing of chiral guests has received considerable attention, because it shows much enhanced sensitivity and provides their fast colorimetric detection even at low concentration. Hence, the synthesis of silver nanoparticles stabilized with chiral receptors **XII-XV** and studies of their colorimetric enantioselectivity for TBA salts of chiral guests were carried out. The AgNPs were synthesized by the reduction of $AgNO_3$ by visible light in the presence of these compounds **XII-XV**. The nanoparticles formed by these receptors showed distinct color changes with enantiomers of α-amino acids and tartaric acid, and can be used for their visual enantiomeric recognition.

The fourth chapter deals with the synthesis of steroid-based wheel molecule **XVIII** and ion-pair threads **XIX-XXI** and study of their anion-templated pseudorotaxane formation. Although, the NMR titration and 2D NOESY experiments, showed the binding of the wheel molecule **XVIII** with ion-pair threads **XIX-XX** having Br^- and Cl^- ions, there was no clear evidence of the formation of the pseudorotaxane.



XVIII



XIX: X = Br^-
XX: X = Cl^-
XXI: X = PF_6^-

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