STUDIES ON SYNTHESIS AND CHARACTERISATION OF ARYL ETHERS

A

Thesis submitted

In partial fulfillment of requirement for the

Degree of Master of Science in Chemistry

Submitted by

Gagandeep Bansal

(Regd.No. 300902006)

Supervisor

Dr.Manmohan Chhibber

Assistant Professor

School of Chemistry and Biochemistry

Thapar University

Patiala 14700

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Dated: July 15, 2011.

Gagandeep

Gagandeep Bansal

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled "Studies on Synthesis and Characterization of Aryl ethers", in the partial fulfillment of the requirements for the award of the degree of Masters of Science (Chemistry), School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own work during the period of January to June 2011, under the supervision of Dr.Manmohan Chhibber. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Date: 15 July 2011

Gagandeep

Gagandeep Bansal

This is to certify that the above statement made by candidate is correct and true to the best of our knowledge.

Dr.Manmohan Chhibber

Project Supervisor,

Assistant Professor (SCBC),

Thapar University.

Susheel Mittal 15/7

Dr. Susheel Mittal

Head, SCBC,

Thapar University.

Certificate

This is to certify that the project entitled "**Studies on Synthesis and Characterization of Aryl Ethers**", being submitted by Mr. Gagandeep Bansal in partial fulfillment of the requirement for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Manmohan Chhibber and that no part of this project has been submitted for the award of any other degree by me.

Dr. Manmohan Chhibber
Assistant Professor,
Thapar University, Patiala

Dr. Susheel Mittal
Head,
School of Chemistry and Biochemistry,
Thapar University, Patiala

Dr. S.K Mohapatra
Dean, Academic Affairs,
Thapar University, Patiala

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Introduction

Introduction

Nature has played and continues to play a major role in development and progress of organic chemistry. All life processes are essentially achieved by arrays of molecules working together in synchronization rather than by discrete molecules acting in isolation. There are a number of supramolecular assemblies in nature. These biological assemblies often provide highly ordered microenvironments and specifically integrated functions. Enzymes and biomembranes are typical examples which have survived in long-term evolution. They include a variety of organic and inorganic components such as proteins, cofactors, lipids, metal cations, ionophores and other functional elements. Molecular recognition is an important term not only in natural but also in artificial systems. Artificial supramolecular assemblies may have advantages over biological assemblies: facile synthesis, high physical stability and versatile molecular structure [1].

Conceptually, supramolecular chemistry can be broadly classified into host -guest chemistry and self assembly [2]. The former involves species combining with one another in small integer ratios, comprising a host that specifically accommodates a guest, thus leading to molecular recognisation.The. According to Cram [2] the host component is a molecule or ion whose binding sites converge in the complex. The guest component is any molecule or ion whose binding sites diverge in the complex. The latter describes the building of noncovalent arrays of defined geometry from specifically engineered molecular components. Supramolecular chemistry is therefore, the chemistry of noncovalent bound species and noncovalent interactions play an important role in self assembly and stabilization of supermolecules [3]. The forces encountered in supramolecular chemistry are hydrophobic comlexation, electrostatic interactions, Vander wall forces, hydrogen bonding, aromatic interactions and charge transfer interactions [4, 5]. Unlike covalent force, the above mentioned forces are much weaker and easily disrupted. Thus next goal is the establishment of general working principles for the design of supramolecular function based on specific recognition. Since crown ether chemistry provides a useful strategy for molecular recognition, its combination with molecular assembly technology offers many opportunities in this new and fascinating field.

Ever since the report of discovery of the first synthetic ionophores by C.J.Pedersen [6, 7, 8] in 1967, and more so since the awarding of noble prize [9] in 1987 to Charles Pedersen, Donald Cram and Jean-Marie Lehn, the pioneers of this field, for synthesizing molecules and compounds with cavities and cages within which metal ions and other molecules could be bound, there has been impetus to synthesise more and more novel structures with fascinating micro and macroscopic architectures endowed with novel functions.

The work presented in this synthesis relates to synthesis of Aryl Ethers Based macromolecules that may be further derivatized to capture metal ions.

Review of Literature

Literature Review

Supramolecular Chemistry also known as Host–Guest chemistry involves two or more molecules, a "host" and a "guest' involved in non-bonding interactions to form a supramolecular complex. There are numerous host molecules reported in literature that can form supramolecular complex with different guest molecules. These supramolecular complexes finds numerous applications in various fields such as receptors for neutral and ionic species [10, 11], in molecular recognition [12], separation procedures [13, 14], as a mimic of biological processes [15], as catalysts [16], in research for artificial enzymes [17], in the design of sensors for determination of trace amount of metals [18] and in aspect of environment protection [19]. For example calixarene complexes with cesium [20] as well as with lanthanides [21] and actinides [21] are aimed at the management of nuclear waste material.

A brief literature review of different host molecules and diphenyl ethers is presented in following lines. In the mid-1960's, Charles Pedersen reported a new class of complexing agents that were capable of binding with alkali metal ions. The first molecule that was accidently discovered by Charles Pedersen was the by product in an attempt for preparing complexing agent for divalent cations [6] by linking two catecholes through one hydroxyl group of each molecule**.** This compound was named as dibenzo-18-crown-6 [8] **(Figure 1).**

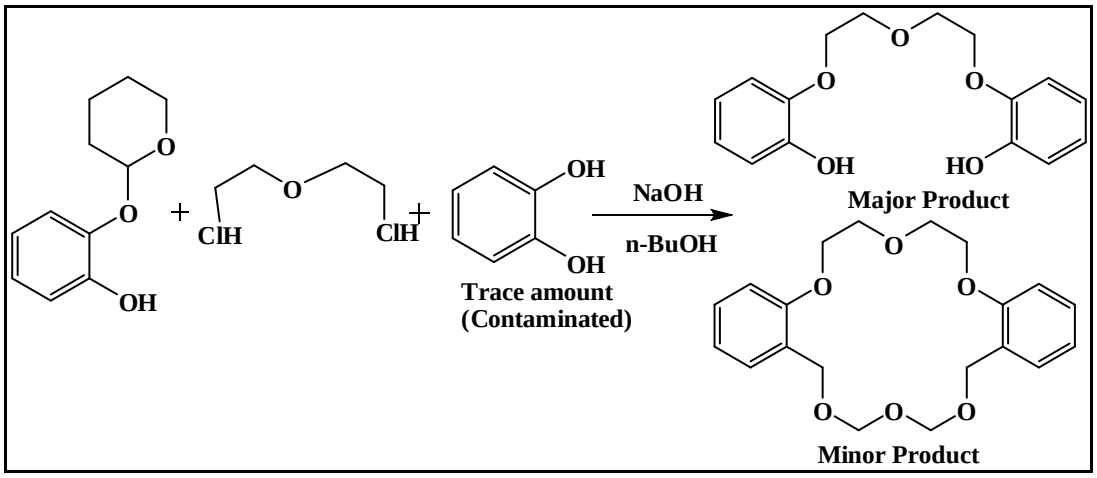


Figure (1): Accidental synthesis of first crown ether by Pederson [8].

In 1978 Vogtlek and Weber reported a new class of acyclic host [22] with pendant binding sites and named them as 'Podand'. Podand host generally exhibit less cation affinity than their cyclic analogs, as a result of lack of preorganisation, but they can adopt similar wrapping conformation to crown ethers in presence of suitable metal ions. Vogtle and Weber reported a variety of Podand ligands such as **(Figure 2)** having quinolene end groups [23].

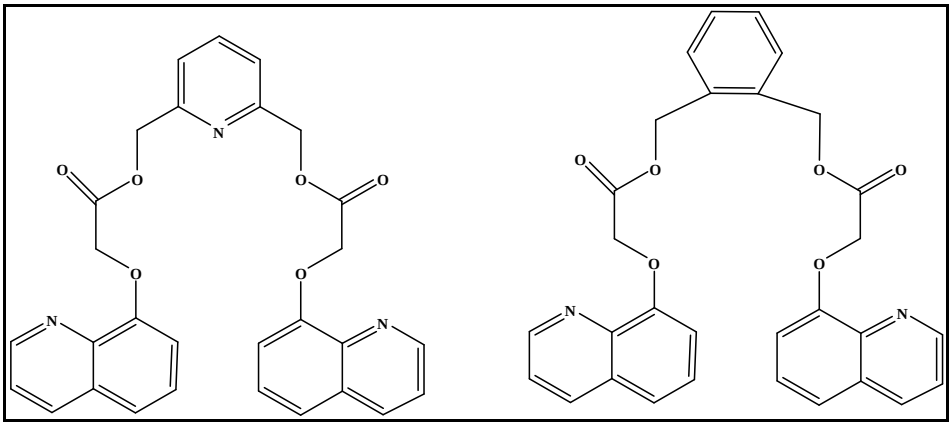


Figure (2): Acyclic hosts (Podand)

Another kind of host molecule reported in literature are 'Calixarenes'. Calixarene [24] is a macrocycle or cyclic oligomer based on a hydroxyl alkylation product of phenol and aldehydes. In 1940's Zinke and Ziegler discovered the base induced reaction of p-alkyl phenols with formaldehyde and reported the synthesis of cyclic oligomers **(Figure 3).** There are two places (phenolic hydroxyl groups and p-positions) which can be modified in calixarenes. Kumar et al [25] reported the single step procedure for prepration of bromocalixarenes and methylene bridged calyx[n]arenes.

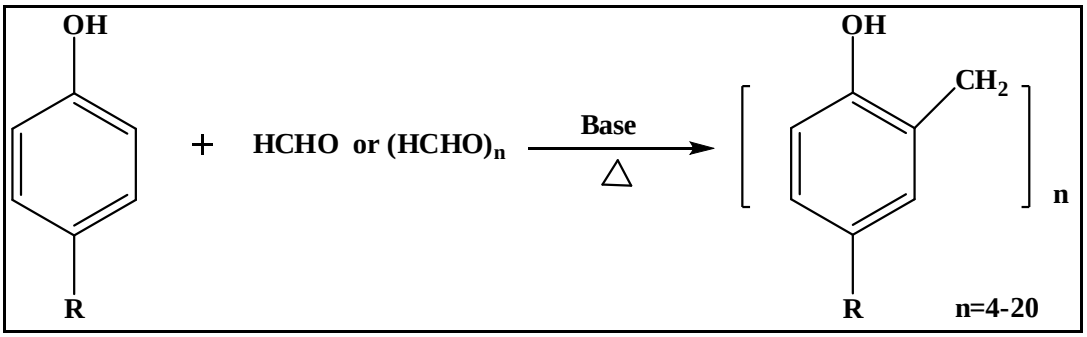


Figure (3): One step synthesis of Calix[n]arenes**.**

Another host molecule reported in literature is Thiacalix[n]arenes. Sone et al. [26] reported the first synthesis of p-tert-butylthiacalix[n]arenes 2_4 in which all four methylenes of parent calix were replaced with sulfur atoms **(Figure 4)**. However, tedious stepwise treatment of p-tertbutylphenol with SCl_2 afforded only poor yield of the desired product.

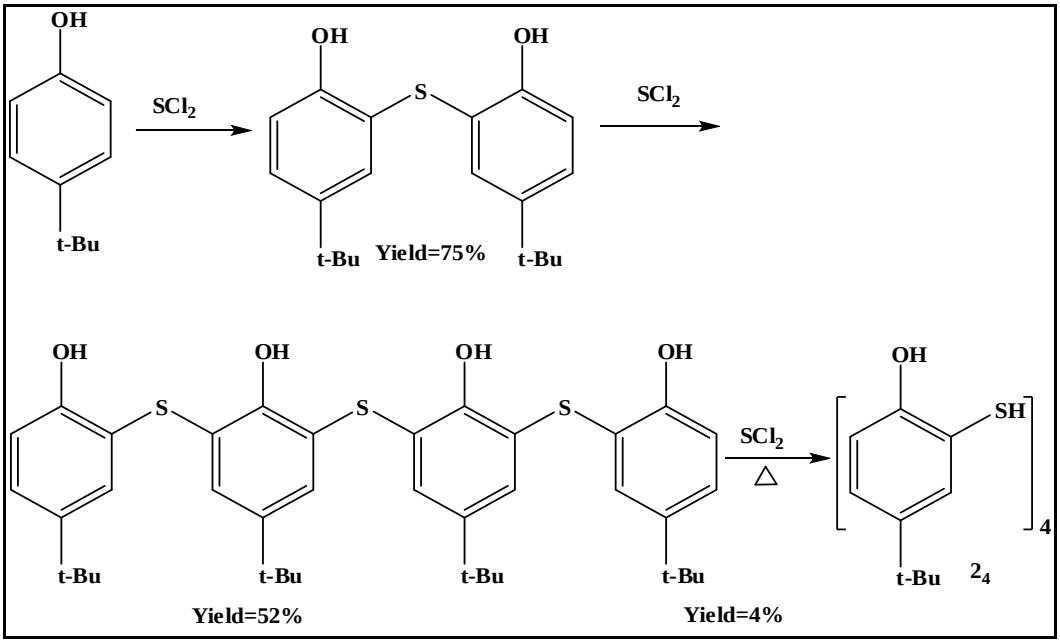


Figure (4): Stepwise synthesis of p-tert-butylthiacalix [4] arene (**2_4**) from p-tert-butyl phenol. [26].

Kumangi et al [27] reported the one step facile synthesis of p-tert-butylthiacalix [4] arene **(Figure. 5).**

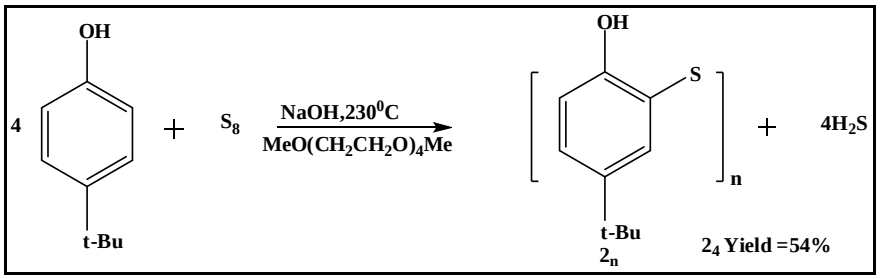


Figure (5): Facile one-step synthesis of p-tert-butylthiacalix [4] arene.

Diphenyl ethers are organic compound with formula $O(C_6H_5)_2$. Diphenyl ethers are structural elements found in biological toxins in the environment such as dioxins as well as in medically useful antibiotics such as Vancomycin. Derivatives of diphenyl ethers can serve as an intermediate for the synthesis of biological active molecules.

Diphenyl ethers can be prepared by copper catalysis based cross coupling reaction of aryl halides with various nucleophiles. Traditional copper catalyzed reactions were pioneered by work of Firtz Ullmann and Irma Goldberg in the early 1900's [28]. These reactions involve the coupling of aromatic halides with amines and phenols, for synthesis of aryl ethers and aryl amines (**Figure 6.**).

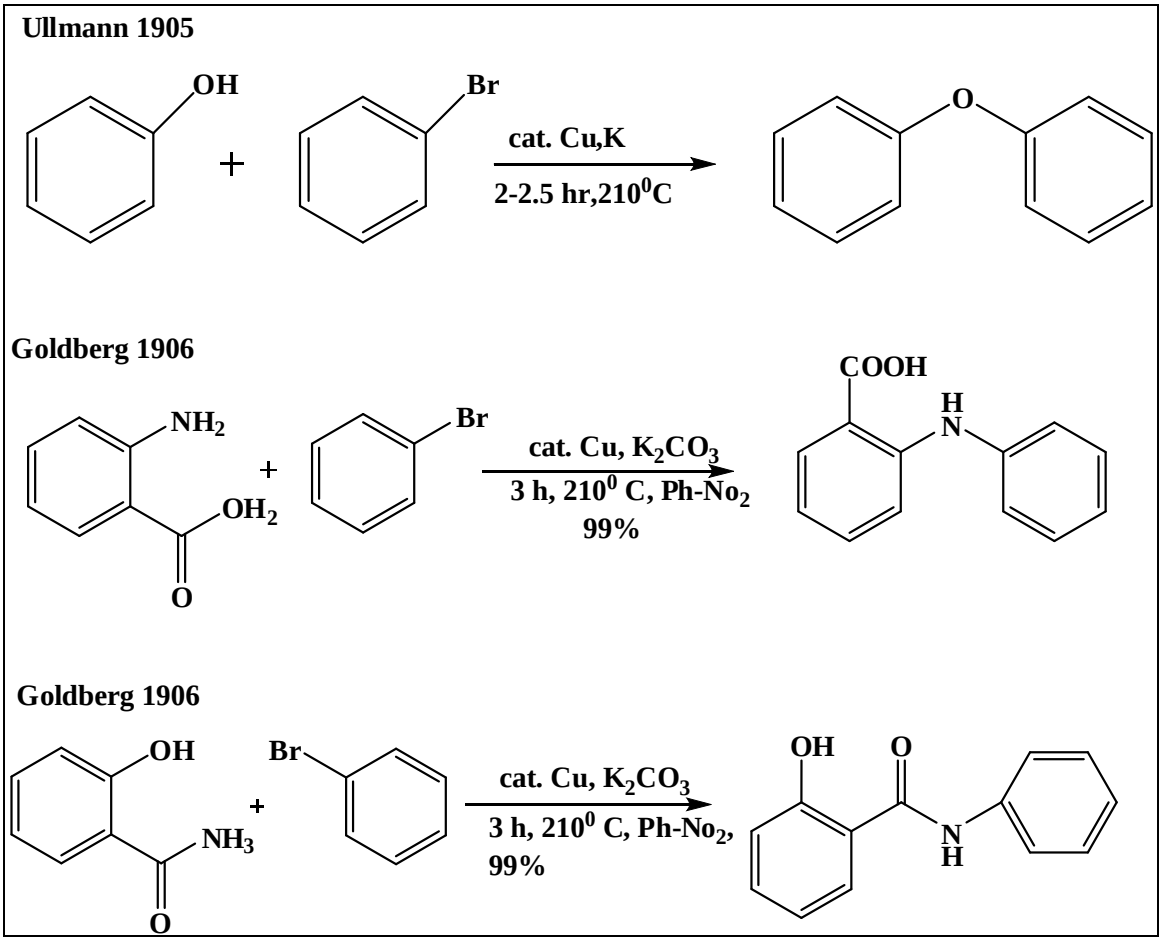


Figure -6: Examples of Ullmann and Goldberg coupling reactions [28].

The term, Ullmann "condensation" is used to describe the copper –catalyzed reaction of aromatic halides with phenol salts or anilines to synthesize aryl ethers and amines. The terminology, Ullmann "coupling", however, is used to describe the synthesis of Biaryls from aromatic halides.

Typical reaction conditions of Ullmann reaction suffers the disadvantages of high reaction temperatures, the used of toxic solvents such as HMPA, and intolerance to a wide-variety of functional groups [29, 30]. The biggest drawback of the classical Ullmann reaction arises from inconsistent results obtained from the use of different copper sources.

The pioneering studies by Weingarten [31], Cohen [32, 33, 34], Van Koten [35], Bowman [36], and Paine [37] established that the active catalytic species in the copper-catalyzed Ullmann coupling is Cu (I).

More importantly, Buchwald reported the coupling of aryl bromides with various phenols, using a soluble copper salt, copper (I) trifluoromethylsulfonate as a *catalyst* with ethyl acetate and 1-napthoic acid as additives in 1997 [38] (**Figure-7**).

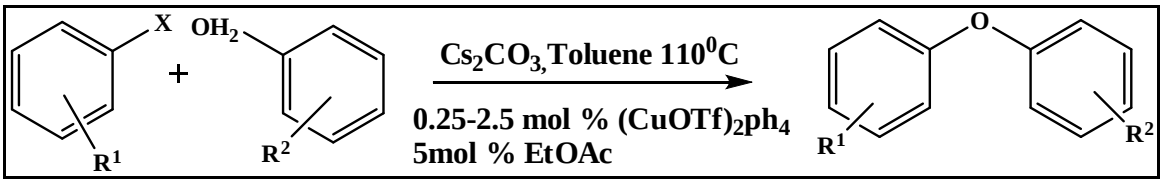


Figure-7: Buchwald's solubilization of copper by using trifluoromethylsulfonate.

The ether linkage of diphenyl ethers can be cleaved by slowly heating diphenyl ether with dilute sodium hydroxide at 300°C [39], with aqueous sodium carbonate [40], or with aqueous sodium phenoxide solution under pressure [41], or by fusing with potassium hydroxide at 300°C [42]. Concentrated sodium hydroxide cannot cleave the ether linkage. The product obtained on cleavage of ether linkage is phenol or phenoxide.

Diphenyl ethers are used as a heat transfer medium due to its extraordinary heat stability. A eutectic mixture of 73.5 percent diphenyl ether and 26.5 percent of diphenyl (Dowtherm A) [43] and a eutectic mixture of 85 percent of diphenyl ether and 15 percent of naphthalene (Dowtherm B) are recommended for this purpose in the temperature range of 230-400°C [44].

Presently we are synthesizing diphenyl ethers derivatives phase transfer catalyst (**Figure - 8**).

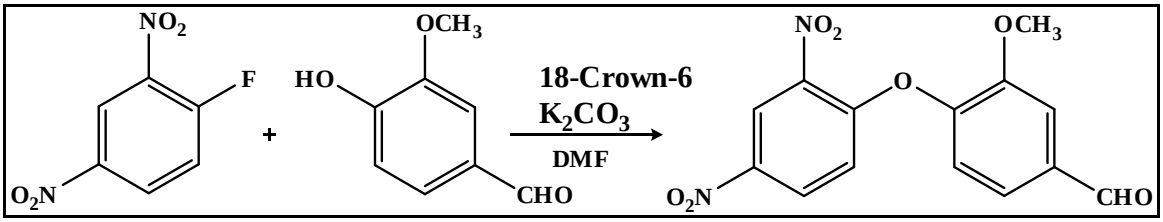


Figure-8: Synthesis of diphenyl ether using phase transfer catalyst.

Diphenyl ether derivatives can be a possible candidate that can display liquid crystal properties. For a molecule to behave as liquid crystal it should have rigid central region and ends that are slightly flexible. Florjanaczyk et al [45] reported that biphenyl esters can display liquid crystalline properties. Liquid crystals may be nematic, smectic or cholesteric; depending on the arrangement of the molecules they are also birefringent, meaning that it possesses two different indices of refraction. One index of refraction correspondents to light polarized along the director of the liquid crystal, and the other is for light polarized perpendicular to the direction. Some of the molecules that acts as liquid crystals are shown in (**Figure-9.)**

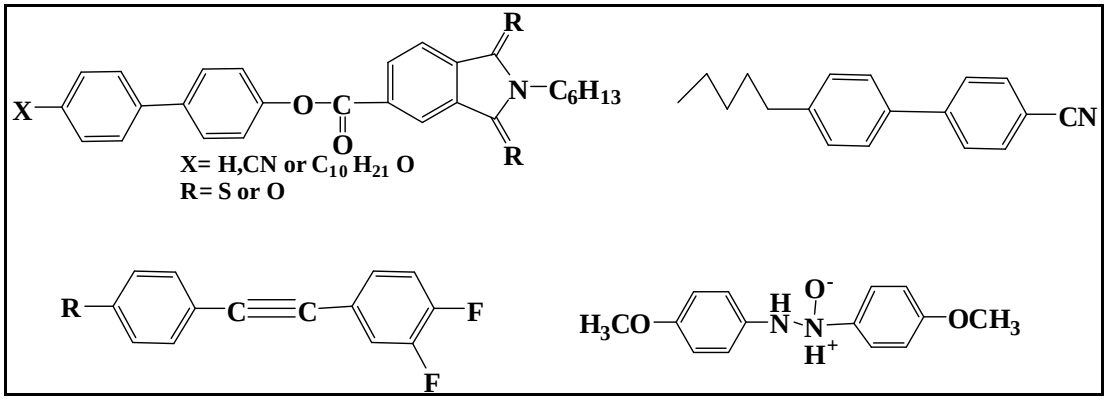


Figure-9. Molecules that can act as liquid crystals.

Some of the derivatives of diphenyl ethers can be used to capture metal ions like crown ethers. These derivatives have a cavity which can bind with the specific metal ion. Specificty of binding is determined by the size of metal ion and cavity and interaction between metal ion and cavity.

The work presented in this thesis relates to synthesis of aryl ether based macromolecules that may be further derivatized to capture metal ions. An attempt has also been made to attach a long flexible chain to diphenyl ethers.

Materials and Methods

MATERIALS AND METHODS

A. Source of reagents and analytical facilities

All the reagents used were procured from Aldrich. LR grade solvents were used for the synthesis and procured from S.D. Fine-Chem. Limited, Mumbai, India. The solvents were distilled before use. NMR Spectral analysis was performed on BRUCKER ADVANCE 2 400MHz spectrophotometer installed at SAIF, Punjab University, Chandigarh.

a. Experimental

4-(2',4'-Dinitrophenoxy)-3-methoxybenzaldehyde (Compound-3):1-Fluoro-2,4 dinitro benzene (1.3 ml,10.5 mmol) was taken in 250 ml round bottom flask containing 10 ml of DMF. To this added K_2CO_3 (2.8 g, 20.9 mmol), 3-methoxy-4-hydroxy benzaldehyde (2.0g, 13.2mmol) and18-Crown-6 (25 mg, 0.1mmol).The mixture was stirred at room temperature for 12 h.After the reaction was complete TLC monitoring was done with ethyl acetate: pet ether (25:75) . The reaction mixture was diluted with CH_2Cl_2 (50 ml), washed with water (25ml), 1N NaOH solution, water (until neutral to litmus paper) and dried over sodium sulphate. The reaction mixture was subjected to rotary evaporator to evaporate organic solvent. Evaporation of organic solvent gives a yellow solid that matched the already analyzed pure compound available in lab.

4-(2',4'-Dinitrophenoxy)-3-hydroxybenzaldehyde (Compound-4): Compound 3 (200 mg, 0.6 mmol) was taken in a 250 ml round bottom flask. To this acetic acid (10 ml) and 48% HBr (1ml) was added .The reaction mixture was refluxed and monitored using TLC. For TLC small amount of reaction mixture was then in appendof and to this added concentrated solution of sodium bicarbonate to neutralize acid and then added few drops of ethyl acetate.TLC monitoring was done by taking sample from ethyl acetate layer.

After the reaction is complete the reaction mixture was cooled acetic acid evaporated using rotator evaporator and vacuum pump. Water was added to dissolve the contents and

the aqueous layer was extracted with ethyl acetate (3x 10 ml).The combined organic layers were dried over Na_2SO_4.Evaporation of organic solvent gives the crude product. The crude product was purified using SiO_2 column chromatography and solvent (Pet ether/ethyl acetate=75:25).Yellow colored product was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5-7.7 (m, 2H), 6.9 (m, 2H), 7.8-7.9 (m, 1H), 7.9 (m, 1H), 9.8 (s, 1H); ^{13}C NMR (DMSO): δ 117.18, 117.85, 121.47, 122.96, 128.66, 129.02, 129.91, 138.12, 140.22, 140.77, 154.74, 155.31, and 189.22.

3,4-bis (2,4-dinitrophenoxy)benzaldehyde (Compound-5): Compound 4 (200 mg, 0.42 mmol) was taken in a 250ml round bottom flask. To this added 1-fluoro-2,4 dinitrobenzene (1.3 ml, 10.5mmol), DMF (10ml), 18-crown-6 (25mg,0.1mmol) and K_2CO_3 (2.8 g, 20.9 mmol).The reaction mixture was refluxed as 80^0C for 10 hours. After the reaction was completed TLC monitoring was done with ethyl acetate: pet ether (25:75). The reaction mixture was diluted with CH_2Cl_2 (50 ml), washed with water (25ml), 1N NaOH solution, water (until neutral to litmus paper) and dried over sodium sulphate. The reaction mixture was subjected to rotary evaporator to evaporate organic solvent. The crude product was purified using SiO_2 column chromatography and solvent (Pet ether/ethyl acetate=75:25).Light yellow colored product was obtained**.** **^{13}** C NMR ($CDCl_3$) δ 112.62, 112.65, 116.70, 116.78, 117.19, 117.25, 120.42, 120.87, 127.60, 128.18, 133.51, 133.80, 141.21, 141.56, 143.95, 145.84, 146.39, 146.75, 189.63.

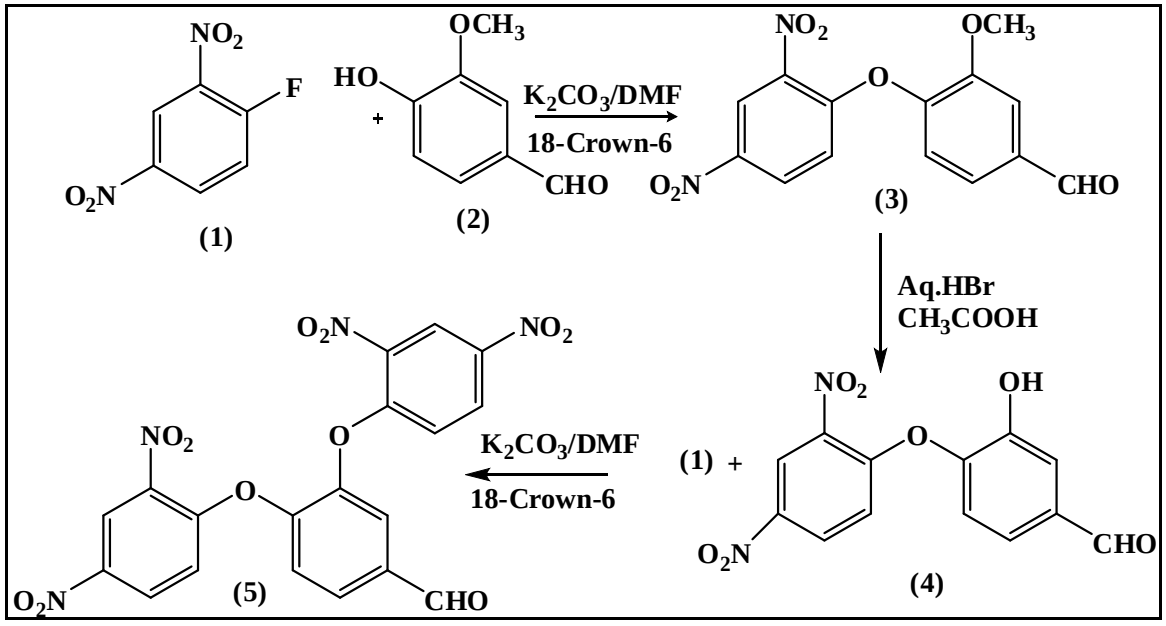
Attempted synthesis of N-(4-(2,4-dinitrophenoxy)-3-methoxybenzylidene)octyl amine : Compound 4 (200mg, 0.6 mmol) was taken in a 250 ml round bottom flask containing methanol (10ml). To this added (154mg, 1.2mmol) octyl ammine. The reaction mixture was heated under reflux for 2 hours. After the reaction was completed TLC monitoring was done ethyl acetate: pet ether. Methanol was evaporated using rotary evaporator. Three product were observed in TLC.The major spot was isolated using silica column chromatography and characterize by ^{1}H NMR that indicate the compound to be 2,4-dinitrophenyl octyl amine.**Figure (13)**

Results and discussion

A. Synthesis and characterization of Aryl ethers for supramolecular assembly

The chemistry of crown ethers is very well studied. Crown ethers are generally alkyl ethers with one or two aromatic rings in the crown sometimes. The study of crown ethers where aliphatic chain is replaced by aromatic rings is so extensively studied. This part of the work deals with the synthesis of aryl ethers motifs the can be developed into a crown so that they can be use to capture metal ion.

A Triphenyl ether moiety was synthesized in two steps starting with 2,4-dinitrofluoro benzene (1) also known as Sanger's reagent. It was made to react with vanillin (2) by Nucleophilic aromatic substitution in the presence of a mild base and DMF at room temperature.18-Crown-6 was used as a phase transfer catalyst. Any unreacted vanillin was removed by washing with aqueous NaOH. Since the vanillin was used in excess no Sanger's reagent was seen in the product that appeared as a single spot in TLC when compared with authentic sample present in the lab.



Compound (3) was converted into corresponding hydroxy by treatment with aqueous HBr in presence of acetic acid by refluxing. Progress of the reaction was monitored using

thin layer chromatography in a solvent system ethyl acetate and pet ether (1:9), that showed the spots of starting material and product with considerable difference in Rf values. Removal of solvent under reducer pressure followed by washing with water gives pure product (4).The ^{1}H and ^{13} C NMR of the compound gave no peak due to –OCH3 that was present in the precursor compound (3).**Figure –10a,10b.**

The synthesis of Triphenyl ether that is compound (5) was carried out using reagents same as those taken for the synthesis of compound (3).However the reaction mixture required refluxing at 800c for 8 hrs. Possible due to stearic hindrance of ortho position. The usual workup followed by column chromatography gave the pure product that has compatible ^{1}H and ^{13}C NMR. The Carbon in ^{13}C spectra due aldehydes appear at 186.9.All other 18 aromatic carbons were observed in the region of 112.6- 146.7.

(Figure –11)

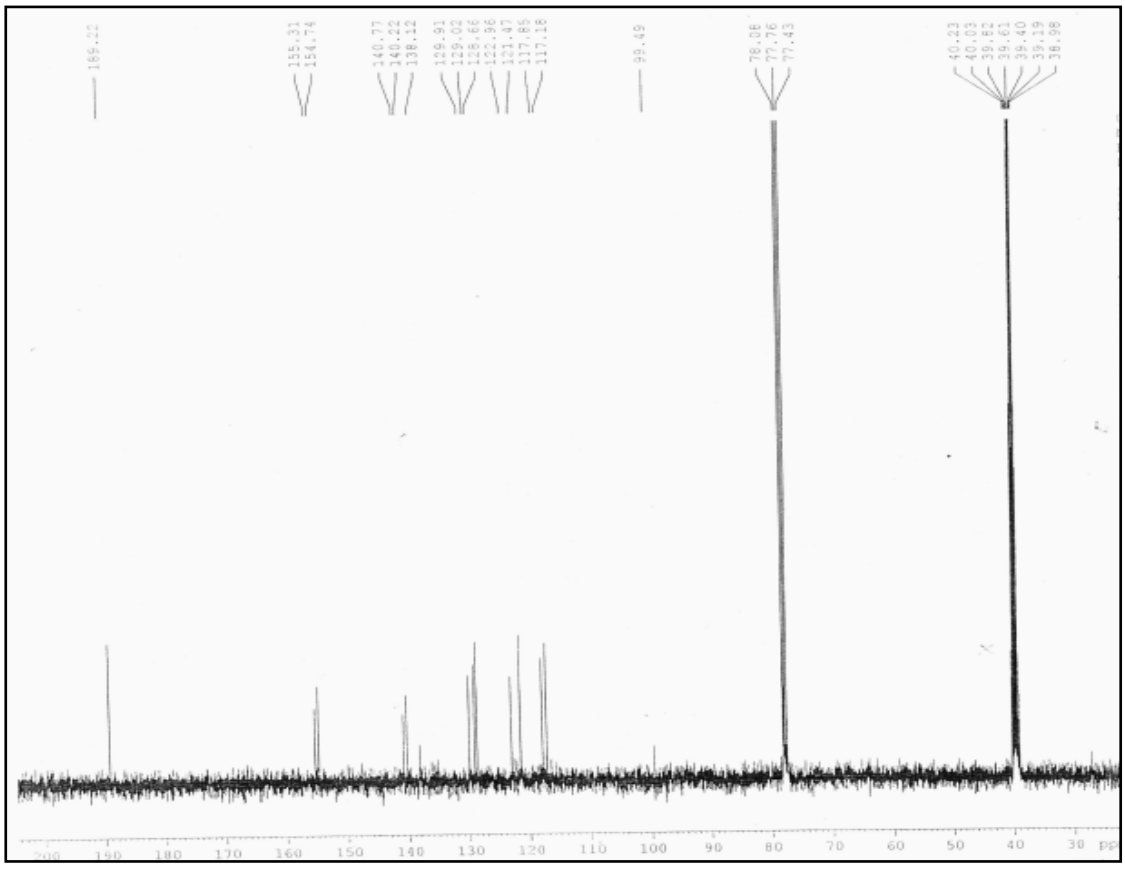


Figure (10a)

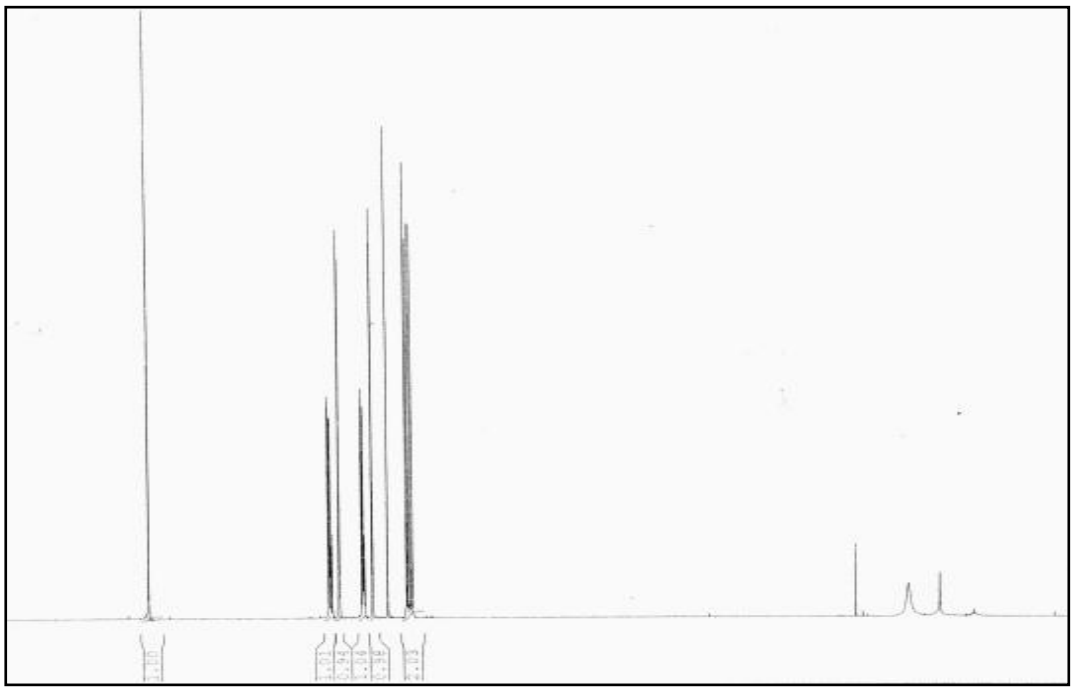


Figure (10b)

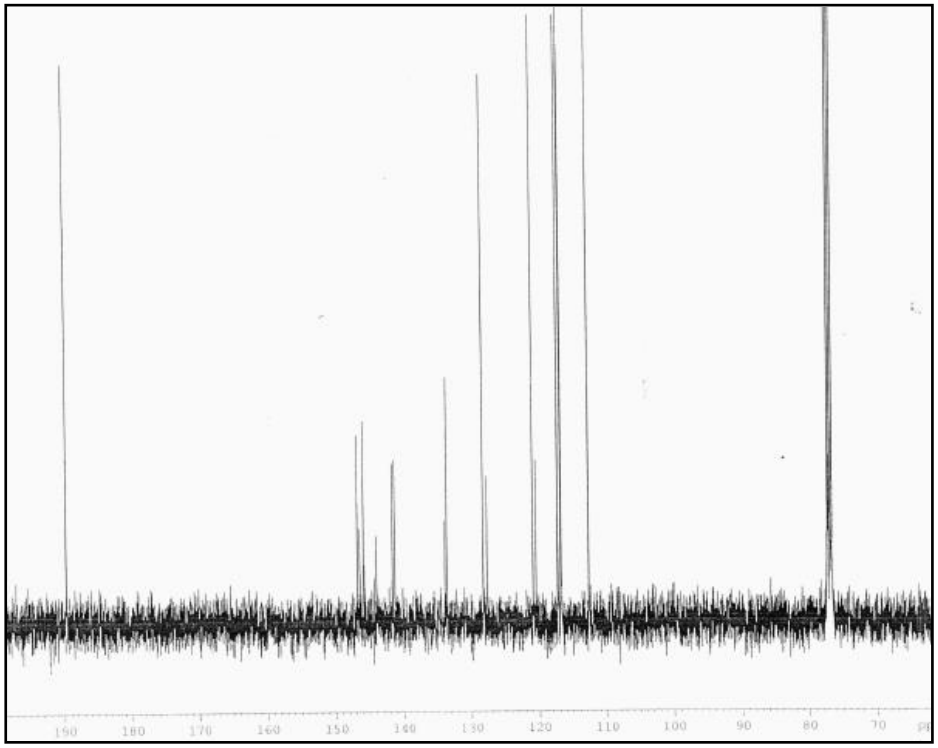


Figure (11)

The Triphenyl ether compound (5) represents a compound with four nitro groups at the tip that may be converted into corresponding ammines so that they can orient themselves and can capture metal ions.

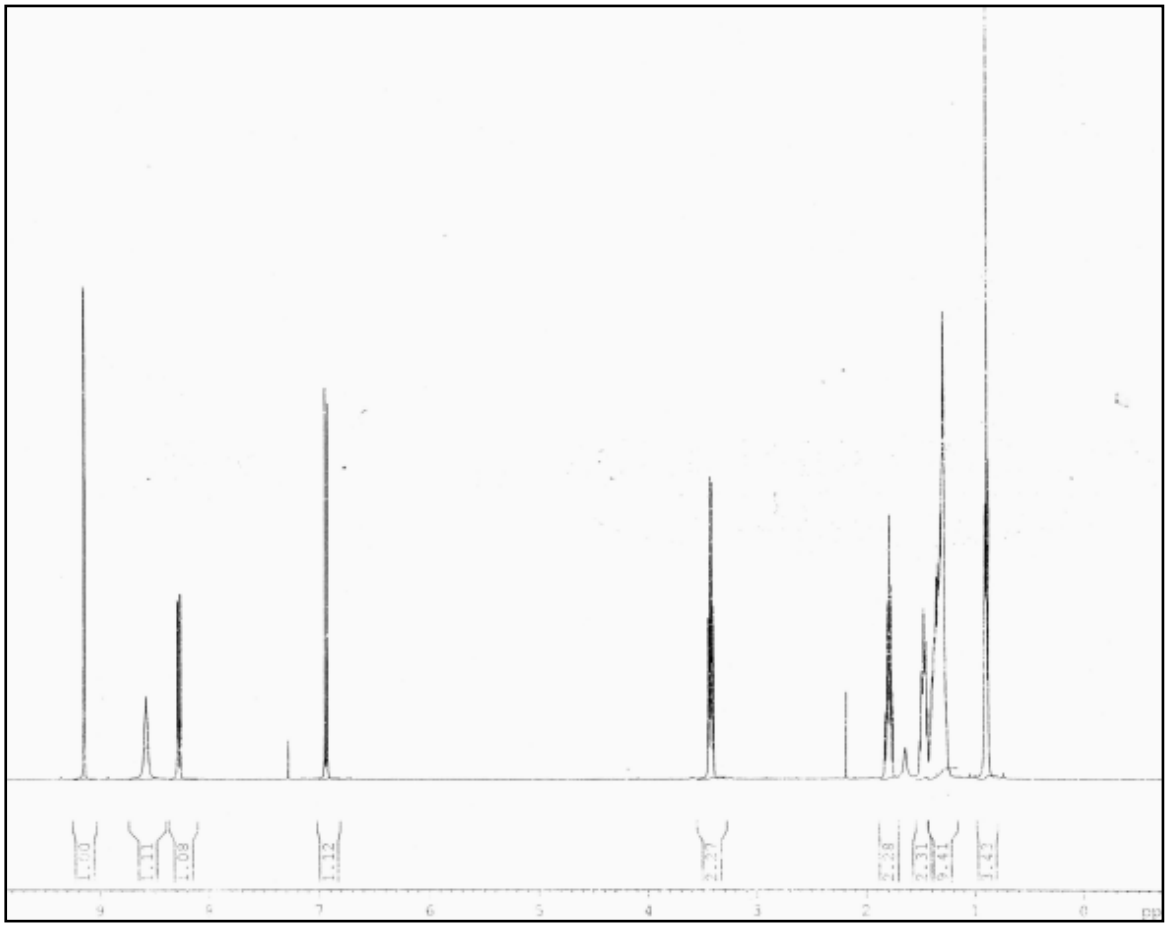


Figure (13)

B. Attempted synthesis of long chain aryl ethers for liquid crystal Properties

The compound that display liquid crystal properties have a stackable core with long hydrophobic chain. This part of work attempted the synthesis of these molecules. Compound (3) synthesized in previous reaction was reacted with octyl amine in presence of methanol at refluxing conditions. The product obtained was not compatible with desired compound as evident from ^{1}H NMR spectroscopy. The 1 H NMR showed

reactions of Sanger's reagent with octyl ammine there by confirming the presence of impurities in the reaction mixture. The presence of aliphatic chain at 1.3-1.9 ppm in 1H NMR spectra and aromatic proton at 9.1 ppm due to Ha **(Figure-12)** along with absence of aromatic protons due to vanillin confirms this.

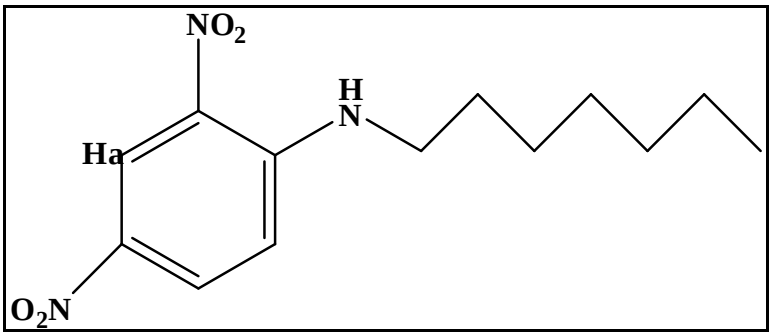


Figure (12)

Conclusion

The work presented above accomplishes the synthesis of a hindered Triphenyl ether that may be use to capture metal ion independently or by making its dimer. Also an unsuccessful attempt has been made to synthesize long chain aromatic ethers that may have displayed liquid crystal properties

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