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Synthesis, Trimerization and Complexation Studies of Benzo-11-Crown-3 Ether

By

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A thesis submitted to the

Faculty of Graduate Studies and Research

In partial fulfilment of the requirements for the degree of

Master of Science

Department of Chemistry

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Ottawa, Ontario, Canada

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Abstract

Benzo-11-crown-3 (B11C3) and dibenzo-22-crown-6 (DB22C6) were synthesized for the first time and characterized using elemental analysis, mass spectrometry (MS), and solution ^1H and ^{13}C Nuclear Magnetic resonance (NMR). B11C3 and DB22C6 were obtained in 19.1% and 5% yields respectively.

Benzo-11-crown-3 ether was trimerized in the presence of FeCl_3 and H_2SO_4 to produce tris(11-crown-3)triphenylene via a radical oxidative coupling reaction in 0.5% yield. It was studied by solution NMR, MS and X-ray crystallography. This molecule crystallizes along with a molecule of diethyl ether and CH_2Cl_2 in the triclinic $p1$ space group. The X-ray crystallography showed two of the three 11-crown-3 ether units of the tris(11-crown-3)triphenylene possess essentially identical geometries, while the third has a significantly different conformation.

The first observed complex of 11-crown-3 ether, $(\text{B11C3})_2 \cdot \text{LiSCN}$ was synthesized and characterized using MS and solution NMR. The ^{13}C CP/MAS (Cross Polarization Magic Angle Spinning) NMR and X-ray crystallographic data were also obtained. The complex crystallized in the monoclinic $P2_1/c$ space group. The ^{13}C CP/MAS NMR of the complex shows a degree of symmetry that is in agreement with the X-ray crystallographic data, ie. there are two inequivalent complexes.

Two complexes of $\text{DB22C6} \cdot \text{NaSCN}$ (1:1), and $\text{DB22C6} \cdot \text{KSCN}$ (1:1) were synthesized and characterized only by MS.

Publications Resulting From This Thesis Work

- 1) Buchanan, G. W., Azad, M. and Yap, G.P.A., X-ray Crystal Structure of Tris(11-crown-3)Triphenylene, J. Mol. Structure, (in press)
- 2) Buchanan, G. W., Azad, M. and Yap, G.P.A., The First Observed Complex of 11-crown-3 Ether. X-ray Crystal Structure and NMR Study of (Benzo-11-Crown-3)₂.LiNCS, Can. J. Chem. (in press)

Acknowledgments

I would like to take this opportunity to thank all the people who have helped and guided me throughout my graduate studies.

First of all, I am most thankful to my thesis supervisor Dr. Gerald W. Buchanan for his helpful guidance, constant encouragement, freedom, and his patience.

I would like to thank Majid Rastegar who generously gave much time in teaching, answering my questions and persistence in assisting me to accomplish this work. Thank you, Majid for everything.

Dr. G.A. Facey for solid-state NMR; Dr. G.P.A. Yap for X-ray crystallography; K. Bourque for running solution NMR samples; C. Kazakoff for mass spectrometry; A. Kiss; C. White and many more.

I would like to acknowledge all my friends Saman Alavi; Farhad Raofie; Mojgan Rasterar, Rana Zoka; and

Finally I would like to thank all those closest to me: my mom, my brother and sisters, my nephews; my nieces and my fiancé, Mahmoud, for their love, support and encouragement over the past two years. Thank you all for everything!

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Introduction

1.1: Crown Ethers

The family of macrocycles has now grown so broad that it is impossible to characterize its full extent in a single introduction. Generally, the crown ethers are classified as macrocyclic polyether compounds composed of oxygen, nitrogen, and / or sulfur heteroatoms separated by two carbon atoms or their equivalent. Considering the vast number of structures and structural variations of crown ethers, probably the most adequate definition presently is that they are macrocyclic systems containing at least one macrocyclic ring. In order to be crown ether, a compound must be cyclic and must contain donor groups such as oxygen. Replacement of oxygen by other heteroatoms such as sulfur and nitrogen has been explored extensively and has led to synthesis of thiacrown ethers, azacrown ethers, and other derivatives. A few examples are shown in figure 1[1].

12-Crown-4

Benzo-12-Crown-4

21-Crown-7

Azacrown Ethers

Thiacrown Ethers

Figure 1: The structure of some typical Crown Ethers

In 1937, Luttringhaus [2] reported the first macrocyclic polyether but it was not until the work of Pedersen thirty years later that the compounds he called crown ethers were found to strongly bind to alkali and alkaline earth metals [3].

In an attempt to find new ways of incorporating vanadium with different ligands for potential use as a catalyst, Charles J. Pedersen working at E.I. Dupont

de Nemours Company in the sixties isolated the crown ether, dibenzo-18-crown-6 (Fig. 2) and presented its complexing potential.

Figure 2: The synthetic scheme of Dibenzo-18-Crown-6 (DB18C6)

Pedersen's method has been used to synthesize majority of crown ethers from glycol or catechol and a dihalide. By using an appropriate sized cation via a "Template Effect" [4], yields have been greatly improved. The synthesis of cyclic materials is achieved by joining the ends of a compound that is nucleophilic on one end and electrophilic on the other end [1]. Pederson observed that the ring closing step in the synthesis of 15-crown-5 was greatly improved by the use of sodium

ions. This is achieved by ion dipole interaction between the lone pairs on the oxygens and the positively charged cation [5].

The geometric arrangement of ligands within the coordination sphere of the metal ion provides constraints, according to the kinetic coordination template hypothesis, that can be used to control the structure of a product formed by reaction of coordinated ligands. In a multistep reaction, the coordination sphere of the metal ion may specifically serve as a template to keep reactive groups in the proper position for a sterically highly selective reaction [6].

The word "crown" ether was used to name the parent member of this class of polyethers, 18-crown-6, because its preferred conformation resembles a crown.

The trivial names of crown ethers are based on the following concept. They consist of, in order: 1) The number and kind of hydrocarbon ring, 2) the total number of atoms in the polyether ring, 3) the class name, crown, and 4) the number of oxygen atoms in the polyether ring [3].

1.2: Triphenylenes

Liquid crystals have been suggested as candidates for highly oriented thin films of one-dimensional molecular electronic conductors for the past few years. Liquid crystals are of interest in fundamental physics as well as for their possible application in devices such as sensors and displays [7,8,9]. Among a wide range of liquid crystals available for this purpose, discotic liquid crystals are important

candidates for new one-dimensional conductors, because of their potential of forming columnar mesophases. Triphenylene compounds are known to exhibit discotic mesophases. These compounds have received special attention because of the discovery of their good one-dimensional electronic conductivity as well as high charge carrier mobility [10,11]. Provided the side chains are of sufficient length, hexaalkoxy-substituted triphenylenes show liquid-crystal properties, hence triphenylenes are promising models for discotic liquid crystals [12]. The structure and columnar packing of Hexamethoxytriphenylene (HMT) are shown in figure 3.

Figure 3: Hexamethoxytriphenylene and a schematic view of its columnar mesophase [13].

A method for making 2,3,6,7,10,11- hexamethoxytriphenylene in near quantitative yield was reported [12] employing oxidative trimerization of 1,2-methoxybenzene in sulphuric acid with iron (III) chloride (FeCl_3). In addition, the

application of this method was recently used by Buchanan [14] to the synthesis of a novel tris(9-crown-3) triphenylene.

In this study, the trimer of benzo-11-crown-3 has been prepared and studied by X-ray crystallography and ^1H and ^{13}C NMR in solution.

1.3: Complexation by crown ethers

Macrocyclic compounds are inherently beautiful and fascinating structures. Their sizes, shapes, and surfaces have intrigued chemists for generations. Although the crowns and cryptands have expanded previously known structural possibilities, it was the complexation processes that have made these compounds very important. The important feature of crown ethers and their relatives has proven to be their ability to capture other species. Pedersen was the first person that recognized this ability even before he synthesized crown ethers [1].

Because of the absence of donor groups in simple aliphatic macrocycles such as cyclotetradecane or even adamantane, direct interaction of them with substrates is prevented except by simple, Van der Waals (lipophilic - lipophilic or hydrophobic- hydrophobic) interaction [1].

Crown ethers have been studied as hosts that bind cations or neutral molecules through dipole-dipole interactions and hydrogen bonding. The term "hole

size selectivity" is generally used to explain the selectivity of crown ethers toward alkali metal ions [15].

The conditions required for the formation and the stability of the complexes are: (1) the relative sizes of the ion and the cavity size of the polyether, (2) the total number of oxygen atoms in the polyether ring, (3) the coplanarity of the oxygen atoms, (4) the symmetrical placement of the oxygen atoms, (5) the basicity of the oxygen atoms, (6) steric hindrance in the polyether ring, (7) the tendency of the ion to associate with the solvent, and (8) the electrical charge on the ion [3].

A complex becomes more stable as the number of its oxygen atoms increases, provided the oxygens are coplanar and symmetrically distributed in the polyether ring. An oxygen atom is considered to be coplanar if it lies in the same plane as all the other oxygens in the ring with the apex of the C-O-C angle centrally directed in the same plane. Maximum symmetry occurs when all the oxygen atoms are equally spaced in a circle. When a polyether ring contains more than six oxygens, the oxygens cannot be arranged in a coplanar conformation, but they can be arranged around the surface of a right circular cylinder with the apices of the C-O-C angles pointed toward the center of the cylinder. This conformation, which is called cylindrically symmetrical, allows the formation of salt complexes. The stability of the complex increases with the increase in the basicity of the oxygen atoms; the oxygen that is attached to an aromatic carbon is less basic than the oxygen that is attached only to aliphatic carbon atoms [3].

Pedersen reported that in general crown ether ligands complex most strongly with those metal cations whose ionic radii best match the radius of the cavity formed by the polyether ring [15]. Figure 4 illustrates the structures of some of the simple crown ethers, presenting an estimate of each cavity diameters and the ionic diameters of some alkali metal ions. Using the simple "lock and key" approach, it is evident that 18-crown-6 has cavity dimensions of the same magnitude as the diameter of the potassium ion, while 15-crown-5 and 12-crown-4 have cavity sizes suited for the ionic diameter of the sodium ion and lithium ion, respectively [16]. Therefore, in principle, particular crowns should be more specific for particular metal ions than for others. It should be emphasized that this does not mean that 18-crown-6 cannot solubilize sodium salts. It only means that it is more specific for potassium ion than sodium ion.

Figure 4: Several cyclic polyether cavity diameters[17]

Table 1: The ionic diameters of some alkali metal ions [14,16]

<u>Ionic diameters (Å)</u>		<u>Ionic diameters (Å)</u>	
K ⁺	2.66	Mg ²⁺	1.44
Na ⁺	1.94	Ca ²⁺	2.00
Li ⁺	1.36	Ba ²⁺	2.72

Stoichiometry and crystalline structure of crown ether complexes are not always easy to predict. If the difference in cavity size and cation diameter is not too big, 1:1 (ligand : salt) complexes may nevertheless be formed. The cation then is either shifted from its ideal position (centered in the ring-plane of the crown ether, type I Fig. 5, or in the middle of the cavity of the cryptand) or the ligand is wrapped around the cation in a nonplanar way, type IIa, and type IIIa in figure 5.

If the cavity is much too large for a cation, then two of them may be embedded therein (type IIb, Fig. 5); on the other hand, if the cation is much too large, a sandwich-type complex may be formed, where the cation is trapped between two ligand units (type IIIb) [18]. The stability of sandwich complexes is higher with respect to the monocyclic analogues owing to the so-called 'bis-crown effect'. Bourgoïn et al., and Handyside et al. reported the first evidence for the existence of sandwich complexes [19].

Figure 5: Schematic representation of several types of crown ether complexes.

1.4: Applications of crown ethers

Crown ethers have found a place in many facts of chemistry, especially synthetic organic and physical organic fields. An enormous amount of work has been reported using ligands in catalyzing synthetic organic reactions and probing reaction mechanisms [17]. They are used extensively as phase transfer catalysts because complexation with alkali and alkaline earth cations yields large lipophilic complexes, which are readily extracted into organic solvents.

Crown ethers show high selectivity in complexation because the macrocycles contain cavities of fixed sizes. This has resulted in a number of potential applications in ion transport [20] and generation of strong bases by charge separation of pairs [21].

The ability of crown ethers to transport biologically significant cations across membranes and their ability to differentiate in their complexation properties between related biologically important cations makes them potentially important. To achieve the goal, crown ethers are normally bonded to a biologically important fragment like carbohydrates [22].

If the binding ability of crown ethers is changed in response to some appropriate input, they could function as efficient ion-transfer carriers. So far four general switching modes have been identified in this regard: "Photoresponse Switching" [23,23,25] which changes bonding ability in response to the light

irradiation, "Redox Switching " [26] which changes the bonding ability in response to the level of redox potentials, "pH Switching" and finally "Thermal Switching"[1].

1.5: Techniques

NMR has found widespread application in the identification of molecular level changes during molecule-molecule and ion-molecule interactions. Nevertheless, when the molecule exhibits many binding sites the analysis becomes very difficult. This problem can easily be overcome for small molecules by using different one- and two-dimensional methods and multinuclear NMR. Further, the molecule should have asymmetry in terms of chemical shifts in order to acquire knowledge about the conformational changes in the various parts of the molecule. Simple crown ether structures such as 24-crown-8 (24C8), 18-crown-6 (18C6) and 15-crown-5 (15C5) are highly symmetric in solution owing to rapid tumbling and segmental motions, and they give a single resonance on the NMR time scale both for ^1H and for ^{13}C . Their mono- and di-benzo counterparts serve as better model compounds, since the crown protons or carbons in these molecules are made inherently non-equivalent by the ring current effect of the benzo group [27].

Using ^1H and ^{13}C NMR, Live and Chan [28] elucidated the structure of the complexes formed by benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6) and dibenzo-30-crown-10 (DB30C10), in solution with Na^+ , K^+ , Cs^+ , or Ba^{2+} in a number of solvents such as water, water-acetone, acetone and chloroform, with different counter ions (ClO_4^- , SCN^- , I^-). The ^1H NMR chemical shifts and vicinal

coupling constants of free crown ethers in various organic solvents indicated that the $\text{-O-CH}_2\text{CH}_2\text{O-}$ fragments are in an all-gauche conformation with rapid interconversion between anti- and syn-gauche rotamers. On complexation, both the ^{13}C resonances and the spin-lattice relaxation time were found to change. The latter effect was attributed to the rigidity of the ether fragments of internal motion when the crown ethers were complexed [28].

1.5.1: Two-dimensional NMR

Two-dimensional NMR is a relatively new technique with a large variety of applications. The basic theory is that instead of having only one time variable a second time variable is introduced. The first, and original, time variable is the time over which the FID is acquired (t_2). The second time variable is the delay between acquisitions (t_1). By varying both time intervals two separate Fourier transforms are acquired thus yielding a two-dimensional spectrum [29].

1.5.1.1: HETCOR experiment

The ^1J -HETCOR (Heteronuclear Correlation) experiments are used to determine which protons are attached to which carbons. This is accomplished by the transfer of magnetization between the ^1H and ^{13}C nuclei, which is caused by the use of two 90° pulses separated by the time t_1 . This spectrum is useful when either a proton or carbon signal for the same molecule has been identified since through the detected coupling if one of the nuclei is identified they both are identified [29].

1.5.1.2: NOESY experiment

In the NOESY (Nuclear Overhauser Enhancement Spectroscopy) experiment attention is paid to the nuclear Overhauser effect, [29] and its effect on signal strengths. Through the use of three 90° pulses, separated by t_1 and a mixing period, a two-dimensional spectrum is produced showing which nuclei are relaxing each other.

1.5.2: Solid State NMR

1.5.2.1: CP/MAS NMR

CP/MAS (cross-polarization magic-angle-spinning) NMR is very useful for characterizing and quantitatively studying diamagnetic organic solids. The relative polarization rates of different types of protonated carbon atoms were shown to be a direct manifestation of the effective magnitude of the ^{13}C - ^1H dipolar interaction. Methyl carbons are especially interesting because they exhibit a wide range of effective dipolar couplings resulting from different degrees of motional freedom. Conventional cross polarization of a carbon is characterized by the time a carbon nucleus receives polarization from the coupled protons [30].

There are three factors, which affect the NMR response of solid samples, which do not arise, or are averaged to zero in liquid phase. These are as follows: 1) line broadening as a result of dipole-dipole interactions; 2) chemical shift anisotropy, again resulting in rather broad, complex patterns. Both these interactions occur in solution but are generally averaged to zero as a result of the

random motion of the molecules. 3) Nuclei in solids generally possess extremely long relaxation times [29].

The chemical shift anisotropy and dipole-dipole interactions are proportional to $\Delta X (3 \cos^2 \theta - 1) / R^3$ where ΔX is the difference between the parallel and perpendicular susceptibilities, θ is the angle between the molecule and the applied magnetic field and R is a bond distance in the molecule. The $3 \cos^2 \theta - 1$ term goes to zero when the angle of 54.44° is used [29,31,32].

By application of CP, there is a considerable enhancement of intensity in the spectrum but no resolution. Dipolar decoupling combined with CP, gives the recognizable features of a number of overlapping chemical shift powder patterns and finally, the CP / MAS technique yields the high-resolution spectrum. Sample spinning can impart an oscillatory time-dependence to the dipolar interaction between the I and S spins that leads to polarization transfer. Care should be taken since, if the dipolar fluctuation energy conserving mutual spin flips of the S spin is close to the spinning rate, the CP process can be affected resulting in appreciable line broadening of the S spin resonance [33].

Solid crown ethers and crown ether complexes with well determined crystal structures have been examined by ^{13}C CP/MAS NMR. Certain carbon atoms in most of the compounds gave single lines in the solution-state spectra, but produced multiplets in the spectra of the solids because of the existence of crystallographically unique molecules in the solid state [34].

Solid-state spectra give rise to line multiplicities not observed in solution NMR. In a single phase (not a mixture of polymorphic forms), peak multiplicities may arise through a number of different effects. The splitting observed in the solid-state ^{13}C spectrum of 2,4-dinitrotoluene arises from the presence of two independent molecules in the crystal whilst benzo-15-crown-5 shows splitting which arise because packing within the crystal renders chemically equivalent pairs of atoms magnetically inequivalent. Peak multiplicities may also arise through the absence of exchange between different conformers; examples are provided by the ^{13}C spectra of certain trans-azabenzenes and p-alkoxybenzoic acids. Splittings may also be observed when the resonant nucleus is very close to a quadrupolar nucleus. This phenomenon is often observed for ^{13}C directly bonded to ^{14}N and occurs because the quadrupole moment prevents magic angle-spinning from eliminating the dipole-dipole interaction between the resonant and the quadrupolar nuclei [34].

1.5.2.2: Dipolar Dephasing

Alla and Lippmaa [35] were the first to use dipolar dephasing to distinguish between carbon atoms with different effective dipolar resonances while producing a spectrum of only minimally attenuated signals for methyl and nonprotonated carbon atoms.

Dipolar dephasing studies measure the time for a polarized carbon nucleus to lose its magnetization after the proton locking field is terminated. Dipolar

dephasing results depend upon the magnitude of the dipolar coupling and generally may be grouped into three cases: CH and CH₂ (strong coupling), CH₃ (moderate coupling), and nonprotonated C (weak coupling).

In studies whose spectra have overlapping resonances, the dipolar dephasing technique discriminates between protonated and nonprotonated carbons. In dipolar-dephased spectra, dipolar and rotational modulation of the resonances can occur for methane and methylene carbons, because of rapid methyl rotation that varies depending upon the structural environment. Dipolar modulation in methyl groups is not observed [29].

1,7-dichloro-4-oxaheptane, **1** Benzo-11-crown-3, **2** Dibenzo-22-crown-6, **3** Tris(11-crown-3)triphenylene, **4** (Benzo-11-crown-3)₂.LiSCN Complex, **5** (1:1) Dibenzo-22-crown-6: KSCN
Complex, **6** (1:1) Dibenzo-22-crown-6: NaSCN
Complex, **7**

Results and Discussion

Chapter 2

2.1: Benzo-11-Crown-3 / Dibenzo-22-Crown-6

Benzo-9-crown-3 [36], benzo-10-crown-3 [37], benzo-12-crown-4 [38], dibenzo-15-crown-5 [39], dibenzo-18-crown-6 [40], and similar compounds have already been synthesized and characterized. A literature search has shown that Benzo-11-crown-3 and its dimer, Dibenzo-22-crown-6 are unknown. Since these molecules may show novel complexation properties due to their increased conformational flexibility, their synthesis was undertaken.

Benzo-11-crown-3 and dibenzo-22-crown-6 were synthesized in the presence of 1,7-dichloro-4-oxaheptane, catechol, and LiOH.H₂O (lithium hydroxide monohydrate) in an isolated yield of 19.2% and 5% respectively. Benzo-11-crown-3 and dibenzo-22-crown-6 were identified by EI MS (electron ionization mass spectroscopy) and ¹H and ¹³C NMR in solution. The molecular weight was confirmed to be 208 for B11C3 (Fig. 22) and 416 for DB22C6 (Fig. 23).

2.2: Solution NMR studies of 2

In the 400 MHz ¹H NMR spectrum of B11C3, multiplets observed for the ether protons are characteristic of AA'MM'XX' spin systems. The spectrum (Fig. 7) shows four sets of peaks as was expected for a symmetric molecule. The peak at 6.97 ppm is quite obviously due to the aromatic protons in the molecule, which are the most deshielded, and the peak at 1.98 ppm, is due to H8, H11, which are the most shielded.

The analysis of ^1H and ^{13}C spectra was performed using both the NOESY and HETCOR experiments (Fig. 8). Assignments of the aliphatic protons 7,12 and 9,11 of B11C3 were made via results from a NOESY experiment. A weak cross peak was noted between the resonance at 4.13 ppm and the aromatic proton resonance. Such a cross peak could only arise from the relaxation between the ortho aromatic protons (H2, 5) and the protons on C7, 12 of B11C3 (Fig.6). No such correlation was found for the aliphatic multiplet centered at 3.85 ppm, since this arises from the more distant (from the aromatic ring) C9, 10. Such a ^1H - ^1H nOe (nuclear Overhauser effect) also has been found in a number of benzo crown ethers [41]. As a matter of fact, the closer the crown ring hydrogen to the benzene ring, the more deshielded they are. The assignment of ^1H methylene peaks in the case of DB18C6, DB24C8, B15C5 [41,28], B18C6 and some other bis(benzo crown ethers) [42] supports this statement. This behavior is thought to originate from an aromatic ring current effect [43,44].

Figure 6: Expected long-range nOe in crown ether (B11C3).

In the proton spectrum, the integration of the three high-field multiplets and one down-field multiplet are almost the same, indicating that each peak contains 4 protons.

The B11C3 molecule shows a reflection plane along a horizontal axis through the molecule, therefore the symmetry reduces the 12 carbon signals down to 6 as seen in the diagram.

The aromatic carbons are the first and easiest to assign. The basic carbon shift for an aromatic carbon is 115-130 ppm [29]. This means that the 3 peaks, in group of two, from 118-152 ppm are the aromatic carbons. Carbons 1,6 are attached directly to the OCH₂ groups, which cause them to be deshielded by the largest amount, therefore the peak at 151.1 ppm corresponds to carbons 1 and 6. Carbons 2 and 5 are both ortho to an OCH₂ substituent, which shields them the most among the aromatic carbons, therefore the peak at 118.6 ppm, belongs to carbons 2 and 5, and the peak at 122.7 ppm corresponds to carbons 4 and 3.

Figure 7: 400MHz ^1H and 100.6MHz ^{13}C NMR spectra of B11C3.

Figure 8: a) NOESY and b) HETCOR spectra of B11C3 by 400 MHz.

Efforts to get single crystals of dibenzo-22-crown-6 (DB22C6) for x-ray study unfortunately failed.

2.3: Solution NMR studies of 3

In solution, the ^{13}C NMR spectrum (Fig. 9) is consistent with the existence of rapid conformational averaging since only six resonances are observed (Table 2), which is similar to the ^{13}C NMR spectrum of the 2 (B11C3), with some chemical shift differences.

The COSY, NOESY and ^1H , ^{13}C , ^1J HETCOR experiments were employed to obtain a partial assignment of connectivities. The combination of COSY and NOESY spectrum (Fig. 10) shows connections between the protons on the ortho carbons in the aromatic ring (C2 and C5) with those on C7 and C12, therefore the resonance at 4.043 ppm is corresponding to the protons on C7 and C12 and the resonance at 3.705 ppm belongs to the protons on C9 and C10. This part of results is similar to the B11C3. The ^1H , ^{13}C , ^1J HETCOR experiment (Fig. 10) shows that ^{13}C resonances at 67.9 and 64.8 ppm connect to the protons on C9, C10 and C7, C12

respectively. These results are opposite to the B11C3, hence the more deshielded ^{13}C resonance was connected to the protons on C7 and C12. There is an upfield shift of 5-6 ppm for C2,5 and C7, 12 which suggests a conformation in which the protons on these carbons are spatially proximate. Such proximity may shield the bonded carbons via sterically induced charge polarization.

According to the result of the ^{13}C NMR spectrum of **3** one can predict that this molecule is symmetric across a vertical axis and horizontal axis.

Table 2: ^{13}C resonances of **2** and **3**

	2	3
C1, C6	151.1	148.5
C4, C3	122.7	120.7
C5, C2	118.5	112.4
C7, C12	69.6	64.8
C9, C10	66.5	67.9
C8, C11	29.5	29.6

2.4: Solid-state CP/MAS NMR of **3**

The solid-phase ^{13}C CP/MAS spectrum (Fig. 11) shows thirteen resolved lines. If **3** possessed a center of symmetry in the crystal, then twelve lines with equal line intensity would be expected in the solid-phase ^{13}C spectrum (6 resonances for the aromatic carbons, 4 for oxygenated carbons and 2 resonances

for non-oxygenated ether carbons). In the region of 30 ppm 2 resonances were expected for C8 and C11, while three absorptions are observed for these carbons at 28.9, 30.0 and 31.4 ppm. In fact these lines are not of equal intensity, reflecting the lack of overall symmetry in **3**. In the case of an asymmetric molecule, one would expect to observe twenty-four resonances in the ^{13}C CP/MAS spectrum. It appears that there are many cases of accidental peak overlap. In the aromatic region, twelve peaks are expected, but six are resolved (2:2 for the quaternary carbons and 2:1:1:4 for the protonated carbons). In the ether region, twelve lines are expected (8 lines for oxygenated carbons and 4 for non-oxygenated carbons), but seven are resolved (1:3:3:1 and 2:1:1). The accidental overlap may be due to conformational similarities in the macrocycle.

Since no X-ray structure for this molecule is presently available, we are not able to assign the resonances.

Non-protonated carbons can be observed, hence identified, in the dipolar-dephased experiment, while the resonances for protonated carbons normally are not observed under such conditions. The dipolar-dephased spectrum (Fig. 11b) shows two strong peaks at 148.5 and 148.0 ppm, which are due to the four quaternary carbons, and one peak at 31.4 ppm for the protonated non-oxygenated carbon resonances ($\text{CH}_2\text{-}\underline{\text{CH}_2}\text{-CH}_2$), indicating large amplitude motion.

a)

b)

Figure 9: a) 400 MHz ^1H and b) 100.6 MHz ^{13}C NMR of 3 in CDCl_3

Figure 10: 400MHz a) NOESY and b) HETCOR spectra of 3

a)

b)

Figure 11: a) 50.3 MHz CP/MAS spectrum and b) dipolar diphased CP/MAS spectrum of 3

Chapter 3

3.1: Tris(11-crown-3)triphenylene

Hexamethoxytriphenylene [12] and tris(9-crown-3)triphenylene [14] have been synthesized and characterized recently.

Tris(11-crown-3)triphenylene **4** was synthesized in the presence of benzo-11-crown-3, FeCl_3 (with a molar ratio of 1:3), as an oxidative reagent, concentrated H_2SO_4 as a catalyst and carbon tetrachloride (CCl_4) as a solvent in a low isolated yield (0.5%). The chemical formula of this compound was confirmed by FAB MS (Fast Atomic Bombardment Mass Spectroscopy) to be $(M+1) m/z = 619$. The melting point of this compound is 285-290 $^\circ\text{C}$, which is significantly very high compared to the starting material (benzo-11-crown-3), which is an oil at room temperature.

The low yield of **4** is due to FeCl_3 , which forms a complex with this compound, **4**. Therefore, the separation of Fe^{3+} from the product **4** was very difficult and causes this low yield.

3.2: Solution NMR studies of 4

Figure 12 shows the ^1H NMR and ^{13}C NMR for **4**, and Table 3 contains the ^1H and ^{13}C chemical shifts in benzo-11-crown-3 and **4**.

In the 400 MHz ^1H NMR spectrum of **4**, one multiplet was observed at 2.10 ppm, which corresponds to CH_2 - CH_2 - CH_2 , two multiplets at 3.94 and 4.35 ppm, which belong to the CH_2 O, and one singlet at 7.99 ppm for the 6 aromatic protons. This peak was deshielded about 1 ppm compared to the aromatic protons of the

free B11C3. This can be due to two reasons, 1) =C-H in B11C3 is connected to one quaternary carbon (C1, C6) and one tertiary carbon (C3, C4), but in **4** this carbon (=C-H) is connected to two quaternary carbons 2) anisotropy in the benzene rings of trimer, **4** that caused this lower field shift.

The solution ^{13}C spectrum (CDCl_3 solvent) contains only six resonances, as expected from the 3-fold symmetry element present in the planar depiction of B11C3.

Table 3: The comparison of the ^{13}C resonances of B11C3 with its trimer **4**.

	B11C3	4
=C-O	151.1	150.4
=C*-C	-----	124.9
=CH	122.7, 118.6	111.6
=C-O-CH ₂ *	69.6	69.8
CH ₂ -O-CH ₂	66.5	66.5
CH ₂ -CH ₂ *-CH ₂	29.5	29.6

By comparing the ^{13}C resonances of tris(11-crown-3)triphenylene with Benzo-11-crown-3, it can be observed that the chemical shift of carbons =C-O, CH₂-O, and CH₂-CH₂-CH₂ are almost the same. But the chemical shift of the two aromatic carbons =C-H in B11C₃ are at 118.6, 122.7 ppm, while in the trimer the =C-H are at 111.6 ppm and the quaternary carbons are deshielded to 124.8 ppm.

Figure 12: 400 MHz ^1H and 100.6 MHz ^{13}C NMR spectra of tris(11-crown-3)triphenylene

3.3: X-ray crystal structure of 4

The ORTEP diagram for **4** is shown in the Figure 13. Structural data for this molecule are given in tables 4 to 8. Table 4 contains the crystallographic data, table 5 contains atomic coordinates and equivalent isotropic displacement factors, atomic bond lengths are collected in table 6, and bond angles are presented in table 7. Selected torsion angles involving non-hydrogen atoms are in table 8. Tris(11-crown-3)triphenylene crystallizes along with a molecule of diethyl ether and CH₂Cl₂ in a p-1 space group (Fig. 14). We were unable to do a solid state ¹³C NMR to compare with X-ray data, because of limited quantities of **4** available.

With respect to bond lengths, there are significant differences found in the aryl C-O units, ranging from the shortest (1.361 Å) for C₃-O₁ to the longest (1.381 Å) for the C₁₀-O₃ moiety. G.W. Buchanan (14) recently noted a similar range of C-O bond lengths for the related tris(9-crown-3)triphenylene. A shorter C-O bond can be viewed as possessing more double bond character, which should lead to a more deshielded ¹³C resonance in the solid- state spectrum.

In examining the bond angle data, it is clear that there are three anomalously large angles involving aromatic carbons and three correspondingly smaller angles involving the same central atoms. The central carbons involved are C₃, C₁₅ and C₃₄. In the case of C₃, the O₁-C₃-C₂ angle is found to be 126.4°, which is ca. 6° larger than expected for an sp² hybridized (120°) center. It appears that the O₁-C₃-C₂ angle "opens up" in an attempt to minimize the effect of steric repulsion resulting from the nearly coplanar (θ = 17.3°) torsional C₄-O₁-C₃-C₂ unit. Such an expansion does not occur in the O₃-C₁₀-C₁₁ unit since the torsion angle

for the $C_9-O_3-C_{10}-C_{11}$ network is -102.7° . The expansion of the $O_1-C_3-C_2$ bond angle is accompanied by a contraction of the $O_1-C_3-C_{10}$ angle to 113.8° with the internal $C_2-C_3-C_{10}$ angle having a normal value of ca. 120° .

At C_{15} , we attribute the anomalously large (125.2°) $O_4-C_{15}-C_{14}$ angle to the same factors as described above for C_3 , since the $C_{14}-C_{15}-O_4-C_{16}$ torsion angle is 14.7° . Similarly at C_{34} , the expansion of the $O_9-C_{34}-C_{35}$ angle to 126.1° can be attributed to the repulsive torsional interactions arising from the nearly coplanar ($\theta = 16.7^\circ$) $C_{33}-O_9-C_{34}-C_{35}$ network.

Unfortunately, benzo-11-crown-3, the starting material of **4** is an oil and no X-ray crystallographic data have been obtained. Therefore, the HyperChem program was used to calculate the preferred geometry of the 11-membered ring of Benzo-11-crown-3 in the gas phase, to compare it with three 11-membered rings in **4**. A comparison of torsion angles for the 11-membered rings is presented in table 4. Two of the three 11-membered rings of **4** have essentially the same geometries, while the third (C_{15} to C_{22}) has a unique conformation. When viewing the ORTEP plot of **4** (Fig. 13) it is clear that there is a "northern" ring (C_3 to C_{10}), an "eastern" ring (C_{15} to C_{22}) and a "western" ring (C_{27} to C_{34}). The "northern" and "western" rings have identical conformations. The primary differences between the conformation of the "eastern" ring and the other two rings are in the region most remote from the central core of the molecule *i.e.* in the $C_5-C_6-O_2-C_7-C_8$ region, where differences in torsion angles up to *ca.* 60° are found.

Table 4: Comparison of calculated 11-membered ring torsion angles (°) in **2** with those in the crystal structure of **4**.

Network	2	C3-C10 (4)	C15-C22 (4)	C27-C34 (4)
C3-C10-O3-C9	61.4	78.4	-65.1	79.4
C10-O3-C9-C8	-148.7	148.6	148.6	-144.3
O3-C9-C8-C7	98.7	71.3	63.4	69.7
C9-C8-C7-O2	-85.9	60.2	-68.7	60.4
C8-C7-O2-C6	161.1	-173.3	156.2	-173.9
C7-O2-C6-C5	-74.3	68.1	-129.5	68.2
O2-C6-C5-C4	-50.1	49.3	81.6	48.8
C6-C5-C4-O1	100.6	-77.3	-50.2	-75.7
C5-C4-O1-C3	-166.6	174.8	-174.5	173.1
C4-O1-C3-C10	109.5	-163.0	-164.7	-163.1
O1-C3-C10-O3	-10.9	3.7	6.4	3.2

Figure 13: The ORTEP diagram of **4**

Figure 14: Unit cell of 4

Table 4. Crystallographic data for **4**

Formula	C₄₁H₄₅O₁₀
Fw	777.74
Crystal system	triclinic
Space Group	P1
a, Å	8.8913 (9)
b, Å	13.5790 (14)
c, Å	17.5244 (17)
Volume, Å ³	1909.6 (3)
Z (molecules/ unit cell)	2
D _c (g/cm ³)	1.353
Crystal dimensions, mm	0.2 x 0.1 x 0.1
Radiation (λ, Å)	MoKα , 0.71073
Octants measured	h(-11 to 11), k(-18 to 17), l (-22 to 17)
Theta range (°)	1.66 to 28.68
Temperature (K)	203 (2)
No. of unique reflections	8624
No. of reflections measured	14,943
No. of reflections with I > 2σ (I)	7724
R ₁ (I > 2σ (I))	0.0547
R ₁ (all data)	0.0998
WR2 (all data)	0.1491
WR2 (I > 2σ (I))	0.1343
GoF	1.04
Largest diff. Peak and hole (e Å ⁻³)	0.600 and -0.680

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	Y	Z	U (eq)
O1	4517 (2)	-1156 (1)	1070 (1)	35 (1)
O2	4380 (2)	-2919 (1)	1611 (1)	36 (1)
O3	4238 (2)	-51 (1)	2625 (1)	29 (1)
O4	8207 (2)	5573 (1)	4580 (1)	41 (1)
O5	9090 (2)	7656 (1)	5839 (1)	35(1)
O6	10513 (2)	6404 (1)	3844 (1)	36 (1)
O7	11755 (2)	3436 (1)	-227 (1)	29 (1)
O8	10255 (2)	1777 (1)	-2386 (1)	35(1)
O9	10504 (1)	1322 (1)	-936 (1)	35 (1)
C1	7378 (2)	1443 (2)	1391 (2)	24 (1)
C2	6508 (3)	348 (2)	998 (1)	27 (1)
C3	5450 (2)	-129 (2)	1395 (1)	28 (1)
C4	4862 (3)	-1949(2)	336 (2)	33 (1)
C5	3688 (3)	-3008 (2)	202 (2)	33 (1)
C6	4038 (2)	-3584 (2)	759 (2)	39 (1)
C7	3103 (3)	-2549 (2)	1999 (2)	37 (1)
C8	3685 (3)	-1747 (2)	2871 (2)	37 (1)
C9	4912 (3)	-758 (2)	2904 (2)	33(1)
C10	5249 (2)	461 (2)	2220 (1)	25 (1)
C11	6033 (2)	1527 (2)	2597 (1)	26 (1)
C12	7093 (2)	205 (2)	2198 (1)	24 (1)
C13	7907 (2)	3208 (2)	2612(1)	24 (1)
C14	7606 (3)	3839 (2)	3406 (1)	29 (1)
C15	8416 (3)	4906 (2)	3810 (1)	31 (1)
C16	7368 (3)	5137 (2)	5110 (2)	35 (1)
C17	7213 (3)	6088 (2)	5872 (2)	39 (1)
C18	8723 (3)	6923 (2)	6264 (2)	42 (1)
C19	10612 (3)	7798 (2)	5600 (2)	36 (1)
C20	10640 (3)	8165 (2)	4882 (2)	35 (1)
C21	9758 (3)	7305 (2)	4092 (2)	35 (1)
C22	9569 (3)	5379 (2)	3426 (1)	29 (1)
C23	9856 (3)	4775 (2)	2648 (1)	29 (1)
C24	9025 (2)	3687 (2)	2214 (1)	24 (1)
C25	9331 (2)	3056 (2)	1382 (1)	25 (1)
C26	10396 (2)	3536 (2)	957 (1)	25 (1)
C27	10722 (2)	2953 (2)	186 (1)	27 (1)
C28	10979 (3)	3677 (2)	-845 (1)	31 (1)
C29	11859 (3)	3519 (2)	-1593 (2)	34 (1)

C30	11837 (3)	2346 (2)	-2104 (2)	33 (1)
C31	10020 (3)	626 (2)	-2812 (2)	39 (1)
C32	10342 (3)	11 (2)	-2281 (2)	35 (1)
C33	9599 (3)	272 (2)	-1488 (1)	33 (1)
C34	10009 (3)	1830 (2)	-192 (1)	27 (1)
C35	8925 (3)	1350 (2)	190 (1)	27 (1)
C36	8544 (2)	1949 (2)	980 (1)	24 (1)

Table 7. Bond lengths (Å) of 4

O1-C3	1.361 (3)	C10-C11	1.364 (3)
O1-C4	1.431 (3)	C11-C12	1.409 (3)
O2-C6	1.418 (3)	C12-C13	1.469 (3)
O2-C7	1.425 (3)	C13-C24	1.405 (3)
O3-C10	1.381 (3)	C13-C14	1.408 (3)
O3-C9	1.450 (3)	C14-C15	1.377 (3)
O4-C15	1.364 (3)	C15-C22	1.405 (3)
O4-C16	1.416 (3)	C16-C17	1.513 (3)
O5-C19	1.419 (3)	C17-C18	1.514 (3)
O5-C18	1.437 (3)	C19-C20	1.511 (3)
O6-C22	1.378 (3)	C20-C21	1.507 (3)
O6-C21	1.453 (3)	C22-C23	1.370 (3)
O7-C27	1.383 (3)	C23-C24	1.410 (3)
O7-C28	1.444 (3)	C24-C25	1.460 (3)
O8-C31	1.428 (3)	C25-C26	1.411 (3)
O8-C30	1.430 (3)	C25-C36	1.411 (3)
O9-C34	1.365 (3)	C26-C27	1.364 (3)
O9-C33	1.440 (3)	C27-C34	1.410 (3)
C1-C12	1.412 (3)	C28-C29	1.510 (3)
C1-C2	1.412 (3)	C29-C30	1.508 (3)
C1-C36	1.466 (3)	C31-C32	1.520 (3)
C5-C6	1.521 (3)	C32-C33	1.505 (3)
C7-C8	1.513 (3)	C34-C35	1.369 (3)
C8-C9	1.517 (3)	C35-C36	1.414 (3)

Table 8. Bond angles (°) of 4

C3-O1-C4	120.2 (2)	C3-C10-O3	119.0 (2)
O4-C16-C17	107.4 (2)	O4-C15-C14	125.2 (2)
C6-O2-C7	114.6 (2)	O4-C15-C22	115.2 (2)
C10-O3-C9	112.1 (2)	O4-C16-C17	107.4 (2)
C15-O4-C16	120.6 (2)	C16-C17-C18	114.3 (2)
C19-O5-C18	115.1 (2)	O5-C18-C17	110.4 (2)
C22-O6-C21	116.3 (2)	O5-C19-C20	109.2 (2)
C27-O7-C28	112.3 (2)	C19-C20-C21	114.1 (2)
C31-O8-C30	114.4 (2)	O6-C21-C20	107.7 (2)
C34-O9-C33	119.5 (2)	C23-C22-O6	119.1 (2)
C12-C1-C2	118.4 (2)	O6-C22-C15	121.1 (2)
C12-C1-C36	119.8 (2)	O7-C27-C34	119.1 (2)
C2-C1-C36	121.7 (2)	O7-C28-C29	111.4 (2)
O1-C3-C2	126.4 (2)	C30-C29-C28	114.5 (2)
O1-C3-C10	113.8 (2)	O8-C30-C29	107.4 (2)
O1-C4-C5	105.6 (2)	O8-C31-C32	115.2 (2)
C4-C5-C6	114.5 (2)	C33-C32-C3	1115.2 (2)
O2-C6-C5	115.5 (2)	O9-C33-C32	106.0 (2)
O2-C7-C8	108.5 (2)	O9-C34-C35	126.1 (2)
C7-C8-C9	113.0 (2)	O9-C34-C27	113.9 (2)
C8-C9-O3	110.9 (2)		
C11-C10-O3	121.5 (2)		

Table 9. Torsion angles (°) of 4

C12-C1-C2-C3	-2.2 (3)	O6-C22-C23-C24	174.3 (2)
C36-C1-C2-C3	178.2 (2)	C15-C22-C23-C24	0.2 (3)
C4-O1-C3-C2	17.3 (3)	C14-C13-C24-C23	2.9 (3)
C4-O1-C3-C10	-163.0	C12-C13-C24-C23	-176.0 (19)
C1-C2-C3-O1	177.5 (2)	C14-C13-C24-C25	-178.5 (19)
C1-C2-C3-C10	-2.1 (3)	C12-C13-C24-C25	2.5 (3)
C3-O1-C4-C5	174.8 (19)	C22-C23-C24-C13	-2.1 (3)
O1-C4-C5-C6	-77.3 (2)	C22-C23-C24-C25	179.4 (2)
C7-O2-C6-C5	68.1 (3)	C13-C24-C25-C26	177.0 (2)
C4-C5-C6-O2	49.3 (3)	C23-C24-C25-C26	-4.5 (3)
C6-O2-C7-C8	-173.3 (19)	C13-C24-C25-C36	-2.1 (3)
O2-C7-C8-C9	60.2 (3)	C23-C24-C25-C36	176.4 (2)
C10-O3-C9-C8	-146.6 (19)	C36-C25-C26-C27	-2.4 (3)
C7-C8-C9-O3	1.3 (3)	C24-C25-C26-C27	178.5 (2)

C9-O3-C10-C11	-102.7 (2)	C14-C15-C22-O6	6.4 (3)
C14-C15-C22-O6	-179.5 (2)	O4-C15-C22-O6	1.0 (3)
C25-C26-C27-O7	179.2 (19)	C25-C26-C27-C34	-1.7 (3)
C9-O3-C10-C3	78.4 (2)	C28-O7-C27-C26	-101.5 (2)
O1-C3-C10-C11	-175.2 (19)	C28-O7-C27-C34	79.4 (2)
C2-C3-C10-C11	4.5 (3)	C27-O7-C28-C29	-144.3 (19)
O1-C3-C10-O3	3.7 (3)	O7-C28-C29-C30	69.7 (3)
C2-C3-C10-O3	-176.6 (19)	C31-O8-C30-C29	-173.9 (19)
O3-C10-C11-C12	178.6 (19)	C28-C29-C30-O8	60.4 (2)
C3-C10-C11-C12	.5 (3)	C30-O8-C31-C32	68.2 (3)
C10-C11-C12-C1	-1.9 (3)	O8-C31-C32-C33	48.8 (3)
C10-C11-C12-C13	179.1 (2)	C34-O9-C33-C32	173.0 (19)
C2-C1-C12-C11	4.2 (3)	C31-C32-C33-O9	-75.7 (3)
C36-C1-C12-C11	-176.3 (19)	C33-O9-C34_C35	16.7 (3)
C2-C1-C12-C13	-176.7 (19)	C33-O9-C34-C27	-163.0 (19)
C36-C1-C12-C13	2.8 (3)	C26-C27-C34-O7	-175.9 (19)
C11-C12-C13-C24	176.1 (2)	O7-C27-C34-O9	3.2(3)
C1-C12-C13-C24	-2.9 (3)	C26-C27-C34-C35	4.3.(3)
C11-C12-C13-C14	-2.8 (3)	O7-C27-C34-C35	-176.6 (2)
C1-C12-C13-C24	178.2 (2)	O9-C34-C35-C36	177.5 (2)
C24-C13-C14-C15	-1.8 (3)	C27-C34-C35-C36	-2.8 (3)
C12-C13-C14-C15	177.1 (2)	C26-C25-C36-C35	3.9 (3)
C16-O4-C15-C14	14.7 (4)	C24-C25-C36-C35	-177.0 (19)
C16-O4-C15-C22	-164.7 (2)	C26-C25-C36-C1	-177.1(19)
C13-C14-C15-O4	-179.6 (2)	C24-C25-C36-C1	2.0 (3)
C13-C14-C15-C22	-0.2 (3)	C34-C35-C36-C25	-1.4 (3)
C15-O4-C116-C17	-174.5 (2)	C34- C35-C36-C1	179.7 (2)
O4-C16-C17-C18	-50.2 (3)	C12-C1-C36-C25	-2.4 (3)
C19-O5-C18-C17	-129.5 (2)	C2-C1-C36-C25	177.2 (2)
C16-C17-C18-O5	81.6 (2)	C12-C1-C36-C35	176.5 (19)
C18-O5-C19-C20	156.2 (19)	C2-C1-C36-C35	-3.9 (3)
O5-C19-C20-C21	-68.7 (3)	C19-C20-C21-O6	-63.4(3)
C22-O6-C22-C23	148.6(2)	C22-C23-C21-O6	120.8(2)
C21-O6-C22-C15	65.1(3)		

Chapter 4

4.1: The 2:1 complex of B11C3 with LiSCN

To date the smallest crown ether complexes of 2:1 benzo-10-crown-3: LiClO_4 and 2:1 naphtho-9-crown-3: LiClO_4 complex have been reported by Buchanan [45,46]. In this study the first complex of 11-crown-3 ether was synthesized.

The complex of 2:1 benzo-11-crown-3 with LiSCN was synthesized in the presence of 2 moles of benzo-11-crown-3 and 1 mole of lithium thiocyanate monohydrate in a yield of 89%. Mass spectroscopy, solution and solid-state NMR and X-ray crystallography confirmed the formation of $(\text{B11C3})_2\text{LiSCN}$ complex, **5**.

The melting point of the complex (110- 114C°) was significantly increased in contrast with the benzo-11-crown-3, which is liquid at room temperature.

For complexation of the biologically important Li^+ ion, the 14-crown-4 ether system has the most nearly "ideal" cavity dimensions [47].

4.2: X-ray structure of **5**

An attempt was made to form and crystallize a 2:1 complex between B11C3 and LiSCN by the use of a stoichiometric amount of each chemical in 1:1 ethyl acetate: acetone.

The ORTEP diagram of the structure obtained is presented in Fig. 15, and clearly represents that of the 2:1 B11C3: LiSCN complex. When the cavity of the

crown ethers is too small to host the alkali metal cation, the crown ether forms stable 2:1 guest-host sandwich complexes with the alkali metal cations [19]. The formation of the (B11C3)₂.LiSCN complex indicates that the diameter of the B11C3 cavity is smaller than the diameter of Li⁺ ion, which is 1.36 Å [15].

In **5** there are two non-equivalent sandwich complexes in the crystal, **5a** and **5b**, each possessing a crystallographic plane of symmetry through the Li⁺ (Fig. 15). Also **5a** is a pseudo-mirror image of **5b**, where the coordination geometry and bond distances from the lithium cation to the ethereal oxygens differs slightly. These differences are small, but larger than the experimental uncertainty and probably caused by crystal packing phenomenon. For example the Li (1)-O1, Li (1)-O2 and Li (1)-O3 bond lengths are 2.043(2), 2.039(2) and 2.131(2) Å respectively, while the Li (2)-O4, Li (2)-O5 and Li (2)-O6 distances are 2.084(2), 2.059(2) and 2.091 (2) Å respectively.

Each complex adopts an octahedral geometry with Li⁺ coordination number six and average O-Li-O bond angle of 84.56° with a standard deviation from the mean of 3.97°. This geometry is thus very close to the ideal geometry expected for octahedral coordination. The average Li-O distance for the ethereal oxygens of 2.07 Å is shorter by 0.04 Å than found in the (benzo-10-crown-3)₂ . LiClO₄ complex (2.11 Å) [45].

A comparison of the torsion angles (Table 15) for the two eleven-membered rings of the complex (ring A involving O1, O2 and O3 vs. ring B involving O4, O5 and O6) shows that the geometries of those two rings are identical.

Figure 15: The ORTEP diagram of 5a and 5b

Figure 16: Unit cell of 5

Table 10. Crystallographic Data of 5

Formula	C ₂₅ H ₃₂ LiNO ₆ S
Formula mass	481.52
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å)	7.7397(8)
b (Å)	18.287(2)
c (Å)	17.4726(19)
β (°)	94.008(2)
V (Å ³)	2466.9(5)
Z (molecules per unit cell)	4
D _c (g cm ⁻³)	1.296
Crystal dimension (mm)	0.20 X 0.20 X 0.20
Radiation (λ , Å)	Mok α . 0.70930
Octants measured	h (-10 to 10), k (0 to 24), l (0 to 23)
Max 2 θ (°)	28.72
Temperature (K)	203(2)
No. of unique reflections	5897
No. of reflections measured	19277
No. of reflections with $I_{\text{net}} > 2\sigma I_{\text{net}}$	5438
R1 ($I > 2\sigma I$)	0.0610
R1 (all data)	0.0875
wR2 ($I > 2\sigma I$)	0.1880
wR2 (all data)	0.1987
GoF	1.036
Largest diff. Peak and hole (e Å ⁻³)	0.848 and -0.642

Table 11: Atomic bond lengths (Å) of 5

Li (1) -O2	2.039 (16)	C1 - C2	1.389 (3)
Li (1) -O1	2.043 (15)	C1 - C6	1.399 (3)
Li (1) -O3	2.131 (17)	C2 - C3	1.382 (4)
Li (2) -O5	2.059 (15)	C3 - C4	1.379 (4)
Li (2) -O4	2.084 (15)	C4 - C5	1.383 (4)
Li (2) -O6	2.091 (15)	C5 - C6	1.384 (3)
N1 - C25	1.059 (5)	C7 - C8	1.513 (5)
O1 - C1	1.372 (3)	C8 - C9	1.489 (5)
O1 - C12	1.450 (3)	C10 - C11	1.489 (5)
O2 - C6	1.381 (3)	C11 - C12	1.484 (5)
O2 - C7	1.453 (3)	C13 - C14	1.385 (3)
O3 - C9	1.429 (4)	C13 - C18	1.386 (3)
O3 - C10	1.437 (4)	C14 - C15	1.388 (4)
O4 - C13	1.385 (3)	C15 - C16	1.382 (4)
O4 - C24	1.451 (3)	C16 - C17	1.395 (4)
O5 - C18	1.378 (3)	C17 - C18	1.388 (3)
O5 - C19	1.454 (3)	C19 - C20	1.502 (3)
O6 - C21	1.427 (3)	C20 - C21	1.507 (3)
O6 - C22	1.440 (3)	C22 - C23	1.524 (3)
S1 - C25	1.670 (5)	C23 - C24	1.520 (3)

Table 12: Atomic bond angles (Å) of 5

O2-Li (1)-O1	79.96 (6)	O1-C1-C6	116.7 (2)
O5-Li (2)-O4	78.72 (6)	O2-C6-C1	116.7 (2)
C1-O1-C12	116.4 (2)	C9-C8-C7	114.9 (3)
C6-O2-C7	116.2 (2)	C12-C11-C10	115.5 (3)
C9-O3-C10	113.4 (2)	C14-C13-O4	122.8 (2)
C13-O4-C24	117.1 (2)	O5-C18-C17	122.8 (2)
C18-O5-C19	116.8 (2)	C19-C20-C21	113.8 (2)
C21-O6-C22	112.4 (2)	C24-C23-C22	114.0 (2)
O1-C1-C2	124.0 (2)	O1Li (1)-O3	85.35 (7)
O2-C6-C5	123.5 (2)	O4- Li (2)-O6	89.08 (6)
O2-C7-C8	111.8 (2)	C12-O1- Li (1)	126.8 (6)
O3-C10-C11	112.6 (3)	C7-O2- Li (1)	122.8(2)
C14-C13-C18	120.7 (2)	C10-O3- Li (1)	121.6 (2)
O5-C18-C13	117.0 (2)	C24-O4-Li (2)	122.3 (1)
O5-C19-C20	109.3 (2)	C19-O5- Li (2)	126.4 (1)
O6-C22-C23	113.1 (2)	C22-O6- Li (2)	115.6 (1)
N1-C25-S1	177.7 (3)	C2-C1-C6	119.9 (2)

O2-Li (1)-O3	88.75 (7)	C5-C6-C1	119.7 (2)
O5-Li (2)-O6	85.52 (6)	O3-C9-C8	114.2 (2)
C1-O1-Li (1)	111.3 (1)	O1-C12-C11	110.4 (2)
C6-O2-Li (1)	110.8 (1)	C18-C13-O4	116.4 (2)
C9-O3- Li (1)	115.6 (2)	C13-C18-C17	120.2 (2)
C13-O4- Li (2)	110.8 (1)	O6-C21-C20	110.8 (2)
C18-O5- Li (2)	111.3 (1)	O4-C24-C23	112.0 (2)
C21-O6-Li (2)	123.4 (1)		

Table 13: Torsion angles of 5

O2-Li1-O1-C1	19.31 (14)	O3-Li1-O1-C1	108.8 (14)
O2-Li1-O1-C12	-133.4 (2)	O3-Li1-O1-C12	-43.9 (2)
O1-Li1-O2-C6	-32 (100)	O3-Li1-O2-C6	-104.5 (15)
O1-Li1-O2-C7	125.0 (2)	O3-Li1-O2-C7	39.5 (2)
O2-Li1-O3-C9	-40.9 (19)	O1-Li1-O3-C9	-120.9 (19)
O2-Li1-O3-C10	103.3 (2)	O1-Li1-O3-C10	23.3 (2)
O5-Li2-O4-C13	19.9 (12)	O6-Li4-O4-C13	105.5 (13)
O5-Li2-O4-C24	-124.7 (17)	O6-Li2-O4-C24	-39.0 (16)
O4-Li2-O5-C18	-20.6 (13)	O6-Li2-O5-C18	-110.5 (13)
O4-Li2-O5-C19	132.1 (2)	O6-Li2-O5-C19	42.1 (19)
O5-Li2-O6-C21	-23.7 (16)	O4-Li2-O6-C21	-102.4 (17)
O5-Li2-O6-C22	121.5 (14)	O4-Li2-O6-C22	42.77 (17)
C12-O1-C1-C2	-42.1 (3)	Li1-O1-C1-C2	162.0 (19)
C12-O1-C1-C6	139.3 (2)	Li1-O1-C1-C6	-16.5 (2)
O1-C1-C2-C3	-177.1 (2)	C6-C1-C2-C3	1.4 (3)
C1-C2-C3-C4	0.0 (4)	C2-C3-C4-C5	0.0 (4)
C3-C4-C5-C6	-1.4 (4)	C7-O2-C6-C5	54.1 (3)
Li1-O2-C6-C5	-159.3 (19)	C7-O2-C6-C1	-130.5 (2)
Li1-O2-C6-C1	16.1 (2)	C4-C5-C6-O2	178.3 (2)
C4-C5-C6-C1	2.8 (3)	O1-C1-C6-O2	0.3 (3)
C2-C1-C6-O2	-178.3 (2)	O1-C1-C6-C5	175.8 (2)
C2-C1-C6-C5	-2.8 (3)	C6-O2-C7-C8	88.3 (3)
Li1-O2-C7-C8	-53.9 (3)	O2-C7-C8-C9	62.8 (4)
C10-O3-C9-C8	-85.6 (3)	Li1 O3-C9-C8	61.5 (3)
C7-C8-C9-O3	-70.6 (4)	C9-O3-C10-C11	167.6 (3)
Li1-O3-C10-C11	22.7 (4)	O3-C10-C11-C12	-74.8 (4)
C1-O1-C12-C11	-138.5 (3)	Li1-O1-C12-C11	13.1 (4)
C10-C11-C12-O1	54.7 (40)	C24-O4-C13-C14	-54.1 (3)
Li2-O4-C13-C14	159.3 (17)	C24-O4-C13-C18	130.2 (2)
Li2-O4-C13-C18	-16.4 (2)	C18-C13-C14-C15	-1.2 (3)

O4-C13-C14-C15	-176.7 (2)	C13-C14-C15-C16	0.1 (4)
C14-C15-C16-C17	0.9 (4)	C15-C16-C17-C18	-0.8 (4)
C19-O5-C18-C13	-137.1 (2)	Li2-O5- C18-C13	18.5 (2)
C19-O5-C18-C17	44.6 (3)	Li2-O5-C18-C17	-159.8 (17)
C14-C13-C18-O5	-177.0 (19)	O4-C13-C18-O5	-1.2 (3)
C14-C13-C18-C17	1.3 (3)	O4-C13-C18-C17	177.1 (19)
C16-C17-C18-O5	177.9 (2)	C16-C17-C18-C13	-0.3 (3)
C18-O5-C19-C20	142.4 (2)	Li2-O5 C19-C20	-9.0 (3)
O5-C19-C20-C21	-58.7 (3)	C22-O6-C21-C20	-169.0 (19)
Li2-O6-C21-C20	-22.9 (3)	C19-C20-C21-O6	77.1 (3)
C21-O6-C22-C23	84.5 (2)	Li2-O6-C22-C23	-64.5 (2)
O6-C22-C23-C24	72.0 (3)	C13-O4-C24-C23	-89.9 (2)
Li2-O4-C24-C23	52.6 (2)	C22-C23-C24-O4	-62.7 (3)

Table 14: Atomic coordinates [$\times 10^4$] and equivalent isotropic displacementparameters [$\text{\AA}^2 \times 10^3$]

	X	Y	Z	U (eq)
Li (1)	0	5000	5000	34 (1)
Li (2)	10000	5000	10000	31 (1)
N1	1593 (6)	2443 (2)	7618 (2)	81 (1)
O1	540 (2)	5816 (1)	5779 (1)	34 (1)
O2	932 (2)	4397 (1)	5920 (1)	36 (1)
O3	-2491 (2)	4975 (1)	5448 (1)	46 (1)
O4	9230 (2)	4222 (1)	9148 (1)	31 (1)
O5	9230 (2)	4128 (1)	10639 (1)	32 (1)
O6	12490 (2)	4559 (1)	10172 (1)	30 (1)
S1	4726 (2)	2642 (1)	7022 (1)	84 (1)
C1	1681 (3)	5585 (1)	6365 (1)	30 (1)
C2	2635 (2)	6052 (1)	6858 (1)	38 (1)
C3	3812 (3)	5769 (2)	7411 (2)	41 (1)
C4	4039 (3)	5023 (2)	7474 (1)	41 (1)
C5	3097 (3)	4551 (1)	6987 (1)	39 (1)
C6	1888 (3)	4828 (1)	6442 (1)	31 (1)
C7	-37 (4)	3892 (2)	6237 (2)	53 (1)
C8	-1823 (4)	4043 (2)	6435 (2)	68 (1)

C9	-2978 (4)	4292 (2)	5766 (2)	63 (1)
C10	-3173 (4)	5597 (2)	5829 (2)	69 (1)
C11	-2358 (5)	6297 (2)	5609 (2)	74 (1)
C12	-572 (4)	6424 (2)	5948 (2)	54 (1)
C13	8366 (3)	3682 (1)	9406 (1)	30 (1)
C14	7363 (3)	3234 (1)	8914 (2)	41 (1)
C15	6258 (3)	2732 (1)	9221 (2)	49 (1)
C16	6153 (3)	2676 (1)	10005 (2)	47 (1)
C17	7146 (3)	3136 (1)	10498 (2)	40 (1)
C18	8249 (3)	3640 (1)	10192 (1)	31 (1)
C19	10127 (3)	3840 (2)	11333 (2)	44 (1)
C20	11871 (3)	4199 (1)	11454 (1)	37 (1)
C21	13011 (3)	4090 (1)	10799 (1)	38 (1)
C22	13326 (3)	4378 (1)	9486 (1)	35 (1)
C23	12403 (3)	3771 (1)	9020 (2)	38 (1)
C24	10692 (3)	4003 (1)	8612 (1)	37 (1)
C25	2805 (5)	2508 (1)	7379 (2)	53 (1)

Table 15: The torsion angles of ring A and ring B

Network A	Torsion angle in A	Network B	Torsion angle in B
C12-O1-C1-C2	-42.1 (3)	C17-C18-O5-C19	44.6 (3)
O1-C1-C6-O2	0.3 (3)	O4-C13-C18-O5	-1.2 (2)
C10-O3-C9-C8	-85.6 (3)	C21-O6-C22-C23	84.5 (2)
C6-O2-C7-C8	88.3 (3)	C13-O4-C24-C23	-89.9 (2)
C7-O2-C6-C5	54.1 (3)	C24-O4-C13-C14	-54.1 (3)
C12-O1-C1-C6	139.3 (2)	C19-O5-C18-C13	-137.1 (2)
C7-C8-C9-O3	-70.6 (4)	O6-C22-C23-C24	72.0 (3)
O3-C10-C11-C12	-74.8 (4)	O6-C21-C20-C19	77.1 (3)

As mentioned before, no X-ray crystal structure of B11C3 is available since it is an oil. The HyperChem program was used to calculate the gas phase geometry of benzo-11-crown-3, **2** and compare it with the geometry of the (B11C3)₂.LiSCN complex **5**. These data are presented in table 16. From

examination of molecular models it is clear that the conformational changes, which occur upon complexation, accompany the reorientation of the oxygen lone pairs on O1, O2 and O3. As a result one pair of electrons on each oxygen becomes available for pseudooctahedral coordination to the lithium cation.

Table 16: The comparison of torsion angles of 2 and 5

Network	Torsion angle In 2 (°)	Torsion angle In 5 (°)
C1-O1-C12-C11	-148.7	-138.5
O1-C12-C11-C10	98.7	54.7
C12-C11-C10-O3	-78.4	-85.9
C11-C10-O3-C9	161.1	167.6
C10-O3-C9-C8	-74.3	-85.6
O3-C9-C8-C7	-70.6	-50.1
C9-C8-C7-O2	100.6	62.8
C8-C7-O2-C6	-166.6	88.3
C7-O2-C6-C1	109.5	-130.5
O2-C6-C1-O1	-10.9	0.3
C6-C1-O1-C12	61.4	139.3

4.3: Solution NMR studies of 5

In most cases down field NMR shifts are observed when the benzo-crown ethers are complexed with alkali metal ions. Live and Chan [28] reported that such shifts might be the result of a change in the dihedral angle on complexation, which affects the position of the ether protons relative to that of the benzo groups.

The ^1H and ^{13}C NMR spectra in solution (Fig. 17) of the complex $(\text{B11C3})_2 \cdot \text{LiSCN}$ show that all the ^1H and ^{13}C chemical shifts were deshielded, as is expected due to the effect of Li cation complexation (Table 17).

Table 17: The ^{13}C NMR (in solution) chemical shifts of benzo-11-crown-3, **2** and its complex with Li^+ , **5**

	Free ligand	Li^+ complex
$=\underline{\text{C}}-\text{O}$	151.1	149.6
$\underline{\text{C}}\text{H}-\text{CH}=\text{C}$	122.6	123.8
$\underline{\text{C}}\text{H}=\text{C}-\text{O}$	118.5	118.2
$\text{C}-\text{O}-\underline{\text{C}}\text{H}_2$	69.6	74.1
$\text{CH}_2-\text{O}-\text{CH}_2$	66.5	70.3
$\text{CH}_2-\underline{\text{C}}\text{H}_2-\text{CH}_2$	29.5	28.2

The change in chemical shift is a result of conformational changes, which occur upon complexation. This is also consistent with a loss of electron density around the ethereal oxygens. The largest chemical shifts were observed on the carbons of $\underline{\text{CH}}_2\text{-O-}\underline{\text{CH}}_2$ and $\underline{\text{CH}}_2\text{-C-O}$ with ca. 3.76 and 4.48 ppm respectively.

The signal assignments in ^1H and ^{13}C NMR spectra of Li^+ complex were also made using a combination COSY and NOESY experiments and HETCOR experiment (Fig. 18) in the same manner as the free ligand (B11C3).

Figure 17: 400 MHz ^1H and 100.6 MHz ^{13}C NMR of 5.

Figure 18: 400 MHz a) NOESY and b) HETCOR spectra of **5**

4.4: Assignment of the solid-state ^{13}C shifts 5

The solid-state ^{13}C CP/MAS spectrum of **5** shows additional multiplicity over that obtained in solution (Table 18) as was expected based on the X-ray crystal structure. An artificial equivalence may exist in solution due to low energy rotational or other conformational processes which do not occur in the solid. Therefore solid-state spectra give rise to line multiplicities that are not observed in solution [47].

Table 18: ^{13}C NMR chemical shifts (δ_{C} from TMS ± 0.1) for (benzo-11-crown-3) $_2\text{LiSCN}$, **5**.

	5(CDCl₃ solution)	5 (solid)
C1	149.6	153.1
C2	118.2	121.5^a
C3	123.8	126.4^b
C4	123.8	127.0^b
C5	118.2	121.0^a
C6	149.6	149.0
C7	74.1	78.0
C8	28.3	28.0
C9	70.3	72.8
C10	70.3	72.8
C11	28.3	28.0
C12	74.1	78.0

^{a,b} Indicate possible interchange of assignments

In the spectrum at 300K (Fig. 19) seven aromatic carbons resonances are observed, however if there was a single symmetrical complex there would be six carbon resonances present in the solid state.

In the dipolar dephased CP/MAS spectrum of **5** (Fig. 19), the protonated carbon resonances disappear completely, indicative of static solid devoid of any large amplitude conformational motion in the macrocycle. The two resonances at 153.1 and 149.0 ppm must arise from the C1 and C6. The C1 and C6 can be distinguished based on their C-O bond lengths. The C1-O1 bond length is shorter than the C6-O2 bond, which are 1.372(3) Å and 1.381(3) Å respectively. The shorter bond length, the more double bond character and more deshielding. Therefore, the resonance at 153.1 ppm likely corresponds to C1 and the resonance at 149.0 ppm corresponds to C6.

In the aliphatic carbon resonance region of a single symmetrical complex, it is expected to have 6 carbon resonances (4 in the region of 70-80 ppm and 2 in the region of 25.30 ppm). The appearance of the aliphatic carbon resonances as broad lines at 300 K appears to be due to the "dipolar washout" phenomenon. The higher temperature broadening can be described as dipolar "washout" and will occur when the molecular motions have rates such that the correlation time for the C-H is equal the inverse of the chemical shift differences. The "dipolar washout" phenomenon was first described about 20 years ago [49] and more recently observed by Buchanan and his co-workers [50,51] in several 18-crown-6 complexes. Apparently, the motion of the C-H vectors of the aliphatic carbons in the solid state is occurring on approximately the same timescale (200MHz) as the

^1H decoupling rf field. Hence interference is set up between the motionally generated rf field and the ^1H decoupler. This renders the decoupler less effective resulting in a dipolar broadened ^{13}C spectrum. When the temperature is increased to 330K (Fig. 20) the increased motional frequency leads to a situation in which there is less interference with the decoupling field and sharper resonances are observed. Coincident with this phenomenon is the observation of very long ^1H spin lattice relaxation times at these sites, with values of ca. 60s at 300K and 120s at 330K. These long T_1 's dramatically increase the time required to obtain spectra for the attached carbons with reasonable signal to noise ratios.

a)

b)

Figure 19: 50.3 MHz (a) normal (300K) and (b) dipolar dephased CP/MAS spectra of **5**

Figure 20: CP/MAS spectrum (330 K) of **5**, spinning rate is ca. 4000 Hz.

X= Spinning sidebands

Chapter 5

5.1:Complexation of 3 with K⁺ and Na⁺

Efforts to make the complexes of **3** with NaSCN and KSCN salts resulted in two complexes (1:1) (DB22C6):NaSCN (mp. 155-160 C°) and (1:1) (DB22C6):KSCN (mp. 145-150). The melting point enhancements in the complexes, in comparison with free **3**, are assumed to be an indication of complex formation. The efforts to obtain X-ray grade single crystals were unsuccessful.

The ESI (Electrospray Impact) MS was run on the complexes and the appropriate molecular ions of the two complexes were observed, a peak at 439.0 (100%) for 1:1 Na⁺ complex (C₂₄H₃₂O₆Na); and a peak at 455.0 (69.7%) due to the 1:1 K⁺ complex (C₂₄H₃₂O₆OK) were detected.

1,7-dichloro-4-oxaheptane

Figure 21: 200 MHz ^1H and 50.3 MHz ^{13}C NMR spectra of 1,7- dichloro-4-oxaheptane.

Figure 22: Mass spectrum of Benzo-11-crown-3

Figure 23: Mass spectrum of Dibenzo-22-crown-6

Figure 24: Mass spectrum of Tris(11-crown-3)triphenylene

Figure 25: Mass spectrum of (Benzo-11-crown-3)₂.LiSCN Complex, 5

Figure 26: Mass spectrum of (Dibenzo-22-crown-6).KSCN Complex

Figure 27: Mass spectrum of (Dibenzo-22-crown-6).NaSCN Complex

Experimental

All the starting materials used in this study were purchased from Aldrich, and used without further purifications

- 1-chloro-3-propanol
- Catechol 99%
- Lithium hydroxide monohydrate
- Iron (III) chloride (FeCl_3)
- Lithium thiocyanate
- Sodium thiocyanate
- Potassium thiocyanate
- Carbon tetrachloride

Figure 28: Synthetic scheme for compounds 1 and 7

Experimental

5.1: Synthesis of 1,7-dichloro-4-oxaheptane

3-chloro-1-propanol (100 g, 1.1 mol) was poured in a 250 ml round bottom flask, which was equipped with a condenser. Concentrated H_2SO_4 (70 g) was then added dropwise via a Pasteur pipet with vigorous stirring. The mixture was refluxed by immersing the flask into an oil-bath at 130 °C for overnight. After cooling the mixture to room temperature, the mixture was poured onto 300 g ice and neutralized with 3 M NaOH. The mixture was extracted with CH_2Cl_2 (4 x300 mL). The combined organic layers were dried over anhydrous sodium sulfate followed by solvent removal using a rotoevaporation, to yield 39.5 g, 22% of crude 1,7-dichloro-4-oxaheptane, as a dark green liquid. The crude product was used for the next step without further purification.

^1H NMR (CDCl_3) δ_{H} : -3.49-3.63 ppm (m, 4H, Cl-CH_2 , O-CH_2), 1.97 ppm (t,

$\text{CH}_2\text{-CH}_2\text{-CH}_2$)

^{13}C NMR (CDCl_3) δ_{C} : 67.5 ppm, ($\text{CH}_2\text{-O-CH}_2$) 42.2 ppm ($\text{CH}_2\text{-Cl}$), 32.9 ppm

($\text{CH}_2\text{-CH}_2\text{-CH}_2$),

5.2: Synthesis of B11C3

In a 3-necked 3 L round bottom flask, that was equipped with a dropping funnel and a condenser, catechol (25.0 g, 0.23 mol), distilled water (2500 mL) and LiOH.H₂O (20.0 g, 0.48 mol) were added. This mixture was then stirred and refluxed for 1 hr. 1,7 dichloro-4-oxaheptane (38.85 g, 0.23 mol) was added dropwise with stirring and the mixture was refluxed for 5 days. After cooling to room temperature, the mixture was acidified to pH 2-3 using concentrated H₂SO₄ and then extracted with CH₂Cl₂ (3 x 300 mL). The combined organic layers were washed with 5% NaOH (3 x 300 mL) followed by water (2 x 300 mL). The organic layers were dried over anhydrous Na₂SO₄. The solvent removal via rotoevaporation yielded an oil, which was then treated with boiling hexane (5 x 300 mL). The hexane extracts were decanted into a clean beaker. After cooling to room temperature, a quantity (0.8 g) of white crystals precipitated. These crystals were collected by vacuum filtration and subsequently identified as dibenzo-22-crown-6 ether. The hexane filtrate was concentrated by rotary evaporation to yield a dark yellow oil. This oil was purified by column chromatography on silica gel using dichloromethane/diethyl ether (95: 5) as eluent to yield 9.0 g, 19.2% of benzo-11-crown-3 ether, as a pale yellow oil.

B11C3

¹H NMR (CDCl₃) δ_H : 6.96 ppm (m, aromatic), 4.13 ppm (t, =C-O-CH₂), 3.98 ppm (t, CH₂-O-CH₂), 1.98 ppm (m, CH₂-CH₂-CH₂)

¹³C NMR (CDCl₃) δ_C : 151.05 ppm (=C-O) , 122.68 ppm (CH=C), 118.56 ppm

(CH-CH=C), 69.6 ppm (=C-O-CH₂), 66.5 ppm (CH₂-O-CH₂), 29.5 ppm (CH₂-CH₂-CH₂)

High resolution MS : m/e for C₁₂H₁₆O₃ , Calc. : 208.2573; Found: 208.1085 (100%)
other peaks at 150.1(63.7%), 121.0 (72.9%), 109.0 (55.9%) and 41.0(41.3%).

Elemental analysis: Calculated	C, 69.26	H, 7.75
Found	C, 69.38	H, 7.83

DB22C6

¹H NMR (CDCl₃) δ_H : 6.83 ppm (m, 8H, aromatic), 4.04 (t, 8H, =C-O-CH₂), 3.71 (t, 8H, CH₂-O-CH₂), 2.09 (t, 8H, CH₂-CH₂-CH₂).

¹³C NMR (CDCl₃) δ_C : 148.5 ppm (=C-O) , 120.7 (CH-CH=C), 112.5 (CH-CH=C), 67.9 (=C-O-CH₂), 64.8 (CH₂-O-CH₂), 29.6 (CH₂-CH₂-CH₂).

+ESI MS : m/z 416 (100%), 151 (56.4%), 121 (41.7%).

Elemental analysis: Calculated	C, 69.26	H, 7.75
Found	C, 69.19	H, 7.21

5.3: Synthesis of tris(B11C3)triphenylene

In a 500ml double necked round bottom flask, which was equipped with a dropping funnel and a condenser with a gas inlet tube, FeCl_3 (10.5 g, 0.065 mol), CCl_4 (120 mL) and concentrated H_2SO_4 (15 drops) were added. To the mixture, B11C3 (4.5 g, 0.022 mol) in CCl_4 (100 mL) was added dropwise with vigorous stirring under N_2 . The mixture was refluxed for 4 days (under N_2). Then 120 mL of methanol were added and the mixture was refluxed for one more day. After cooling, 100 ml distilled water was added to it. The mixture was transferred into a separatory funnel and the crude product was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic layers were washed with distilled water (2 X 300 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation to yield 4.0 g of a dark brown oil, which was a mixture of B11C3 and B11C3 trimer (^1H NMR showed a ratio of 8:1).

The dark brown oil was boiled in hexane (5 x 400 mL) to dissolve the unreacted B11C3. After separation of almost all the B11C3 a brown precipitate was produced. The precipitate was collected by vacuum filtration, and washed with further 300 mL of hot hexane. Subsequently the resulting brown powder was transferred to a beaker and a small amount of acetone (~30 mL) were added to produce a light yellow precipitate. This light yellow solid was dissolved in 40 mL of CH_2Cl_2 and boiled with activated charcoal. After gravity filtration, the volume of the solvent was reduced to ca. 10 mL by boiling, and then anhydrous diethyl ether (20 mL) was added. After 3 days 0.007 g (0.5% yield) of 4, mp 285-290 °C were obtained as light yellow needles.

^1H NMR (CDCl_3) δ_{H} : 7.98 ppm (s, aromatic), 4.34 (t, $=\text{C}-\text{O}-\text{CH}_2$), 3.94 (t, $\text{CH}_2-\text{O}-\text{CH}_2$), 2.11 (m, $\text{CH}_2-\text{CH}_2-\text{CH}_2$)

^{13}C NMR (CDCl_3) δ_{C} : 150.4 ppm ($=\text{C}-\text{O}$), 124.9 ($=\text{C}-\text{C}$), 111.6 ($=\text{CH}$), 29.6 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$)

+ESI MS : m/z 418

5.4: 1:2 complex of Benzo-11-crown-3 with LiSCN

Benzo-11-crown-3 (0.400g, 1.92 mmole) in 15 mL ethyl acetate was added to LiSCN (0.100g, 0.99 mmole) in hot ethyl acetate (10 mL). The solvent volume was then reduced to ca. 7 mL by boiling. Crystallization proceeded by standing overnight at room temperature to give yellow opaque crystals. The crystals were recrystallized by dissolving in 20 mL 1:1 ethyl acetate:acetone. After 4 days, 0.72g (89%), mp 110-113 C° of light yellow needle crystals was obtained.

^1H NMR (CDCl_3) δ_{H} : 7.02 ppm (s, aromatic), 4.34 ppm (t, $=\text{C}-\text{O}-\text{CH}_2$), 3.82 ppm (t, $\text{CH}_2-\text{O}-\text{CH}_2$), 2.02 ppm (m, $\text{CH}_2-\text{CH}_2-\text{CH}_2$).

^{13}C NMR (CDCl_3) δ_{C} : 149.6 ppm ($=\text{C}-\text{O}$), 123.8 ppm ($\text{CH}=\text{C}$), 118.2 ppm ($\text{CH}-\text{CH}=\text{C}$), 74.1 ppm ($=\text{C}-\text{O}-\text{CH}_2$), 70.3 ppm ($\text{CH}_2-\text{O}-\text{CH}_2$), 28.3 ppm ($\text{CH}_2-\text{CH}_2-\text{CH}_2$)

+ESI MS: 423.1 (11.92%), 273 (100%), 256 (96%),

5.5: 1:1 Complex of Dibenzo-22-crown-6 with KSCN

Dibenzo-22-crown-6 (0.14 g, 0.336 mmol) was dissolved in hot methanol (10 mL), and potassium thiocyanate (0.03 g, 0.336 mmol) was also dissolved in methanol (10 mL), and it was then added to the DB22C6 solution. The volume of the solvent was reduced by boiling to ca. 10 mL, and left aside to room temperature. The crystallization started after 6 hr. The crystals (precipitates) were collected by suction filtration, yielded 0.12 g (78%), mp. 145-150C°.

ESI MS: m/z, 455.0 (69.7%)

5.6: 1:1 complex of Dibenzo-22-crown-6 with NaSCN

Dibenzo-22-crown-6 (0.13 g, 0.312 mmol) and NaSCN (0.025 g, 0.312 mmol) were dissolved in hot ethyl acetate (25 mL). The volume was then reduced to ca. 15 mL, and left aside to room temperature. The precipitation formed after one day, which was filtered off to give 0.096 g (70% yield), mp. 155-160 C°.

ESI MS : m/z, 439.0 (100%)

Characterization

Nuclear Magnetic Resonance

Solution NMR:

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer with a 5mm inverse probe and an Aspect X32 computer. All samples were run in CDCl_3 with tetra methyl silane (TMS), used as an internal reference. Routinely ^{13}C spectra were obtained with complete ^1H noise decoupling. All the microprograms used are in the Bruker Software Library.

NOESY experiment

The ^1H ^1H nOe experiments were performed with a 0.5 M CDCl_3 solution and a mixing time selected to be consistent with the $1/T_1$ criterion (It was set to 0.3 s for all of the samples).

HETCOR (HMQC) experiment

For the ^1H ^{13}C HETCOR experiment, the free induction decays (FID) were acquired over 1024 data points for the evolution time, with a digital resolution of ca. 8 HZ / point in F_2 and 4 HZ / point in F_1 . The raw data were zero filled in F_1 prior to the transformation using the qsine window function for both F_1 and F_2 . The proton relaxation decays were set to 1 s. Delays were chosen to emphasize J values of 135-140 Hz.

Solid state NMR experiments

¹³C CP/MAS spectra

The ¹³C CP/MAS spectra were acquired at 50.32 MHz on a Bruker ASX-200 solid state NMR spectrometer, equipped with a Bruker 7 mm triple resonances MAS probe. The magic angle was accurately set using the ⁷⁹Br resonance of KBr by maximizing the number of rotational echoes in the free induction decay. ¹H 90° pulse lengths were typically 3.5-3.8 μ sec with contact times of 1 ms. Chemical shifts were referenced to the ¹³C resonance of tetrakis(trimethylsilyl) silane, Si(Si(CH₃)₃)₄, which was assigned a chemical shift of 3.7 ppm relative to TMS. The spin rates were typically between 4 and 6 KHz.

¹³C CP/MAS Dipolar dephased spectra

The ¹³C CP/MAS Dipolar dephased spectrum of Dibenzo22-crown-6 and (Benzo-11-crown-3)₂ LiSCN complex were recorded with a dephasing delay time of 40 μ sec.

Mass spectrometry Techniques

Electron Impact

The MS spectra of some samples were recorded on a VG 7070E Mass Spectrometer at 70 eV, with 6KV accelerating voltage.

High resolution

B11C3 was analyzed on a KRATOS CONCEPT II H mass spectrometer with the resolution of 8000 and ionization of 70 eV. The sample was scanned by 10 sec/dec., with ac voltage of 8 KV using perfluorokerosene as reference.

Electrospray impact (ESI)

Most of the compounds were analyzed on a Quattro LC, Micromass with the fluorine flow of 20 μ L/min and ac voltage of 3.5-5 KV.

X-ray Crystallographic Measurement

Single crystals of Tris(11-Crown-3)triphenylene, **4** and (B11C3)₂.LiSCN, **5** were mounted on thin glass fibers, and measured on a Bruker AX SMART 1K CCD diffractometer with MoK α radiation, using 0.3° scans at 0, 90, 180°. Unit cell parameters were determined from 60 data frames collected at different sections of Ewald sphere. All the atoms were refined anisotropically except the hydrogen atoms, which were refined isotropically. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . All scattering factors and anomalous dispersion facts are contained in the SHELXTL 5.1 program library. The unit cell parameters and systematic absence are constant with the space group P2(1)/c for **4** and P-1 for **5**.

Conclusion and Future Work

In tris(11-crown-3)triphenylene, **4** two of the three 11-crown-3 ether units contain essentially identical geometries, and in the tris(9-crown-3)triphenylene all the three 9-crown-3 ether units contain different geometries. The three aromatic rings of **4** are essentially coplanar, in contrast to the situation for tris(9-crown-3)triphenylene, where up to ca. 14° deviations from coplanarity were found.

The isolated yield of **4** (0.5%) is very low compared to tris(9-crown-3)triphenylene (25%). This is more likely due to the difficulty in freeing the trimeric compound **4** from its complex with FeCl₃, where the crude yield was about 12%.

The X-ray crystallography and solid-state NMR show that the two benzo-11-crown-3 units of the (benzo-11-crown-3)₂. LiSCN complex, **5** are equivalent as oppose to the 1:2 complex of benzo-10-crown-3 with LiClO₄, where the two crown rings possess different geometries.

In the solid-state ¹³C CP/MAS spectrum of **5** when the temperature was increased from 300 to 330 K, the increased motional frequency leads to a situation in which there is less interference with the decoupling field and sharper resonances are observed.

In conclusion, we have found the complex of 11-crown-3 to be a 2:1 complex of benzo-11-crown-3 with LiSCN. X-ray data show that the complex is rigid, but solid-state ¹³CNMR indicates C-H vector motion in the 11-membered rings with a frequency of ca. 200 MHz.

As a future work, it would be of interest to trimerize the asymmetric benzo-10-crown-3 to determine if both possible trimeric products are observed.

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