การศึกษาโฟโตไอโซเมอไรเซชันของเอโซเบนซีนคราวน์อีเทอร์คาลิก[4]ซารีน สำหรับประยุกต์ในการสกัดไอออนของโลหะแอลคาไล

นางสาวบงกช พิภูษณะนาคทนต์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาเคมี ภาควิชาเคมี

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2542

ISBN 974-333-670-2

Photoisomerization Studies of Azobenzene Crown Ether Calix[4] arenes for Applications in Alkali Metal Ion Extraction

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A Thesis Submitted in Patial Fullfillment of the Requirements
for the Degree of Master of Science in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University

Academic year 1999
ISBN 974-333-670-2

Thesis Title : Photoisomerization Studies of Azobenzene Crown Ether Calix[4] arenes for Applications in Alkali Metal Ion Extraction

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บงกช พิภูษณะนาคทนต์ : การศึกษาโฟโตไอโซเมอไรเซชันของเอโซเบนซีนคราวน์อีเทอร์คาลิก[4] ซารีน สำหรับประยุกต์ในการสกัดไอออนของโลหะแอลคาไล (Photoisomerization Studies of Azobenzene Crown Ether Calix[4]arenes for Applications in Alkali Metal Ion Extraction) อ.ที่ปรึกษา : ผศ.ดร.ธวัชชัย ตันฑุลานิ, อ.ที่ปรึกษาร่วม : อ.ดร. มงคล สุขวัฒนาสินิทธิ์; 102 หน้า. ISBN 574-333-670-2

ทำการสังเคราะห์สารใหม่สองชนิด คือ อนุพันธ์ของเอโซเบนซีนคราวน์อีเทอร์คาลิก[4]ซารีน, 5 และ 8 ได้ 2 วิธี วิธีแรกเตรียมได้จากการนำไนโตรฟีนอกซีไกลโคลิก 2 สายมาเชื่อมต่อกับวงของคาลิก[4]เอรีนในตำแหน่งที่ 1 และ 3 แล้วนำผลิตภัณฑ์ที่ได้มาทำปฏิกิริยารีดักชันโดยใช้ Zn เป็นตัวรีดิวส์ในสารละลายอัลคาไลน์ ได้ผลิตภัณฑ์ 5 และ 8 ปริมาณ 8 % และ 12 % ตามลำดับ ในวิธีที่ 2 ได้ทำการเตรียมเอโซเบนซีนที่ประกอบด้วยสายของไกลโคลิก 2 สายขึ้นก่อนแล้วนำไปต่อเข้ากับวงของคาลิก[4]เอรีน เปอร์เซนต์ผลิตภัณฑ์ที่ได้ (5% และ 8% สำหรับลิแกนด์ 5 และ 8 ตามลำดับ) จากวิธีนี้น้อยกว่าวิธีแรกเล็กน้อย ผลึกของลิแกนด์ทั้งสองได้มาจากการตกผลึกซ้ำในเมธานอล ผลึกของลิแกนด์ 5 เท่านั้นที่สามารถทำเอ็กซเรย์คริสตัลโรกราฟี ผลที่ได้จากทั้งเอ็กซเรย์และเอ็นเอ็มอาร์ชี้ให้เห็นว่า สเตอริโอไอโซเมอร์ของส่วนเอโซเบนซีนของลิแกนด์ 5 อยู่ในรูป*ทรานส์*และส่วนของคาลิก[4]เอรีนยังคงอยู่ในรูปโคนคอนฟอร์เมชัน ในทางตรงกันข้าม ผลจากเอ็นเอ็มอาร์ของ 8 บอกเป็นนัยว่า ลิแกนด์ 8 ที่ตกผลึกออกมาได้อยู่ในรูป*ซิส*ไอโซเมอร์และมีคอนฟอร์เมชันเป็นโคน การศึกษาไอโซเมอไรเซชันของลิแกนด์ทั้งสองชนิดพบว่า สารละลายของลิแกนด์ 5 เกิด*ซิส-ทรานส์*ไอโซเมอไรเซชันได้หลังจากวางไว้ภายใต้แสงปกติที่อุณหภูมิห้องและภายใต้แสงยูวี แต่สำหรับลิแกนด์ 8 มีการเปลี่ยนแปลงคอนฟอเมชันของวงคาลิกเอรีนเกิดขึ้น ทำให้การสังเกตการเกิด*ซิส-ทรานส์*ไอโซเมอไรเซชันทำได้ยากและไม่อาจสรุปได้ชัดเจนว่าเกิด*ซิส-ทรานส์*ไอโซเมอไรเซชันหรือไม่ สำหรับการศึกษาการเกิดสารประกอบเชิงซ้อนพบว่าโซเดียมไอออนชอบจับกับลิแกนด์ทั้งสองชนิดในรูป*ซิส*ไอโซเมอร์ ในขณะที่โปแตสเซียมไอออนชอบจับในรูป*ทรานส์*ไอโซเมอร์ในตอนแรก

ภาควิชา เคมี ลายมือชื่อนิสิต บงกช พิภูษณะนาคทนต์

สาขาวิชา เคมี ลายมือชื่ออาจารย์ที่ปรึกษา ธวัชชัย ตันฑุลานิ

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

4072294123 : MAJOR CHEMISTRY.

KEY WORDS : AZOBENZENE, CROWN ETHER, CALIXARENE, PHOTOISOMERIZATION, AND ION-SENSOR

BONGKOT PIPOOSANANAKATON : PHOTOISOMERIZATION STUDIES OF AZOBENZENE CROWN ETHER CALIX[4] ARENES FOR APPLICATION IN ALKALI METAL ION EXTEACTION. THESIS ADVISOR : ASSIST. PROF. THAWATCHAI TUNTULANI, Ph.D.; THESIS CO-ADVISOR : MONGKOL SUKWATTANASINITT, Ph.D. 102 pp. ISBN 574-333-670-2

Two new compounds, derivatives of azobenzene crown ether calix[4]arenes **5** and **8** were prepared by two pathways. In the first pathway, two nitrophenoxy glycolic chains were attached to *t*-butylcalix[4]arenes ring in a 1,3 alternated position. Subsequent reduction of the nitro groups by Zn in an alkaline solution afforded **5** and **8** in 8% and 12% yields, respectively. In the second pathway, the azobenzene containing two glycolic chains was prepared prior to its couple to the *t*-butylcalix[4]arenes. The yields from the second approach (5%, 8%) were a little lower than those from the former approach. Single crystals of both **5** and **8** can be obtained by recrystallizations in methanol. However, only the crystal of **5** was suitable for X-rays crystallography. Both X-rays and ^{1}H-NMR results indicated that, in the crystal, the stereoisomer of azobenzene moiety of **5** was *trans* and the calixarene platform existed as a *cone* conformation. On the other hand, the ^{1}H-NMR spectrum of **8** suggested that ligand **8** was initially isolated as a *cis*-azobenzene with *cone*-calixarene. Ligand **5** underwent an observable *cis-trans* isomerization upon standing in the chloroform solution under the room light or a UV mercury lamp. The concurrent conformational change of the calixarene platform complicated the observation of the *cis-trans* isomerization of ligand **8** under the same condition and it was difficult to justify if the *cis-trans* isomerization had occurred. The complexation studies suggested that Na^{+} preferred a binding with the *cis*-form of both ligands while K^{+} initially preferred a binding with *trans*-form.

ภาควิชา เคมี ลายมือชื่อนิสิต .....

สาขาวิชา เคมี ลายมือชื่ออาจารย์ที่ปรึกษา .....

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

Acknowledgements

First of all, I would like to express my gratitude to my family for their encouragement and support throughout the course of my education. Especially, my mother gave an opportunity to study and also financial support.

This thesis could not be succeeded without kindness of many people. First, I would like to thank Prof. Somsak Ruchirawat and Dr. Poolsak Sahakitpichan at Chulabhorn Research Institute for a permission to use a photochemical equipment and Miss. Siriporn Wongbundit for ^{1}H-NMR results, the Scientific and Technological Research Equipment Center of Chulalongkorn University for mass spectroscopy, elemental analysis and ^{1}H-NMR results and the Department of Physics, Faculty of Science, Thammasat University for X-ray Crystallography. In addition, I would like also express to Mr.Sanchai Akethawatchai at National Science and Technology Development Agency for ^{1}H-NMR (400 MHz) results. The Thailand/Research Fund and the Department of Chemistry, Faculty of Science, Chulalongkorn University are gratefully acknowledged for financial support.

Moreover, I would like to thank my friends and staffs in Supramolecular Physico-Chemical Laboratory: Miss. Sudarath Verawong for early training and Miss Gamolwan Tumcharean for advices in NMR spectroscopy. I also thank Dr. Roderick W. Bates and Dr. Teerayuth Wilaiwan for research equipments and chemical materials.

Finally, I would like to express my debt of gratitude to my thesis advisor, Dr.Thawatchai Tuntulani and Dr. Mongkol Sukwattanasinitt, for suggestions and assistance in this research and persuasion into the world-wide of azobenzene and photoisomerization. Furthermore, I would like to thank my committees for their valuable suggestions.

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List of Abbreviations and Signs

Å .	Angstrom
^{O}C	Celcius
δ	Chemical shift
J	Coupling constant
G	Gram
Hz	Hertz
mp	Melting point
mmol	Millimol
ppm	Part per million
M^{-1}	Per mole
^{1}H-NMR	Proton Nuclear Magnetic Resonance
RT	Room Temperature

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CHAPTER I

INTRODUCTION

1.1 Biological Ion Transportation

In animal cells, ion-equilibrium is essential and influenced on several biological processes such as glucose metabolism, protein synthesis and activation of some enzymes. Potassium ions (K^+) are concentrated inside cells and sodium ions (Na^+) are mainly in the blood plasma and the interstitial fluids of the body. The concentrations inside and outside of the cells are controlled and promoted by magnesium and phosphate ions[1].

The transport of glucose and amino acids in plasma membrane of cells of kidney tubule and intestinal epithelium can be brought into cell together with Na^+, by facilitating diffusion. So the amount of Na^+ in inner cell is increased. In order to control an ion-equilibrium, Na^+/K^+pump or Na^+/K^+-ATPase is necessary to push moving Na^+ out and K^+ into the cell. Carrier ionophores or specific carrier proteins are responsible to maintain the high K^+ and low Na^+ concentrations in a mammalian cell. ATP-binding site on the carrier protein is at the inner surface of the membrane in which hydrolysis occurs only if ATP, Na^+ and Mg^+ are inside the cell. For each ATP hydrolyzed, three ions of Na^+ are moved out of the cell but solely two ions of K^+ moved in, which lead to external positive charge (Figure 1.1).

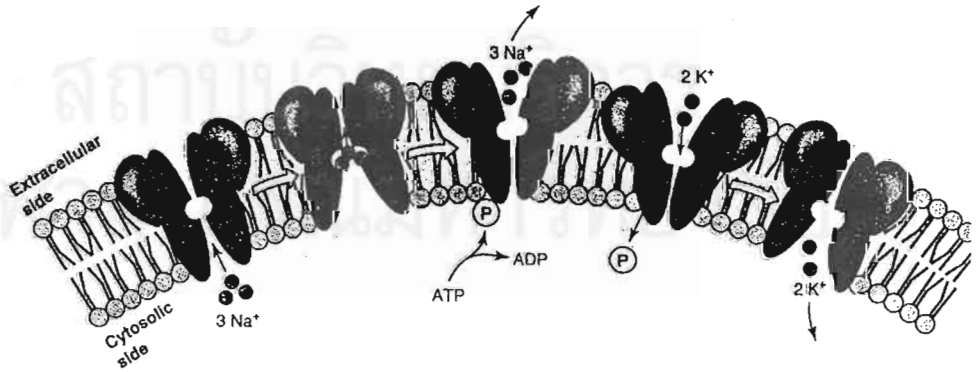


Figure 1.1 Hypothetical model for the translocation of Na^+ and K^+ across the plasma membrane by the Na^+/K^+-ATPase

Although the details of the transfer mechanisms are still uncertain, it was found that the ions were able to complex with specific ligands that moved through the hydrophobic cell wall. For example, valinomycin[1c,1d], a cyclic-oligopeptide with 12 carbonyl groups and a number of hydrophobic branching groups, can easily form a complex with K^+. However, Na^+ is too small to coordinate to several oxygen atoms in the core of the ionophore. The potassium complex thus passes through the cell easily (Figure 1.2).

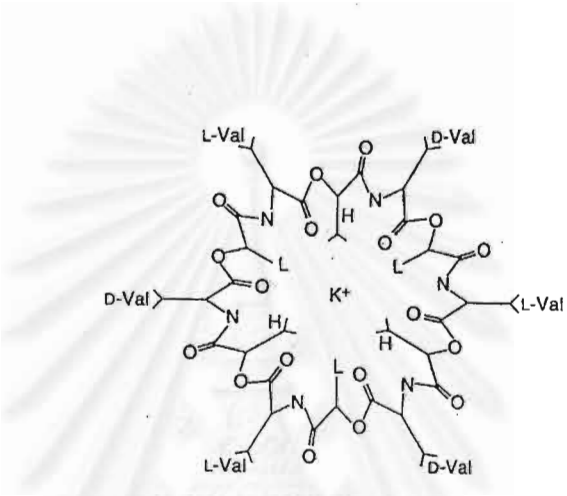


Figure 1.2 Structure of the valinomycin-K^+ complex

From this concept, chemists try to mimic biological systems which have different selectivity of the complexation between Na^+ and K^+. It is known that crown ethers that are antibiotically active increase the permeability of cations through cell membrane. The chelating ligand as shown in Figure 1.3 binds both Na^+ and K^+ ions but favor K^+ ions because K^+ can perfectly fit into the cavity of crown-6. Thus selectivity between Na^+ and K^+ can be regulated by the sizes of the ligands.

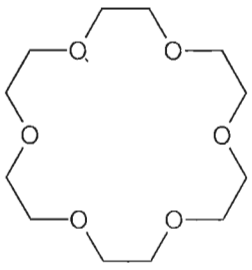
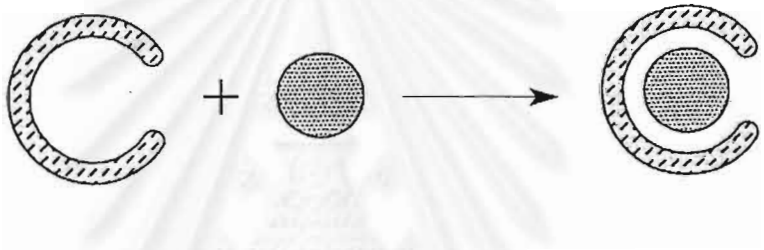


Figure 1.3 An example of chelating ligand, a crown ether

1.2 Host-guest systems

Biological systems such as enzymes, antibodies and ionophores, etc. can bind substrates depending on noncovalent intermolecular forces (electrostatic interactions, hydrogen bonds, π-π interactions etc)[1b-1d]. In 1967, Pedersen reported the fundamental discovery of synthetic macromonocyclic polyethers (crown ethers)[2a]. Three researchers received the 1987 Nobel Prize in chemistry : Charles J. Pedersen, Donald J. Cram and Jean-Marie Lehn. Thus, in the last two decades, there has been increasingly interested in crown ether and their complexes[3]. Specific hosts can bind metal ions, organic cations, organic and inorganic anions and organic molecules[2b].



host molecule guest molecule host-guest complex

Scheme 1.1 Representation of a host-guest complexation and decomplexation

1.3 Photoresponsive systems

Complexation behavior and selectivity can be reversibly controlled by external stimulation as shown in Scheme 1.2.

Scheme 1.2 The external stimulation influences on the host-guest complexation

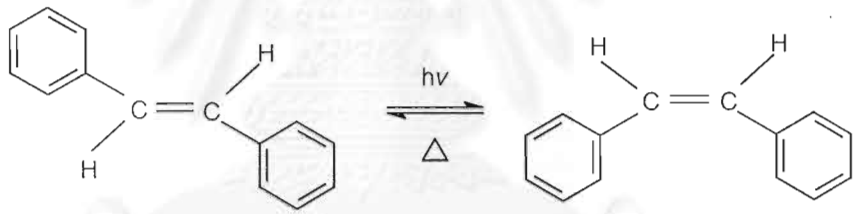
A supramolecular molecule incorporated with a photochromic component has introduced interesting photoresponsive properties[r]. This concept can be applied to build model systems for theoretical studies and for photochemical molecular devices.

1.3.1 Photoactive components

The photoinduced *trans-* to *cis*-isomerization of an olefin compound is an important process[4]. In general, the *trans*-isomer is the more stable form. The rate of thermal *cis-trans* isomerization depends on structures of molecules and conditions. If the rate of thermal isomerization is slow, the reversible isomerization can be controlled by simple irradiation using different wavelength.

1.3.1.1 Stilbene

A basic example of a double bond twist is stilbene (ethylene compound), (Scheme 1.3). The mechanism of *trans-* to *cis*-isomerization of stilbene was proposed as a rotation of the weaken double bond by an excitation of high-amplitude torsional vibration or by excitating an electron from a π-bonding to a π* antibonding orbital as rotation[5].



Trans- *Cis-*

Scheme 1.3 *Trans- to cis*-isomerization of stilbene

1.3.1.2 Azobenzene

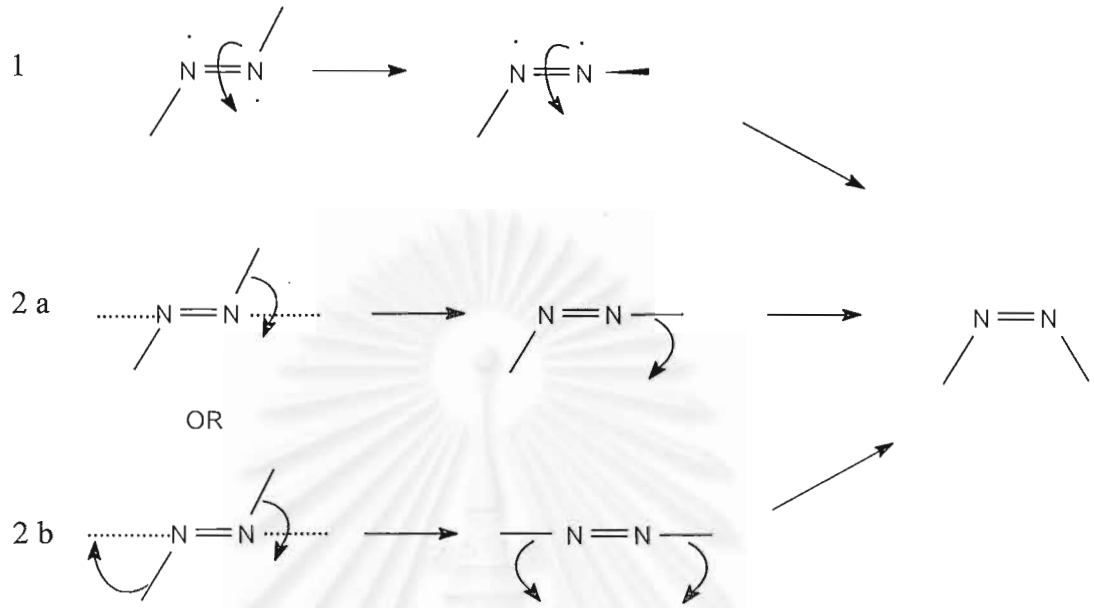
Azobenzene is quite similar to stilbene. The *trans*-isomer (Scheme 1.4) of azobenzene is more stable than the *cis*-isomer. Both isomers of azobenzene have the high absorption band (π-π*) in the near-ultraviolet region (~320 nm) and the weak band (n-π*) in the visible regioin (~450 nm). The *cis*-isomer has the π-π* band shifted to a shorter wavelength and the n-π* band increased in the intensity[5].

There are two well accepted isomerization mechanisms of azobenzene :

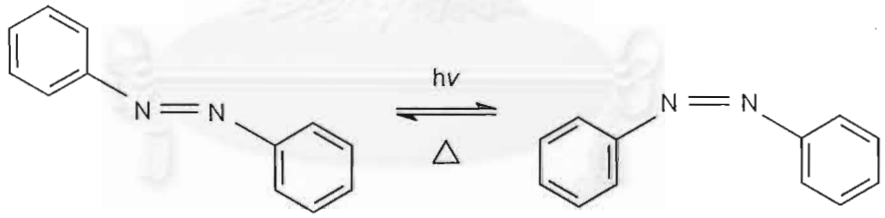
1. Twisting around the -N=N- bond (rotation mechanism), as in stilbene

2 a In plane inversion at one of two nitrogen atoms (inversion mechanism)

2 b In plane inversion at both nitrogen atoms



The in-plane inversion mechanism is responsible for the dark isomerization, while rotation can usually occur upon light excitation[5]. However, it is not clear whether photoisomerization occurs through only rotation or along with inversion.



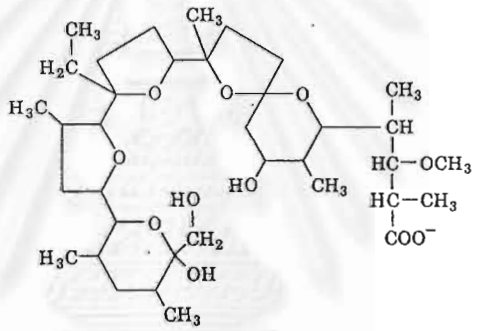
Trans- *Cis-*

Scheme 1.4 *Trans- to cis*-isomerization of azobenzene

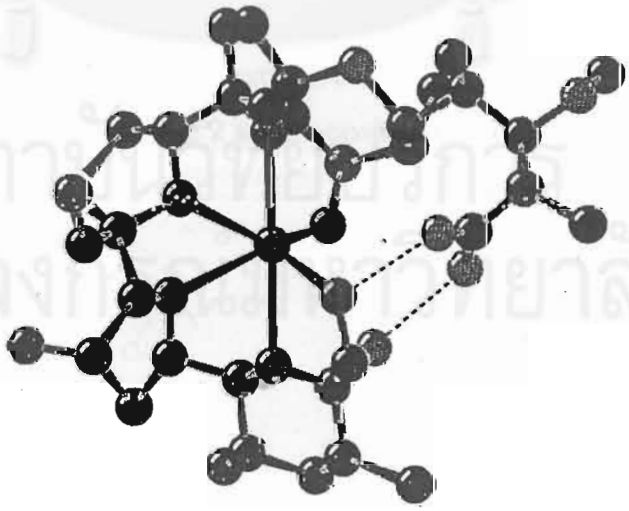
Photoinduced isomerization of azobenzene bring to changes in dipole moment and geometry[6]. The distance between the *para* carbon atoms in azobenzene of the *trans* form is 9.0 Å changing to 5.5 Å upon isomerization to the *cis* form. *Trans*-azobenzene has no dipole moment while the dipole moment of the non planar of the *cis*-form is 3.0 D. These properties are useful for probes of conformational dynamic of macromolecules by site-specific photo labeling.

1.3.2 Systems involving crown ethers

Crown ethers[2,7] are macrocyclic polyethers which can form complexes with metal ions and organic cations. The formation constants of complexes depend on the fitting of a cavity of a crown with a metal ion. Crown ethers can be designed to be selective towards particular cations. Lehn *et al.*[7a,8] have found that the best carrier for ion transport is a ligand which has a moderately stable rather than a very stable complex. The very stable complex, which extracts ions into membrane phase, cannot release the ion from the complex. A natural ionophore, monensin[8b,1c], as changing from the noncyclic to the cyclic form, has a different binding ability between the ion-complexation site and the ion-decomplexation site as shown in Figure 1.4(a) and (b), respectively.



(a)

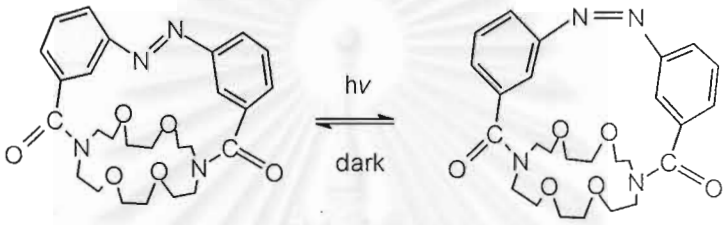


(b)

Figure 1.4 Monensin (a) The structure formula (b) The octahedral Na^+ complex

1.3.2.1 Crown ethers with an intramolecular bridge

The *trans*-azobenzene capped with crown ether preferably binds small metal ions such as Li^+ and Na^+. After UV-irradiation, the *trans*-form changes to *cis*-form which preferably binds large metal ions such as K^+ and Rb^+. It is indicated that light induced the expansion of the crown ether cavity[9] (Scheme 1.5). The rate of the conformational changes of crown ethers is studied by cation complexation, and followed by spectrophotometry.

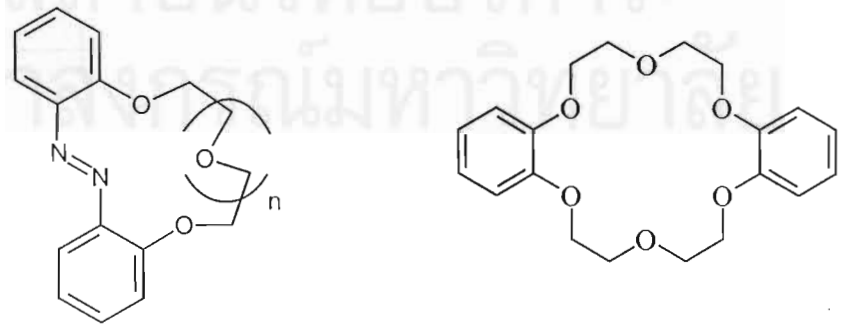


Trans- *Cis-*

Scheme 1.5 *Trans- to cis-* isomerization of azobenzene capped with crown ether

1.3.2.2 Cylindrical and phane-type crown ethers

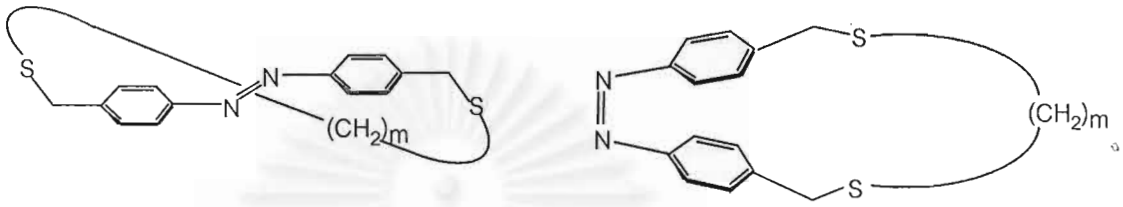
Shiga *et al.*[10] synthesized several azobenzene crown ether compounds, Figure 1.5(a), and studied their complexing properties with alkali and alkaline earth metal ions. The complexation constants of azobenzene-crown ethers (as n = 1-4) are less than those of dibenzo-18-crown-6, Figure 1.5(b) in aprotic solvents. The azo group is not a favorable component of a crown ether for stabilizing the metal complexes because of the steric strain in the 2 and 2' -positions of azobenzene.



(a) (b)

Figure 1.5 (a) Azobenzo-crown ethers and (b) Dibenzo-18-crown-6

Funke *et al.*[11] synthesized the dithia-diaza[n.2]paracyclophane-enes, **a-h** (m = 2-12) by starting from *p*-hydrazotoluene and using the rigid group and high dilution techniques (Figure 1.6). The *cis/trans* ratio of compound **a-h** at various photo stationary state (PSS) and conditions is shown in Table 1.1.



Trans-(**a-h**) *Cis*-(**a-h**)

Figure 1.6 *Trans and cis* isomers of dithia-diaza[n.2]paracyclophane-enes, **a-h**

Table 1.1 *Cis/trans* ratio of dithia-diaza[n.2]paracyclophane-enes at various photo stationary states (PSS) and wavelengths[a]

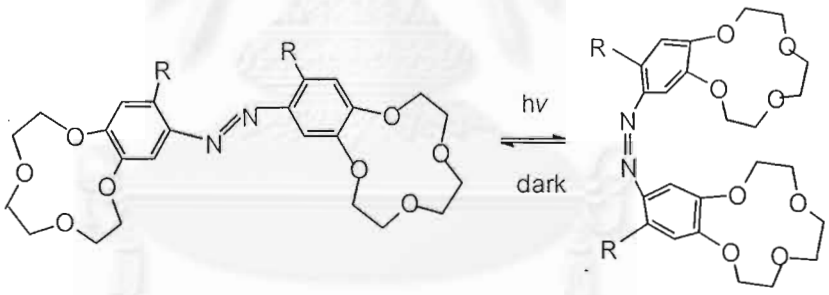
Compound	m	Day light cis/trans	λ=369 nm cis/trans	λ=443 nm cis/trans
a	2	100/0	decomposition	
b	4	100/0	decomposition	
c	5	100/0	decomposition	
d	6	77/23	100/0	50/50
e	7	22/78	100/0	22/78
f	8	0/100	100/0	0/100
g	9	0/100	90/10	0/100
h	12	0/100	90/10	0/100
p-azotoluene		0/100	85/15	0/100

[a] determined by ^{1}H-NMR

As a result, only **a-c** are in the *cis*-azo configuration, while **d** and **e** are mixtures of *cis* and *trans*-forms. Moreover, **f-h** are formed as pure *trans*-azobenzene compound. This implies that the length of the chain effected on the configuration of the azobenzene unit.

1.3.2.3 Phototweezer : Butterfly

Shinkai and co-workers[12] synthesized azobis(crown ethers), shown in Scheme 1.5, which possessed a butterfly-like motion. In the absence of metal ions, the *trans*-form was isomerized by the UV light to the *cis*-form and thermally reversible to the *trans*-form. The photostationary state of the *cis*-isomer was able to increased by adding alkali metal ions especially Rb^+ and Cs^+ (> 90% cis) and the rate of the thermal *cis*- to *trans*-isomerization was suppressed. Furthermore, influence of treatment methods on thermal isomerization rates were studied. The rate constants of method A, adding metal cations before photoisomerization, were almost identical with those of method B, adding metal cations after photoirradiation. The result indicated that the *cis*-isomer was able to occur as a sandwich 1:2 cation/crown complex with metal ions that were too large to fit in only one crown ring. The extraction ability and the concentration of the *cis*-form at the photo stationary state (PSS) are maximum and the rate of the thermal isomerization became minimum.

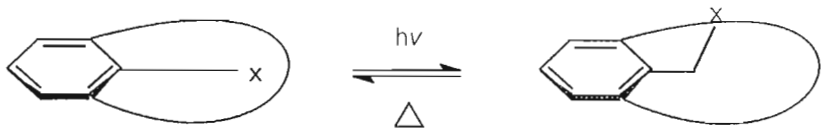


Trans- *Cis-*

Scheme 1.6 *Trans-cis* isomerization of bis(crown ether) as butterfly-motion.

1.3.2.4 Intra-annular azobenzene substituent capped crown ethers

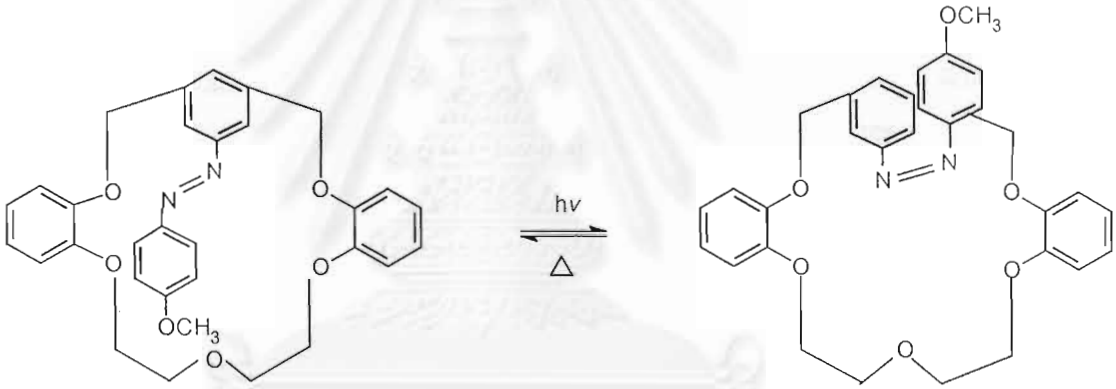
An intra-annular azobenzene substituent X cappped with crown ether as shown in Scheme 1.7 can prevent, promote, and switch ion coordinations, depending on its specific natures[13].



Trans- *Cis-*

Scheme 1.7 An intra-annular azobenzene substituent X cappped crown ethers

When the substituent is a phenyl azo group, it can be stimulated to change the structure by light as shown in Scheme 1.8. A methoxyphenylazo substituent (*trans*-form) occupies the crown cavity and prevents complexation with Na^+ ion. Only *cis*-form of the compound can interact with Na^+ since the azo group is removed from the ring. This system has been used to transport Na^+ ions across a liquid membrane, under the UV-irradiation.



Trans- *Cis-*

Scheme 1.8 A methoxyphenylazo substituent occupied the crown cavity

1.3.3 Systems involving calix[4]arenes

Introduction to Calixarenes

Calixarenes are useful macrocyclic ligands in supramolecular chemistry. They are made up of phenolic units linked with methylene bridges and formed basket-shape cavities[14]. The name "calixarene" has been given by Gutsche[15]. The word "calix" came from "calice" means *cuplike* in Greek and the suffix "arene" means *aryl rings of molecules*. The number of aromatic units is specified by a blanklet between calix and arene.

Two diffferent regions can be distinguished in calixarene : the hydroxyl groups region or the "lower rim" and the *para*-position of the phenol or the "upper rim" of the calix. They are suitable to be building blocks in supramolecular chemistry[3, 16]. Ester, amides, crown ethers, etc on the lower rim of derivatives of calixarenes can bind to cations. Because of their unique molecules and well preorganized cavity, modified calixarenes are designed for complexation with cations, anions or neutral guest molecules.

Gutsche[15] has introduced the term "cone", "partial cone", "1,2-alternate" and "1,3-alternate" which are accepted today for basic conformation. The four possible conformations shown in Figure 1.7 are differrent at OH-groups of the phenolic units and *para*-positions. The most stable conformation of calix[4]arene is the cone conformation because of intramolecular hydrogen bond formation in which OH groups at the lower rim act as both donors and acceptors. If there are bulky substituents at the lower rim, a structure may be interconverted among possible conformations due to the breach of hydrogen bonds and easily free rotation of C-atom of methylene bridges ($Ar\text{-}CH_2\text{-}Ar$).

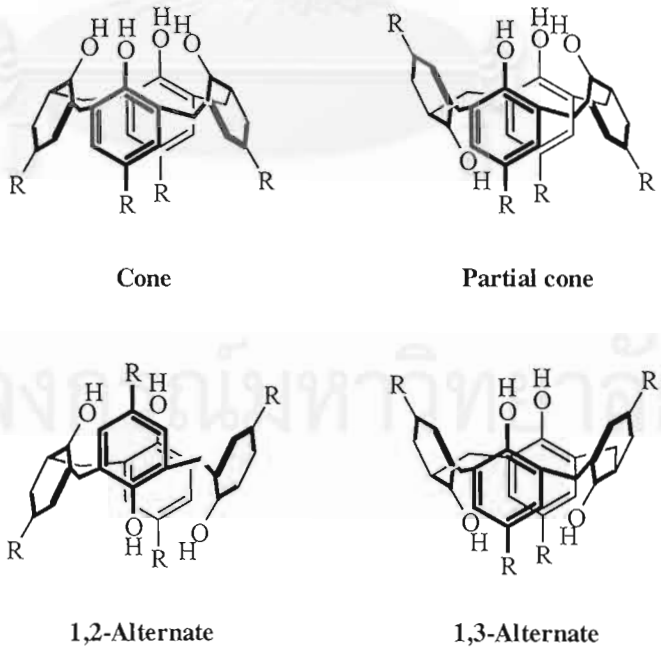
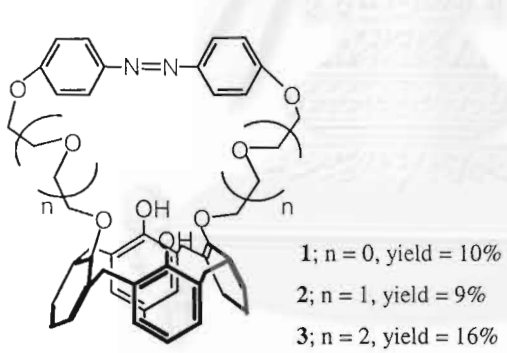


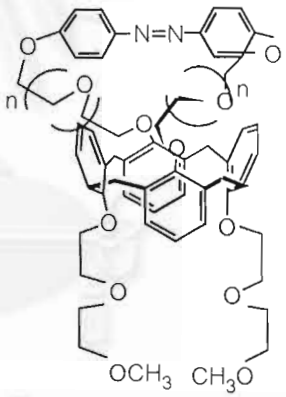
Figure 1.7 Structures and conformations of calix[4]arene.

1.3.3.2 Azobenzene crown ether calixarenes

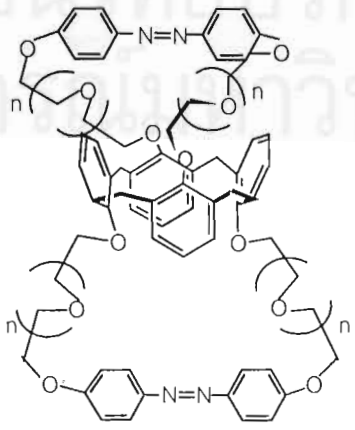
In 1996, Saadioui and co-workers synthesized a series of *trans* and *cis*-azobenzene linked with glycolic chains of the calix[4]crowns[17a]. The products prepared from the 1,3 dialkylation of calix[4]arene through glycolic chains whose terminals are nitrophenyl groups. Reduction of the nitro groups into diamino groups was achieved by $NH_2NH_2.H_2O$ in the presence of graphite in ethanol[17b]. The coupling of diamino groups to azobenzene was prepared by activated MnO_2[17c] in benzene. The *trans-cis* structures of new ligands were characterized by ^{1}H-NMR spectroscopy and the yields of these ligands were reported in Figure 1.8. As a result from long glycolic chains(n = 0, 1, 2), *trans*-isomer was mainly obtained in case of compounds **2**, **3**, **5**, **6**, **7**, and **8** while compounds **1**, and **4** which have shorter glycolic chains were obtained as *cis*-isomers. It can be concluded that the length of glycolic chain effected on the isomer of compounds.



1; n = 0, yield = 10%
2; n = 1, yield = 9%
3; n = 2, yield = 16%



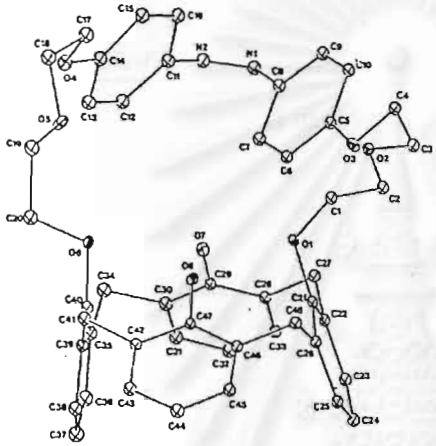
4; n = 0, yield = 55%
5; n = 1, yield = 29%
6; n = 2, yield = 15%



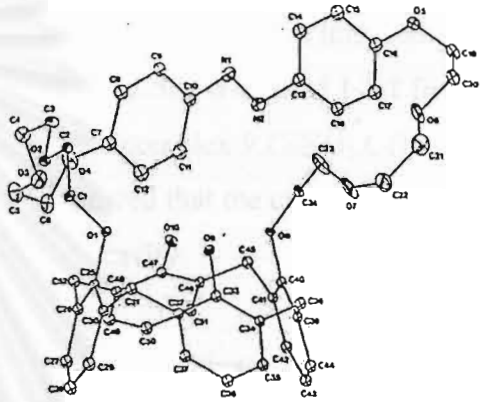
7; n = 0, yield = 6%
8; n = 1, yield = 2%

Figure 1.8 Azocrown derivatives of 1, 3 dialkylation of calix[4]arene

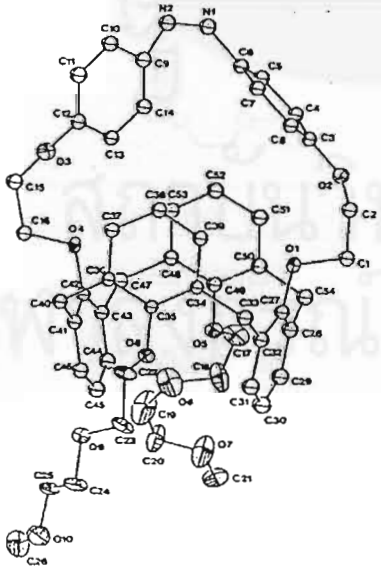
Later, crystal structures[18] of *cis*-**2**, *trans*-**3**, cis-**4** and *trans*-**5**.were reported (Figure 1.9). The structure of **2** obtained from X-ray crystallography was quite contradicted to that deduced from ^{1}H-NMR. The X-ray structure suggested that the crystallized compound was *cis*-**2** while the ^{1}H-NMR spectrum of the solution of **2** indicated that the *trans*-isomer was the major component. However, the X-ray crystallography structures of *trans*-**3**, *cis*-**4**, and *trans*-**5** agreed well with ^{1}H-NMR spectra.



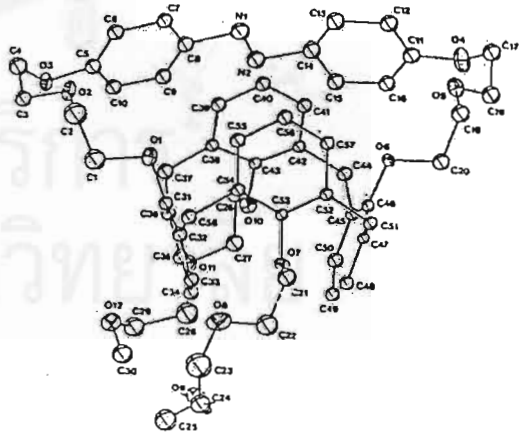
cis-**2**; n = 1



trans-**3**; n = 2



cis-**4**; n = 0

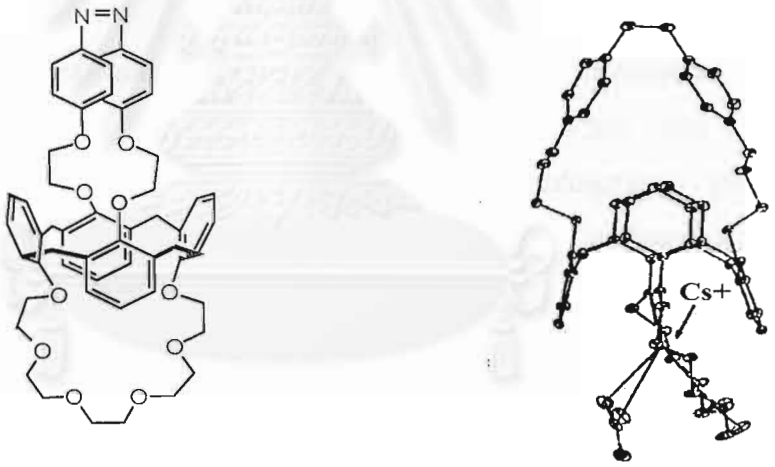


trans-**5**; n = 1

Figure 1.9 *ORTEPII* plots of the molecular units of compounds **2, 3, 4** and **5.**

In the same year, Vicens *et al.*[19] reported the synthesis of compound **9** (Figure 1.10(a)) which contained both crown-6 and azobenzene moieties attacted to the calix [4]arene unit in the 1,3-alternate conformation. The synthetic approach was similar to the synthesis of compounds **2-5**. The authors proposed the structure of **9** to be the *cis*-isomer based on UV-Visible and ^{1}H-NMR spectra. The UV-Visible and ^{1}H-NMR spectra of compound **9** compared favorably to the results of the published azobenzene calixarene[17a] to be in the *cis*-isomer.

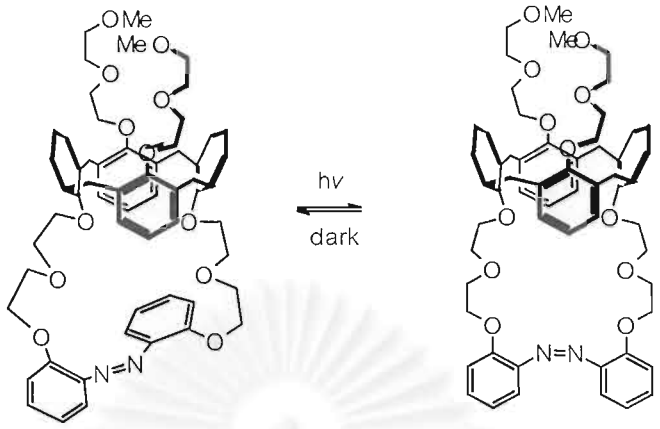
The complexation between the alkali picrates (Na^+, K^+, Rb^+ and Cs^+) and the $CDCl_3$ solition of **9** was followed by ^{1}H-NMR for 8 days. From the area integration, the ratios of metal to ligand in the complexes were 0.2:1, 1.5:1, 0.4:1 and 1.1:1 for Na^+, K^+, Rb^+ and Cs^+, respectively. The single crystal of complex **9**.$CsNO_3$.CH_3NO_2 was obtained (Figure 1.10(b)). The crystal structure showed that the complex was in the *cis*-form and the Cs^+ cation was located in crown-6 cavity.



(a) (b)

Figure 1.10 (a) compound **9** (b) the complex of **9** and $CsNO_3$

In 1997, Vicens and coworkers[20] reported the synthesis of azo-calix[4]crown 1,3-alternated, **10**, as shown in Scheme 1.9 and studies of its complexation with alkali cations. *Cis-trans* ratio of **10** under the photostationary state to be 55/45. It was found that both *trans*- and *cis*-forms can bind alkali metal ions. The percentage of *cis*-isomer increased in the following order : $Cs^+ > Rb^+ > K^+ > Na^+$. From the result, it was concluded that the complexations of **10** with Rb^+ and Cs^+ ions are more stable than that of Na^+ and K^+.



Trans- *Cis-*

Scheme 1.9 *Trans* to *cis* isomerization of azo-modified calix[4]crown ether, **10**, in the 1,3-alternate conformation

1.4 Objective and scope of the research

Azobenzenes make up an interesting class of compounds that exhibit photoresponsive properties. They have been incorporated into supramolecular frameworks in order to produce photofunctional extractants, photo-switchable receptor and ionophores for transports[19]. Currently, we are interested in constructing a photo-switchable molecular system which can selectively bind to Na^+ or K^+ ions to mimic the biological Na^+, K^+pump[1].

This project is thus to develop a new class of carrier ionophores, azobenzene crown ether *p-tert*-butyl calix[4]arene, **5** and **8** (Figure 1.11) which azobenzene acted as photo-antenna and *tert*-butyl groups as hydrophobic parts. Studies of *cis-trans* isomerization under the day light and the UV-irradition will then be pursued. Furthermore, our interest is also concentrated on the influence of alkali metal ion on the percentage of *cis*- and *trans*-isomer of these ligands under the equilibrium.

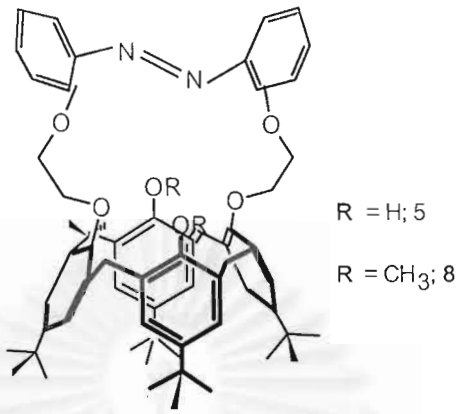


Figure 1.11 Structure of derivative of azobenzene crown ether *p-tert*-butyl calix[4] arene, **5** and **8**.

CHAPTER II

EXPERIMENTAL SECTION

2.1 General Procedure

2.1.1 Materials for synthesis

All reagents were standard analytical grade, purchased from Fluka, J. T. Baker or Merck, and used without further purification. Commercial grade solvents such as acetone, dichloromethane and methanol were distilled and stored over 4 Å molecular sieves. Chromatographic seperations were performed on silica gel column (kieselgel 60, 0.063-0.200 mm Merck). Thin layer chromatography (TLC) was carried out using silica gel plates (kieselgel 60 F_{254}, 1mm, Merck). Calix[4]arene, **3**, was prepared according to the literature[21(a)]. Unless otherwise noted, all reactions were carried out under nitrogen. The products were characterized by ^{1}H-NMR spectroscopy and elemental analyses.

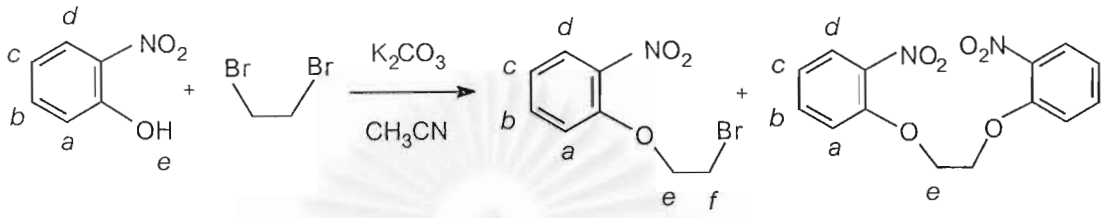
2.1.2 Analytical Instruments

Elemental analyses were analyzed on a Perkin Elmer CHON/S analyser (PE2400 series II). Mass spectra were recorded on a Fisson Mass Spectrometer Model Trio 2000. Melting points were taken on an Electrothermal 9100 apparatus. The ^{1}H-NMR spectra were recorded on a Bruker ACF 200 MHz nuclear magnetic resonance spectrometer, Variance 200 MHz nuclear magnetic resonance spectrometer and 400 MHz on a Bruker AM 400 spectrometer. Variable temperature NMR experiments were carried out on a JEOL 500 MHz NMR spectrometer. UV-Visible spectra were recorded on a Spectronic 3000 ARRAY Spectrophotometer. In all cases, samples were mixed in deuterated chloroform and chemical shift were recorded using a residual chloroform signal as internal reference.

2.2 Synthesis of Calix[4]arene Derivatives

Method I

2.2.1 Preparation of 2-(2-bromoethoxy)nitrobenzene, **1**



1 **2**

In a 500 mL two-necked flask equipped with a magnetic bar and a reflux condenser, *o*-nitrophenol (4.45 g, 32.0 mmol), 1,2-dibromoethane (60.11 g, 320.0 mmol) and potassium carbonate (8.85 g ,64.0 mmol) were mixed in acetonitrile (150 mL). The mixture was refluxed for 24 hours and then allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was then evaporated by a rotary evaporator to give a yellow solid residue. Methanol was subsequently added to this residue, and it was chilled in an ice bath to precipitate a white solid. The white precipitate, **2**, was filtered out and washed with cold methanol (0.55g, 7%). The combined filtrate was condensed by a rotary evaporator until the solution started to become cloudy. The residue was then redissolved in ether. Hexane was added and the solution was chilled in an ice bath. The desired product crystallized as a light yellow solid, **1**, (5.80 g, 74%). The ^{1}H-NMR spectrum of **1** and **2** are shown in Figure A.1 and Figure A.2, respectively and the assignments of the signals are presented in Table 2.1 and 2.2.

Anal. Caled for $C_8H_8BrNO_3$; C, 39.05%; H, 3.28%; N, 5.69. Found : C, 39.07%; H, 3.21%; N, 5.65%. mp : 164-165 °C.

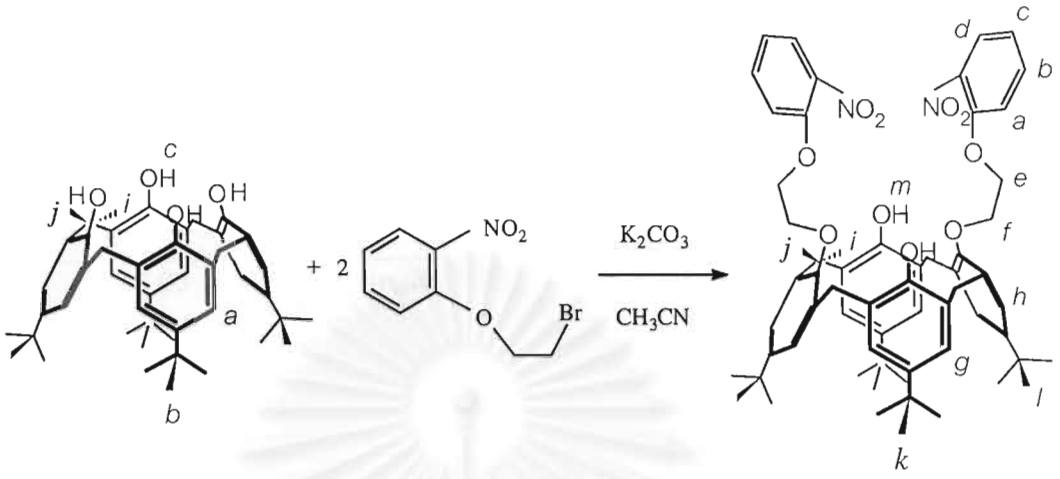
Table 2.1. Assignments of ^{1}H-NMR signals of 2-(2-bromoethoxy)nitrobenzene, **1** (The spectrum is shown in Figure A.1)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.81	doublet (J=8.0 Hz)	1H	*d*
7.52	triplet (J=8.0 Hz)	1H	*b*
7.10-7.02	multiplet	2H	*a, c*
4.40	triplet (J=6.0 Hz)	2H	*e*
3.65	triplet (J=6.0 Hz)	2H	*f*

Table 2.2. Assignments of ^{1}H-NMR signals of 1,2-dinitrophenoxyethane, **2** (The spectrum is shown in Figure A.2)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.82	doublet (J=7.0 Hz)	2H	*d*
7.56	triplet (J=8.0 Hz)	2H	*b*
7.23	doublet (J=7.0 Hz)	2H	*a*
7.11	triplet (J=8.0 Hz)	2H	*c*
4.53	singlet	4H	*e*

2.2.2 Preparation of 25, 27-bis-2-(2-nitrophenoxy)ethoxy-*p-tert*-calix[4]arene, **4**



3 **1** **4**

In a 500 mL two-necked flask equipped with a magnetic bar and a reflux condenser, *p-tert*-butylcalix[4]arene, **3,** (6.48 g, 10.0 mmol) and potassium carbonate (1.45 g, 10.5 mmol) were mixed in acetonitrile (230 mL) and refluxed for 3 hours. Into this mixture, 2-(2-bromoethoxy)nitrobenzene, **1**, (4.92 g, 20.0mmol) in acetonitrile (20 mL) was then added dropwise through an addition funnel. The reaction mixture was refluxed for 4 days and was then allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was then evaporated by a rotary evaporator to give a yellow solid residue. The residue was subsequently mixed in water. The mixture was extracted with dichloromethane (3x20 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed under vacuum to afford a yellow solid. The solid was redissolvedl in dichloromethane to get clear yellow solution. A small quantity of acetone was then added into this solution. Upon slow evaporation of the solvent, sugar-like crystals were obtained (6.51g, 66%). The ^{1}H-NMR spectrum of **3** and **4** are shown in Figure A.3 and A.4, respectively and the assignments of the signals are collected in Table 2.3 and 2.4.

Anal. Caled for $C_{60}H_{70}N_2O_{10}$; C, 73.60%; H, 7.21%; N, 2.86%. Found : C, 73.62%; H, 7.27%; N, 2.73%. mp : 205-207 °C.

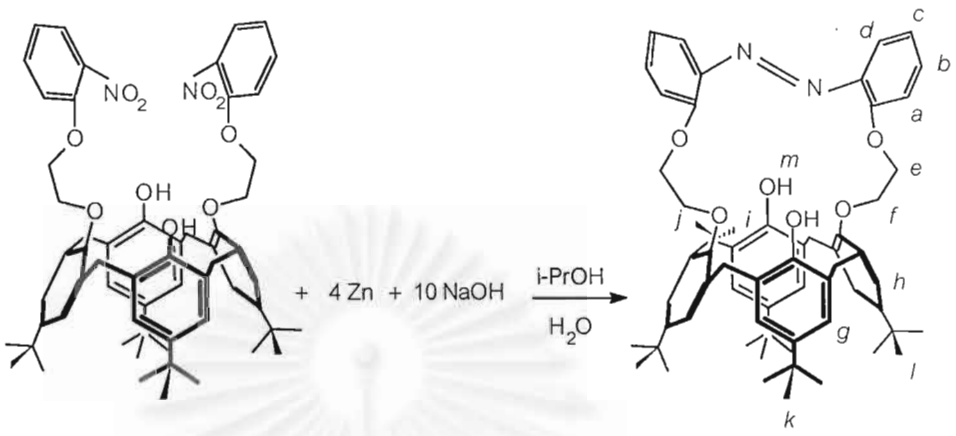
Table 2.3. Assignments of ^{1}H-NMR signals of *p-tert*-butylcalix[4]arene, **3** (The spectrum is shown in Figure A.3)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
10.34	singlet	4H	*c*
7.05	singlet	8H	*a*
4.25	doublet (J=8.0 Hz)	4H	*i*
3.50	doublet (J=8.0 Hz)	4H	*j*
1.21	singlet	36H	*b*

Table 2.4. Assignments of ^{1}H-NMR signals 25, 27-bis-2-(2-nitrophenoxy)ethoxy-*p*-*tert*-calix[4]arene, **4** (The spectrum is shown in Figure A.4)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.74	doublet (J=8.0 Hz)	2H	*d*
7.46	triplet (J=8.0 Hz)	2H	*b*
7.24	doublet (J=8.0 Hz)	2H	*a*
7.03, 6.75	singlet	8H	*h, g*
6.95	triplet (J=8.0 Hz)	2H	*c*
6.85	singlet	2H	*m*
4.47-4.45	broad peak	4H	*e*
4.33-4.26	multiplet	8H	*i, f*
3.28	doublet (J=13.0 Hz)	4H	*j*
1.28, 0.94	singlet	36H	*l, k*

2.2.3 Preparation of azobenzene crown ether *p-tert*-butyl calix[4]arene, **5**



4 **5**

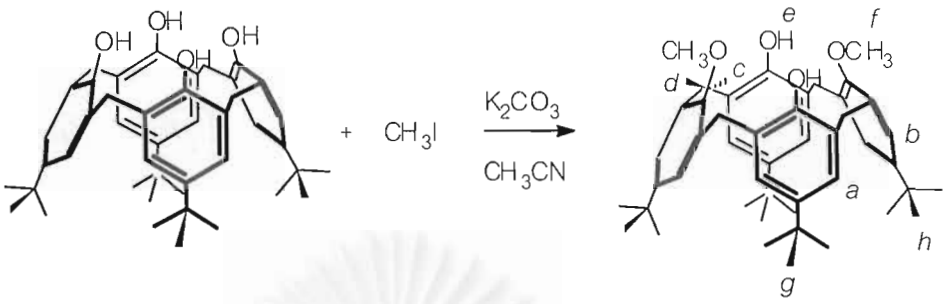
In a 50 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser, a mixture of 25,27-bis-2-(2-nitropnenoxy)ethoxy-*p-tert*-calix[4]arene, **4**, (0.70 g, 0.71 mmol) in isopropanol (8 mL), sodium hydroxide (0.28 g, 7.0mmol) in H_2O (4 mL) and zinc (0.20 g, 3.06 mmol) was stirred. The mixture was refluxed under nitrogen atmosphere for 48 hours and it was then allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was evaporated by a rotary evaporator to give an orange residue. The residue was dissolved in dichloromethane (20 mL) and it was then extracted with 2 M HCl (2x20 mL). The organic phase was separated, and the aqueous layer was extracted again with dichloromethane (2x30 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed to give an oily orange residue. The residue was redissolved in a minimum amount of dichloromethane. The orange solution was eluted through silica gel column with 15 % ethyl acetate/hexane as eluent. The first orange solution eluted out of the column was the desired product. It was crystallized by adding methanol to give orange needle crystals (0.05g, 8%) upon standing for 3 days. The ^{1}H-NMR spectrum of **5** is shown in Figure A.5 and the assignments of the signals are collected in Table 2.5. (Only data of *trans*-isomer was reported)

Anal. Caled for $C_{60}H_{70}N_2O_6$; C, 78.74%; H, 7.71%; N, 3.06%. Found : C, 77.21%;H, 7.51%; N, 2.72%. mp : 195-197 °C (decomposed)

Table 2.5. Assignments of ^{1}H-NMR signals of azobenzene crown ether *p-tert*-butyl calix[4]arene, **5** (The spectrum is shown in Figure A.5)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.67	doublet (J=8.0 Hz)	2H	*d*
7.61	singlet	2H	*m*
7.32	triplet (J= 5.5Hz)	2H	*b*
7.15-7.02	multiplet	4H	*a, c*
6.92, 6.86	singlet	8H	*h. g*
4.84	triplet (broad peak)	4H	*e*
4.38	triplet (broad peak)	4H	*f*
4.15	doublet (J=13.0 Hz)	4H	*i*
3.20	doublet (J=13.0 Hz)	4H	*j*
1.20, 1.03	singlet	36H	*l, k*

2.2.4 Preparation of 26,28-dimethoxy-*p*-*tert*-butylcalix[4]arene[21(b)], **6**



3 **6**

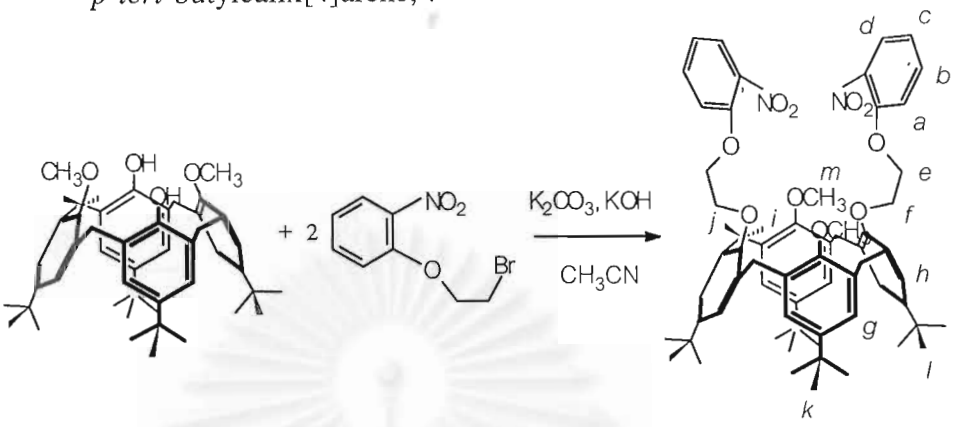
In a 250 mL two-necked flask equipped with a magnetic bar and a reflux condensor, calix[4]arene, **3**, (1.40 g, 2.16 mmol) and potassium carbonate (0.60 g, 4.32 mmol) were mixed in acetonitrile (50 mL). After stirring at room temperture for 12 hours, methyl iodide (2 mL) was added dropwise into the mixture. It was then refluxed under nitrogen atmosphere for 6 hours and was allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was then evaporated by a rotary evaporator to give a white solid residue. The residue was dissolved in dichloromethane.(30 mL) and was extracted with saturated ammonium chloride (2x20 mL) solutions and water (2x20 mL). The organic phase was separated, combined, and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed to leave a white solid residue. The residue was dissolved in hexane with an aid of small quantity of dichloromethane. The mixture was chilled in an ice bath. The product crystallized as a white solid (1.06 g, 73%). The ^{1}H-NMR spectrum of **6** is shown in Figure A.6 and the assignments of the signals are collected in Table 2.6.

Anal. Caled for $C_{46}H_{60}O_4$; C, 81.61%; H, 8.93%. Found : C, 81.75%; H, 8.93%. mp : 248-250 °C.

Table 2.6. Assignments of ^{1}H-NMR signals of 26,28-dimethoxy-*p-tert*-butylcalix[4] arene, **6** (The spectrum is shown in Figure A.6)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.22	singlet	2H	*e*
7.06	singlet	4H	*b*
6.75	singlet	4H	*a*
4.27	doublet (J=13.0 Hz)	4H	*c*
3.93	singlet	6H	*f*
3.32	doublet (J=13.0 Hz)	4H	*d*
1.29, 0.92	singlet	36H	*h, g*

2.3.5 Preparation of 25,27-bis-2-(2-nitrophenoxy)ethoxy-26,28-dimethoxy-*p-tert*-butylcalix[4]arene, **7**



6 **1** **7**

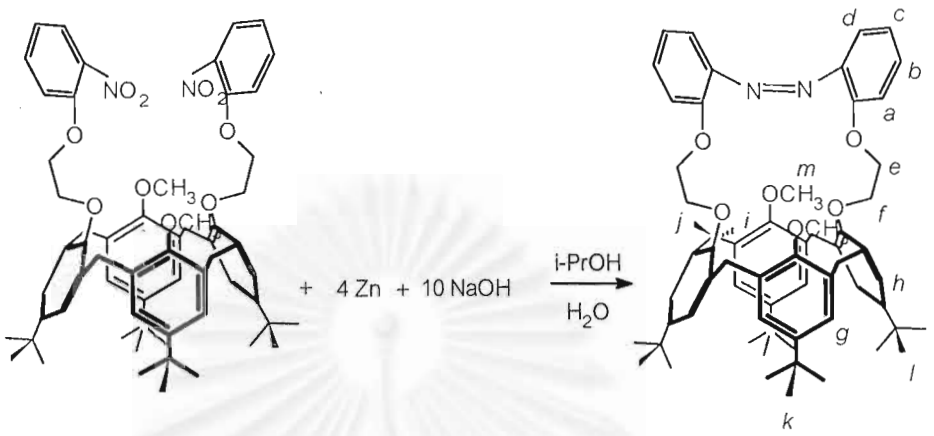
In a 250 ml two-necked flask equipped with a magnetic bar and condenser, **6**, (1.37 g, 2.03 mmol), potassium carbonate (1.12 g, 8.11 mmol), potassium hydroxide (3-5 pellets) were mixed in acetonitrile (50 mL). After stirring at 35-40^{O}C for 4 hours, compound **1** (1.0 g, 4.06 mmol) in acetonitrile (40 mL) was then slowly added into the mixture. It was refluxed under nitrogen atmosphere for 48 hours. The mixture was filtered and the solid residue was washed with dichloromethane. The filtrate was combined and the solvent was removed to give a brown viscous residue. The residue was dissolved in dichloromethane and it was then extracted with saturated ammonium chloride solution (2x20 mL) and water (2x20 mL). The organic phase was subsequently separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed to give a dark-brown solid residue. The residue was redissolved in a minimum amount of dichloromethane. The dark-brown solution was chromatographed on a silica gel column with 10% ethyl acetate/hexane. The desired product eluted out of the column as the 4th band as an orange solution. The solvent was removed and the product was crystallized in methanol to give orange crystals (0.41 g, 20%). The ^{1}H-NMR spectrum of **7** is shown in Figure A.7 and the assignments of the signals are collected in Table 2.7.

Anal. Caled for $C_{62}H_{74}N_2O_{10}$; C, 73.93%; H, 7.40%; N, 2.78%. Found : C, 73.92%; H, 7.46%; N, 2.76%. mp :189-191 °C.

Table 2.7. Assignments of ^{1}H-NMR signals of 25,27-bis-2-(2-nitrophenoxy)ethoxy-26,28-dimethoxy-*p-tert*-butylcalix[4]arene, **7** (The spectrum is shown in Figure A.7)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.81	doublet (J=8.0 Hz)	2H	*d*
7.51	triplet (J=8.0 Hz)	2H	*b*
7.30-6.92, 6.69-6.40	broad peak	12H	*a, c, h, g*
4.60-4.28	broad peak	4H	*e*
4.28-4.00	broad peak	4H	*f*
4.00-3.60	broad peak	4H	*i*
3.47	singlet peak	6H	*m*
3.40-3.00	broad peak	4H	*j*
1.28, 1.05, 0.84	three of singlets	36H	*l, k*

2.3.6 Preparation of azobenzene crown ether dimethoxy-*p*-*tert*-butylcalix[4] arene, **8**



7 **8**

Compound **7** (0.51 g, 0.5 mmol) in isopropanol (10.0 mL), sodium hydroxide (0.20 g, 5.0 mmol) in H_2O (2 mL) and zinc (0.13 g, 2.0 mmol) were placed in a 50 mL round-bottomed flask equipped with a magnetic bar and a reflux condenser. The mixture was refluxed under nitrogen atmosphere for 2 days and it was allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was evaporated by a rotary evaporator to obtain an orange residue. The residue was dissolved in dichloromethane and it was then extracted with saturated ammonium chloride solution (2x20 mL) and water (2x20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the filtrate was evaporated to afford an orange oily residue. The orange residue was subsequently chromatographed on a silica gel column with 5% ethyl acetate/hexane as eluent. The desired product was the first orange band eluted out of the column. The product was crystallized in methanol and ethyl acetate to give orange needle-shape crystals (0.06 g, 12%). The ^{1}H-NMR spectrum of **8** is shown in Figure A.8 and the assignments of the signals are collected in Table 2.8 (Only data of *trans*-isomer was reported).

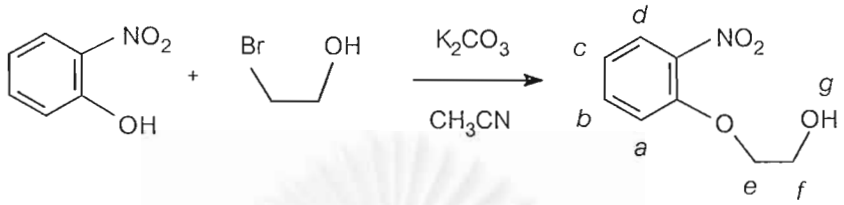
Anal. Caled for $C_{62}H_{74}N_2O_6$; C, 78.95%; H, 7.91%; N, 2.97%. Found : C, 79.06%; H, 7.91%; N, 2.97%. mp : 228-230 °C

Table 2.8. Assignments of ^{1}H-NMR signals of azobenzene crown ether dimethoxy-*p*-*tert*-butylcalix[4]arene, **8** (The spectrum is shown in Figure A.8)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.41-6.88	multiplet	8H	*a, b, c, d*
7.01, 6.42	singlet	8H	*h, g*
4.65-4.63	broad peak	4H	*e*
4.34-4.25	broad peak	4H	*f*
4.22	doublet (J=12.5 Hz)	4H	*i*
3.44	singlet	6H	*m*
3.10	doublet (J=12.5 Hz)	4H	*j*
1.26, 0.79	singlet	36H	*l, k*

Method II

2.3.7 Preparation of 2-(2-hydroxoethoxy)nitrobenzene, **9**



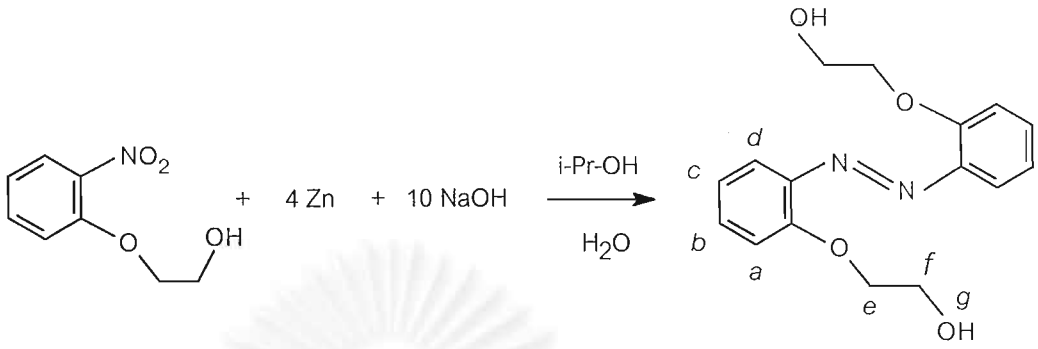
9

In a 500 mL two-necked flask equipped with a magnetic bar and a reflux condensor, *o*-nitrophenol (2.78 g, 20.0 mmol) and potassium carbonate (2.90 g, 21.0 mmol) were mixed in acetonitrile (170 mL). The mixture was stirred for 3 hours at 35-40 °C and 2-bromoethanol (7.50 g, 60.0 mmol) was subsequently added dropwise. The mixture was refluxed for 24 hours and it was then allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined solution was evaporated by a rotary evaporator to yield a residue. The residue was dissolved in dichloromethane and the solution was extracted with 2M NaOH solution (3x20 mL). The organic phase was then separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed to give the desired product as yellow liquid (2.30 g, 63%). The ^{1}H-NMR spectrum of **9** is shown in Figure A.9 and the assignments of the signals are collected in Table 2.9. EI MS (mz):183 (M^+)

Table 2.9. Assignments of ^{1}H-NMR spectrum of 2-(2-hydroxoethoxy)nitrobenzene, **9** (The spectrum is shown in Figure A.9)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.68	doublet (J=8.0 Hz)	1H	*d*
7.40	triplet (J=8.0 Hz)	1H	*b*
7.01	doublet (J=8.0 Hz)	1H	*a*
6.91	triplet (J=8.0 Hz)	1H	*c*
4.41	singlet	1H	*g*
4.10	triplet (J=4.5 Hz)	2H	*e*
3.83	triplet (J=4.5 Hz)	2H	*f*

2.3.8 Preparation of bis-2-(2-hydroxoethoxy)azobenzene, **10**



10

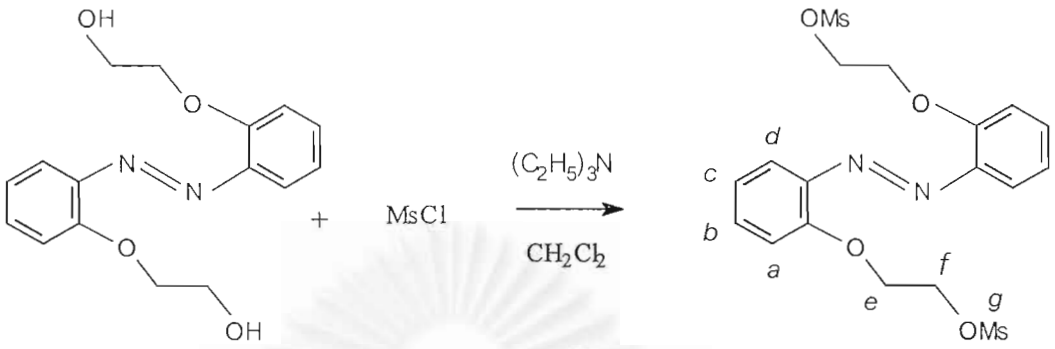
A mixture of **9** (2.01 g, 10.92 mmol) in methanol (10 mL), sodium hydroxide (4.37 g ,109.3 mmol) in H_2O (6 mL) was stirred in a 50 mL round-bottomed flask, and zinc (2.86 g, 43.74 mmol) was subsequently added. The mixture was refluxed under nitrogen atmosphere for 48 hours and was then allowed to cool to room temperature. The mixture was filtered and the solid residue was washed with dichloromethane. The combined filtrate was evaporated to give an orange residue. The residue was dissolved in dichloromethane and it was then extracted with saturated ammonium chloride solution (2x20 mL) and water (2x20 mL). The combined organic phase was separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the solvent was removed to give a viscous orange residue. The residue was redissolved in a minimum amount of dichloromethane and chromatographed on a silica gel column with 15% ethyl acetate/dichloromethane as eluent. The orange solution was obtained. Upon addition of methanol and slow evaporation of the solvent, the product crystallized as orange needle-shape crystals (0.51 g, 30%). The ^{1}H-NMR spectrum of **10** is shown in Figure A.10 and the assignments of the signals are collected in Table 2.10.

Anal. Caled for $C_{16}H_{18}N_2O_4$; C, 63.56%; H, 6.00%; N, 9.27%. Found : C, 63.56%; H, 6.19%; N, 9.29%. EI MS mz:302 (M^+)

Table 2.10. Assignments of ^{1}H-NMR signals of bis-2-(2-hydroxoethoxy)azobenzene, **10** (The spectrum is shown in Figure A.10)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.70	doublet (J=8.0 Hz)	2H	*d*
7.38	triplet (J=8.0 Hz)	2H	*b*
7.12-7.65	multiplet	4H	*a, c*
5.04	broad peak	2H	*g*
4.25	triplet (J=4.0 Hz)	4H	*e*
3.28	broad peak	4H	*f*

2.3.9 Preparation of bis-2-(2-mesyloxyethoxy)azobenzene, **11**



10 **11**

In a 100 mL two-necked flask equipped with a magnetic stirring bar, methane sulfonylchloride (0.67g, 5.83 mmol) and triethylamine (1.07 g, 10.60 mmol) were dissolved in dichloromethane (20 mL) and stirred for 30 min at 0-5 °C. Compound **10** (1.21 g, 2.65 mmol) in dichloromethane (5 mL) was then added slowly into the mixture. The stirring was continued for 1 hour at 0-10°C. The mixture was extracted with 1M HCl solution (2x20 mL) and water (2x20 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the filtrate was evaporated to give an orange-brown residue. The residue was chromatographed on a silica gel column with 30% ethyl acetate/hexane as eluent. The first orange band eluted out of the column was the desired product. It was crystallized by adding dichloromethane and ethyl acetate (0.40g, 33%). The ^{1}H-NMR spectrum of **11** is shown in Figure A.11 and the assignments of the signals are collected in Table 2.11.

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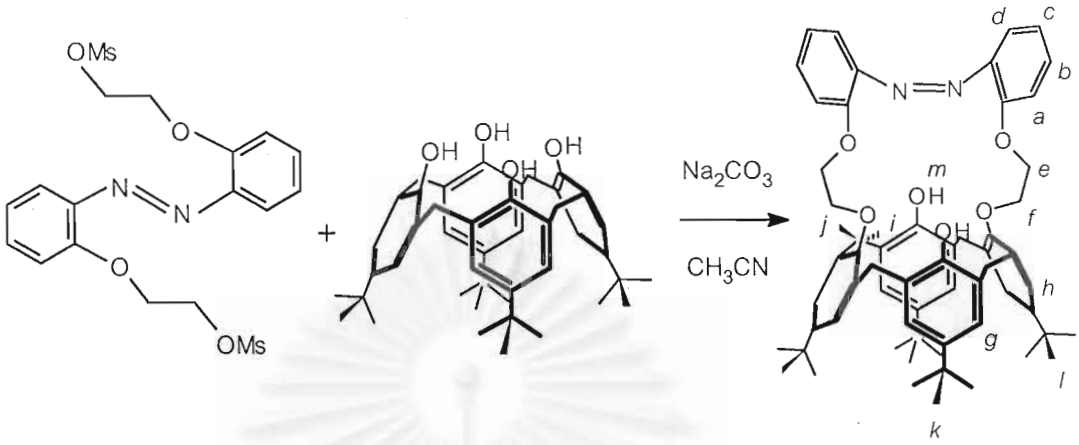
Anal Caled for $C_{18}H_{22}N_2O_8S_2$; C, 47.15%; H, 4.84%; N, 6.11% .Found : C, 47.11%; H, 4.85%; N, 6.12%.

Table 2.11. Assignments of ^{1}H-NMR signals of bis-2-(2-mesyloxyethoxy) azobenzene, **11** (The spectrum is shown in Figure A.11)

Chemical shift (ppm)	Multiplicity (J_{HH})	Number of protons	Assignments
7.60	doublet (J=8.0 Hz)	2H	*d*
7.50	triplet (J=8.0 Hz)	2H	*b*
7.09-7.05	multiplet	4H	*a, c*
4.69	triplet (J=4.0 Hz)	4H	*e*
4.44	triplet (J=4.0 Hz)	4H	*f*
3.04	singlet	6H	*g*

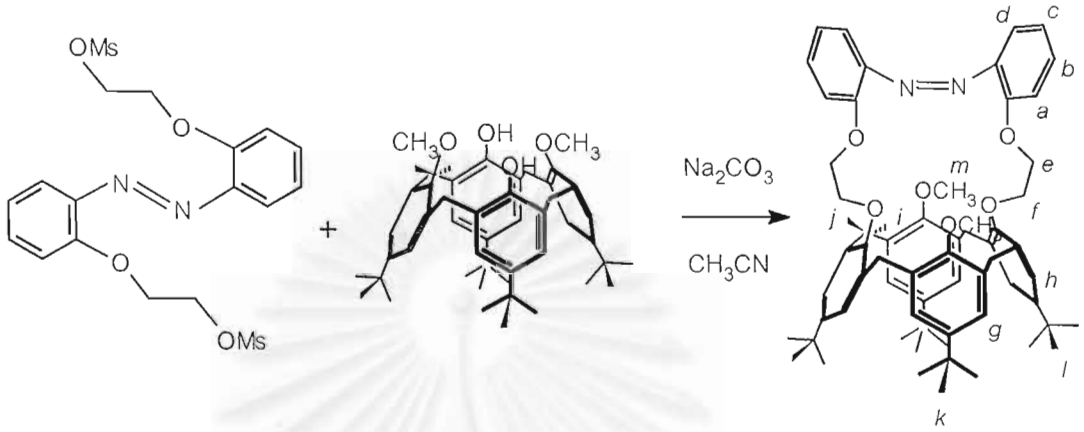
2.2.10 Preparation of azobenzene crown ether *p-tert*-butylcalix[4]arene, **5**



11 **3** **5**

In a 250 mL two-necked flask equipped with a magnetic bar and a reflux condensor, *p-tert*-butylcalix[4]arene, **3**, (1.02 g, 1.54 mmol) and sodium carbonate (0.16 g, 1.55 mmol) were mixed in acetonitrile (100 mL). The mixture was stirred for 24 hours at 35-40 ^{O}C. Compound **11** (0.84g, 1.84 mmol) in acetonitrile (20mL) was then slowly added into the mixture. The reaction mixture was then refluxed for 1 days. The solid was seperated by filtration and washed with dichloromethane. The combined filtrate was evaporated to give an orange residue. The residue was dissolved in dichloromethane (30 mL) and the solution was extracted with 1M HCl solution (2x30 mL). The organic phase was then separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4. The solvent of filtrate was evaporated to give an orange oily residue which was purified by chromatography on a silica gel column with 10% ethyl acetate/hexane as eluent. The first orange band eluted out of the column was the desired product. It was crystallized in methanol to give orange needle-shape crystals (0.07g, 5%). The ^{1}H-NMR spectrum of **5** is shown in Figure A.5 and the assignments of the signals are collected in Table 2.5 (only data of the *trans*-isomer was reported).

2.3.11 Preparation of azobenzene crown ether dimethoxy-*p*-*tert*-butylcalix[4] arene, **8**



11 **6** **8**

In a 250 mL two-necked flask equipped with a magnetic bar and a reflux condenser, compound, **6**, (0.82 g, 1.18 mmol) and sodium carbonate (0.25 g, 2.36 mmol) were mixed in acetonitrile (120 mL). The mixture was stirred for 24 hours at 35-40 ^{O}C. Compound **11** (0.65 g, 1.42 mmol) in acetonitrile (20mL) was then slowly added into the mixture. The reaction mixture was then refluxed for 2 days. The solid was separated by filtration and washed with dichloromethane. The combined filtrate was evaporated to give an orange residue. The residue was dissolved in dichloromethane and the solution was extracted with 1M HCl solution. The organic phase was then separated and dried over anhydrous Na_2SO_4. After filtration of Na_2SO_4, the filtrate was evaporated solvent to give an orange oily residue which was purified by chromatography on a silica gel column with 10% ethyl acetate/hexane.as eluent The first orange band eluted out of the column was the desired product. It was crystallized in methanol and ethyl acetate to give an orange solid (0.09 g, 8%). The ^{1}H-NMR spectrum of **8** is shown in Figure A.5 and the assignments of the signals are collected in Table 2.8 (only data of the major-isomer was reported).

2.3 Variable temperature ^{1}H-NMR (500 MHz) experiments of the compound 7 in $CDCl_3$

The conformational behavior of compound 7 in $CDCl_3$ was studied by variable temperature ^{1}H-NMR experiments using a Jeol 500 MHz NMR spectrometer (Figure 3.3). The spectra were recorded at room temperature, 0, -10, -20 and -30°C and shown in Figure 3.4.

2.4 The percentage of *cis*-isomer under the photostationary state of ligands 5 and 8

2.4.1 Photoisomerization of ligands 5 and 8

The investigated ligand (~3 mmol) was dissolved in $CDCl_3$ (2.5 mL) in an NMR tube and was irradiated with a 180 W low pressure Hg lamp at room temperature. The distance between the lamp and the sample tube was 4 cm. The ^{1}H-NMR (200 MHz) spectra of ligands **5** and **8** were then recorded at 0.5, 1.0, 2.0, 4.0, 8.0, 24.0, and 48.0 hours as shown in Figures 3.5 and 3.6, respectively. The percentage of *cis*-isomer of ligand **5** was calculated from the area integration of the AB system of the methylene bridge protons of calix[4]arene (Table C.1).

2.4.2 Isomerization of ligands 5 and 8 under the day light

The investigated ligand (~3 mmol) was dissolved in $CDCl_3$ (2.5 mL) in an NMR tube and was allowed to stand under the day light at room temperature. The ^{1}H-NMR (200 MHz) spectra were then recorded at 2.0, 12.0, 24.0, 48.0, 96.0, 144.0, and 192.0 hours of ligand **5** (Figure 3.7). The percentage of *cis*-isomer of ligand **5** was calculated from the area integration of the AB system of the methylene bridge protons of calix[4]arene (Table C.2). The ^{1}H-NMR (400 MHz) spectra were then recorded at 0.17, 0.25, 0.50, 1.00, 2.00, and 4.00 hours of ligand **8** (Figure 3.8).

2.5 Effect of CH_3CN towards conformation of ligand 5

CH_3CN (10 μL) was added into the $CDCl_3$ (2.5 mL) solution of isomerized ligand **5** (~3 mmol). The spectrum of the mixture of *cis*- and *trans*-**5** in the presence of CH_3CN compares the spectrum of the mixture of *cis*- and *trans*-**5** without CH_3CN (Figure 3.9) and the inclusion induced shifts of protons on *trans*- and *cis*-**5** in the presence of CH_3CN are shown in Table 3.5.

2.6 Influence of alkali cations on the *cis-trans* isomerization of ligands 5 and 8

2.6.1 Complexation studies of sodium and potassium picrates with ligands **5** in the $CDCl_3$ solution under PSS (Figure 3.10).

Sodium and potassium picrates were prepared as procedure described by Coplan and Fuoss[22]. The metal picrate (~10 mmol) was added into the $CDCl_3$ (2.5 mL) solution of the isomerized ligand **5** (~3mmol). The isomerization was then followed by ^{1}H-NMR (400 MHz) spectroscopy at 2, 5, 12, 19 and 30 days. The ^{1}H-NMR spectra of sodium and potassium picrates were shown in Figures B.1-B.5 and Figures B.6-B.10, respectively.

2.6.2 Complexation studies of sodium and potassium picrates with ligands **8** in the $CDCl_3$ solution under PSS (Figure 3.11).

Complexation studies of sodium and potassium picrates with ligand **8** were carried out in the same manner as that of **5**,. The ^{1}H-NMR spectra of sodium and potassium picrates at various times were shown in Figures B.11 - B.15 and Figures B.16 - B.20, respectively.

2.7 UV-Visible analysis

The electronic absorption spectra of **5** (1.8×10^{-5}mol/l) and **8** (1.5×10^{-5}mol/l) in chloroform, both before and after irradiation, were recorded on a Spectronic 3000 ARRAY Spectrophotometer (Figure 3.12). Absorption spectra of the irradiated ligands and after their complexation with Na^+ and K^+ were depicted in Figure 3.13 and Figure 3.14 for ligands **5** and **8**, respectively.

2.8 X-ray analysis

The investigated crystals were mounted on the end of a hollow glass fiber approximately parallel to the long dimension of the crystal using cyanoacrylate glue. Preliminary examination and data collection were performed using MoK_α X-radiation (λ = 0.71073 Å) on a Bruker AXS SMART area detector diffractometer. Cell constants and a preliminary orientation matrix were obtained from a least-square refinement with a θ range of 1.34 to 30.53° and 2.06 to 30.42° for **4** and **5**, respectively. The final cell parameters were obtained from refinement based on peak positions of 42992 and 21144 strong reflections with $2\theta < 30.53°$ and $2\theta < 30.42°$ for **4** and **5**, respectively. The program used to solve the structures was SHELX86. Data were corrected for Lorentz and polarization effects. The structure were solved by direct method. All remaining non-hydrogen atoms were found by iterative cycles of full-matrix least squares refinement. All hydrogen atoms were included in calculated positions and their parameter fixed during the refinement. Crystallographic parameters of both **4** and **5** are described in Table 3.1.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis and characterization of azobenzene crown ether calix[4]arenes 5, 8

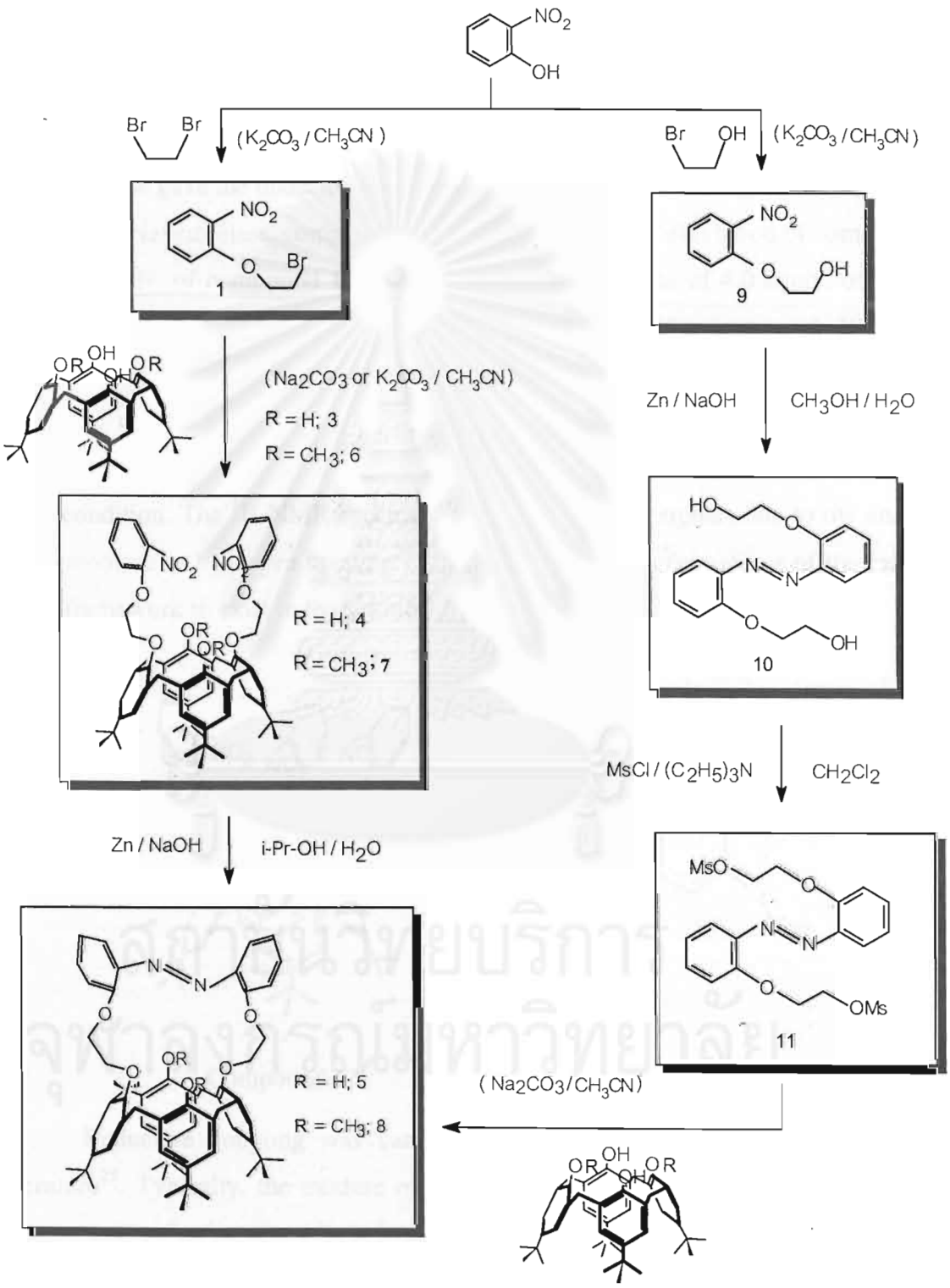
The synthesis of compounds **5** and **8** was conducted according to Scheme 3.1. In the first pathway, two ethoxy nitrobenzene groups were attached to the calix[4]arene framework by a nucleophilic substitution between *o*-nitrophenol and 1,2-dibromoethane. A reductive coupling of nitrobenzene groups was then carried out to afford the azobenzene crown ether calix[4]arenes.

Alkylation of *o*-nitrophenol with 10.0 equiv. of 1, 2-dibromoethane in the excess of K_2CO_3 and acetonitrile as solvent gave yellow needle-shaped crystals of **1** as a major product (74%) and **2** as a minor product (7%). The ^{1}H-NMR spectrum of **1** showed a triplet signal of metylene protons (-O-$CH_{2(e)}$-$CH_{2(f)}$-Br) at 4 .40 ppm and 3.65 ppm, respectively, instead of the singlet peak of methylene protons of starting material (Br-CH_2-CH_2-Br) at 3.64 ppm. Furthermore, the signals of aromatic protons shifted upfield and the singlet peak of the hydroxy proton was dissappeared. The ^{1}H-NMR spectrum of **2** possesses a singlet peak at 4.53 ppm due to a symmetric structure.

A nitrobenzene derivative of calix[4]arene, 25, 27-bis-2-(2-nitrophenoxy) ethoxy-*p-tert*-butylcalix[4]arene, **4** was prepared by alkylation of calix[4]arene, **3** with 2.0 equiv.of compound **1** in acetonitrile in the presence of 1.05 equiv. K_2CO_3 as a base. Compound **4** was crystallized in dichloromethane and acetone to give sugar-like and needle-like crystals. The sugar-like crystals were identified as the desired product, like crystals. The sugar-like crystals were identified as the desired product, **4** in 66% by ^{1}H-NMR and X-ray crystallography in Figure A.4 and Figure 3.1, respectively. The needle-like crystals were the undesired trisubstituted product, **12**. The undesired trisubstituted products were difficult to be seperated from the disubstituted product. Unfortunately, the repeatability of this reaction was quite low and we felt that the selectivity of the reaction highly depeneded on the conditions. The ^{1}H-NMR spectrum of **4** showed the signals of nitroaromatic protons at 6.95-7.74 ppm.

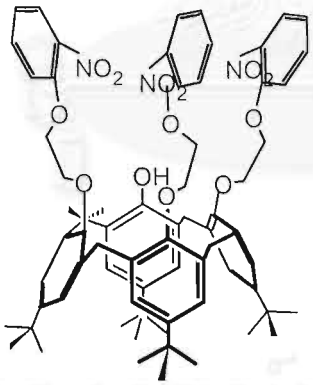
Tert-butyl protons of compound **4** appeared as two singlet signals at 1.28 ppm and 0.94 ppm, while that of the starting material possessed one set at 1.21 ppm. The product has intra-molecular hydrogen bonds indicated by a singlet peak of OH proton at 6.85 ppm.

Scheme 3.1 Two different pathways for synthesis ligands **5** and **8**

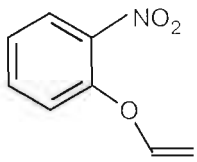


The spectrum also possesses two doublet signals at 3.50 ppm and 4.25 ppm, and integration of two sets of *tert*-butyl groups are equivalent (18 H each), indicating that the calix[4]arene unit is in a cone conformation.

In early attempts, we tried to prepare compound **7** from alkylation reaction of **6**[21(b)] with **1** in various conditions. A preparation by using potassium *tert*-butoxide as a base in THF gave the elimination product of **1,** compound **13**. Another method, using NaH as a base gave the undesired elimination of product (24%) along with compound **7** in only 8%. Nevertheless, compound **7** can be synthesized by alkylation of compound **6** with 2.0 equiv. of compound **1** in acetonitrile in the presence of 4.0 equiv. of K_2CO_3 and KOH. The desired product was separated on a silica gel column with 10% ethyl acetate/hexane as eluent to afford compound **7** in 20%. The yield was quite low due to the steric congestion of the methyl group which may decelerate the substitution reaction rate[23] and the elimination product, **13** was an inevitable side reaction under basic condition. The ^{1}H-NMR spectrum of **7** showed broad signals due to the absence of intramolecular hydrogen bonding[24] causing in various conformations of the calix[4] arene framework to exist in the solution.



Compound **12**



Compound **13**

Reductive coupling was carried out with a modified procedure from the literature[25]. Typically, the mixture of bis-nitrobenzene calix[4]arene, **4**, in *i*-PrOH in the presence of aqueous sodium hydroxide and zinc was stirred and refluxed under nitrogen atmosphere for 48 hours. The crude product was obtained as an orange solid in 8% yield after an extensive purification by chromatography and recrystallization. The orange solid was analyzed by TLC (20% ethyl acetate/hexane) and two orange

spots were found, R_f = 0.59 and 0.35, corresponding to the *trans*- and *cis*-isomers of **5**, respectively. The ^{1}H-NMR spectrum of mainly *trans*-**5** was shown in Figure A.5. The groups of signals at 7.02-7.67 ppm belong to azo aromatic protons, a doublet of doublet at 7.67 ppm (J=8.0 Hz, coupling between $H_{(d)}$ and $H_{(c)}$, and J=2.0 Hz, coupling between $H_{(d)}$ and $H_{(b)}$) assigned for the $H_{(d)}$ aromatic protons of the azobenzene[8(b),11,12, 17(a)].

A similar coupling reaction of compound **7** gave compound **8** was purified by crystallization in methanol and ethyl acetate/hexane to give orange crystal of **8** (12%). The orange solid was analyzed by TLC (20% ethyl acetate/hexane) and two orange spots were found, R_f = 0.68 and 0.57 for the *major*- and *minor*-conformers. The signal of aromatic protons of compound **8** in Figure A.8 appeared as a pair of sharp singlet peaks at 7.01 ppm and 6.42 ppm unlike the broad peaks of compound **7**. The result implied that compound **8** became more rigid and the calix[4]arene framework resumed the cone conformation.

Alternatively, 2-(2-hydroxyethoxy)nitrobenzene, **9** can be synthesized and then reduced to ethoxy azobenzene before attaching to calix[4]arene to produce the desired azobenzene calix[4]arene as shown in Scheme 3.1. Compound **9** was prepared from a nucleophilic substitution reaction between *o*-nitrophenol with 3.0 equiv. of 2-bromoethanol in the presence of 1.05 equiv. of K_2CO_3 in acetonitrile. After separation and purification, a yellow liquid was obtained in 63%. The ^{1}H-NMR spectrum of **9** was shown in Figure A.9. The groups of signals at 6.91-7.68 ppm are of aromatic protons. The triplet signal of methylene protons ($OCH_{2(e)}$-$CH_{2(f)}$-OH) at 4.10 ppm and 3.83 ppm were shifted downfield (methylene protons of starting material, -$CH_{2(e)}$-$CH_{2(f)}$-OH, at 3.74 ppm and 3.33 ppm as shown in Figure A.14). The singlet peak at 4.41 ppm belongs to hydroxy protons as proved by D_2O exchange.

A reductive coupling of compound **9** with zinc in *i*-PrOH in the presence of sodium hydroxide solution (48 hours, reflux) and purification of the crude by silica gel column chromatography with 15% ethyl acetate/dichloromethane as an eluent gave an orange viscous liquid which was crystallized out as an orange solid, compound **10**, from a methanol solution 30% (The ^{1}H-NMR spectrum and the mass spectrum as shown in Figure A.10 and Figure A.16, respectively). The groups of signals at 7.65-7.70 ppm correspond to aromatic protons. The broad peak at 5.04 ppm belongs to the

hydroxy protons as proved by D_2O exchange. Methylene protons (-CH_2-$CH_{2(l)}$-OH) at 3.28 ppm also became broad peak because of intra-molecular hydrogen bonding.

In order to facilitate the nucleophilic substitution reaction compound **10** and compound **3** or **6**, compound **10** was converted into a methane sulfonate ester, **11**. The mesylation of **10** with 2.2 equiv. methane sulfonylchloride and excess triethylamine in dichloromethane gave the desired product in 33% after purification (Figure A.11).

The nucleophilic substitution of **11** with **3** or **6** in the presence of Na_2CO_3 in acetonitrile gave azobenzene calix[4]arenes **5** and **8**, respectively. In a typical reaction, compound **3** and 1.05 equiv. Na_2CO_3 in acetonitrile were mixed in acetonitrile. Compound **11** was then added (24 hours, reflux). After workup procedure, **5** was obtained in a quite poor yield as orange crystals (5%). In the same way, the reaction between compound **11** and **6** gave **8** solely in 8%. The low yield of nucleophilic substitution reactions may stem from the competing polymeric formation during the reactions.

3.2 X-ray Studies

The solid state structure of compound **4** was determined by X-ray crystallography. The structure of **4** showed that the disubstituted groups located on the lower rim in the 1,3 position and still be in the cone conformation because of intramolecular hydrogen bonding. Since it was crystallized from dichloromethane and acetone, the inclusion of a molecule of acetone into the upper rim of the calixarene unit was observed. The coupling reaction of this compound to form ligand **5** is thus too difficult to obtain a good yield since two nitro-aromatic groups are pointing in the opposite direction.

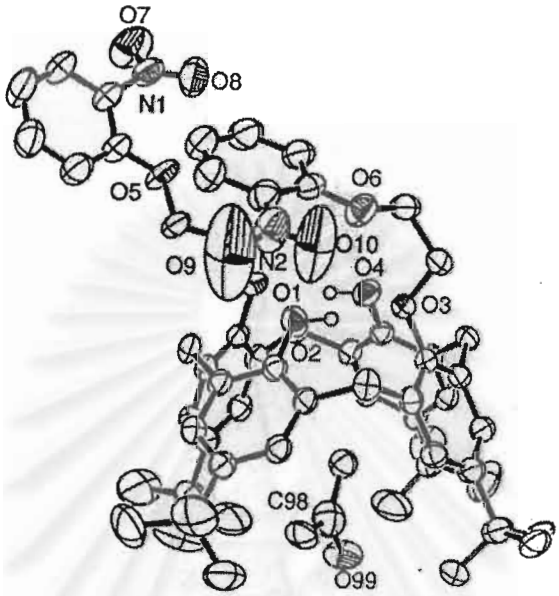


Figure 3.1 X-ray crystallographic structure of compound **4**•C_3H_6O

We can obtain crystals of both ligands **5** and **8**. Unfortunately, only crystals of **5** are suitable for single crystal X-ray analysis. The X-ray structure of ligand **5** was isolated in a pure *trans*-form (Figure 3.2). The X-ray structure indicates that a molecule of ethyl acetate has included into the calix[4]arene unit of **5** pointing the -CO-CH_3 moiety into the upper rim cavity. The *trans*-form of **5** has -Ar-N=N-Ar- unit bended towards the calix[4]arene unit.

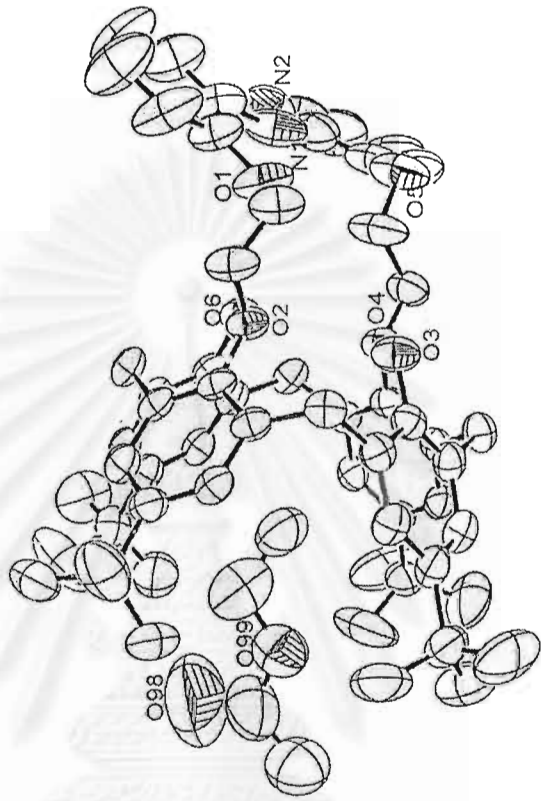


Figure 3.2 X-ray crystallographic structure of ligand **5**•$C_4H_8O_2$. Hydrogen atoms were omitted for clarity

The X-ray crystallographic data for compounds **4**•C_3H_6O and **5**•$C_4H_8O_2$ are presented in Table 3.1. The selected bond lengths and bond angles of compounds **4**•C_3H_6O and **5**•$C_4H_8O_2$ are shown in Table 3.2 and 3.3 respectively.

Table 3.1 Summary of X-ray crystallographic data for compounds 4•C_3H_6O and 5•$C_4H_8O_2$

Compound	4	5
crystal habit and color	sugar-like, yellow	needle-shape, orange
crystal dimension, mm	? x ? x ?	? x ? x ?
formula	$C_{60}H_{70}N_2O_{10}$	$C_{64}H_{88}N_2O_8$
fw	979.18	1013.36
crystal system	monoclinic	monoclinic
space group	P2(1)/c	Cc
T, K	293 (2)	293 (2)
cell parameter		
a (Å)	16.1437(2)	15.1260 (3)
b (Å)	21.0292(2)	31.1347 (4)
c (Å)	18.9685(3)	12.6692 (8)
α (deg)	90.0	90.2091 (10)
β (deg)	110.3080 (10)	98.4968 (10)
γ (deg)	90.0	89.9261 (10)
V (^{3})	6039.31(13)	5900.9 (4)
Z	5	4
ρ (calcd) (mg/m^3)	1.346	1.141
radiation (λ,)	0.71073	0.71073
abs coeff (μ, mm^{-1})	0.091	0.074
no. of reflections measd	+,- *h, k, l*	+,- *h, k, l*
no. of unique total data	42992	21144
no. of unique obsd data	17323	13447
agreement between equiv. obsd data		
no. of variables		
R	0.0923	0.0740
R_w	0.2653	0.1551

Table 3.2 Selected bond lengths (Å) and bond angles (deg) for compound **4**

Atoms	bond lengths (Å)	Atoms	bond angles (deg)
O (1) - C (1)	1.400 (3)	C (1) - O (1) – C (29)	115.9 (2)
O (1) – C (29)	1.437 (3)	C (20) - O (3) – C (21)	116.3 (17)
O (2) – C (13)	1.391 (3)	C (31) – O (5) – C (30)	118.2 (2)
O (3) – C (20)	1.433 (3)	C (23) – O (6) – C (22)	120.3 (2)
O (3) – C (21)	1.359 (3)	O (8) – N (1) – O (7)	123.3 (3)
O (4) – C (43)	1.434 (3)	O (8) – N (1) – C (32)	119.7 (3)
O (5) – C (30)	1.348 (3)	O (7) – N (1) – C (32)	116.9 (3)
O (6) – C (23)	1.433 (3)	O (10) – N (2) – O (9)	116.9 (5)
O (6) – C (22)	1.233 (4)	O (10) – N (2) – C (28)	125.2 (3)
O (7) – N (1)	1.195 (4)	O (9) – N (2) – C (28)	117.0 (4)
O (9) – N (2)	1.155 (6)	O (3) – C (21) – C (22)	105.3 (2)
O (10) – N (2)	1.131 (5)	O (1) – C (29) – C (30)	111.4 (2)

Table 3.3 Selected bond lengths (Å) and bond angles (deg) for ligand **5**

Atoms	bond lengths (Å)	Atoms	bond angles (deg)
N (1) - N (2)	1.162 (6)	N (2) - N (1) – C (1)	110.9 (6)
N (1) – C (1)	1.533 (7)	N (1) - N (2) – C (53)	115.5 (6)
N (2) – C (53)	1.467 (8)	C (6) – O (1) – C (7)	120.5 (3)
O (1) – C (6)	1.381 (5)	C (48) – O (5) – C (47)	116.6 (5)
O (1) – C (7)	1.433 (6)	C (5) – C (6) – O (1)	123.7 (4)
O (2) – C (9)	1.403 (4)	O (1) – C (6) – C (1)	115.8 (4)
O (2) – C (8)	1.454 (5)	O (1) – C (7) – C (8)	113.1 (5)
O (4) – C (60)	1.409 (4)	O (2) – C (9) – C (10)	118.6 (3)
O (4) – C (46)	1.454 (5)	O (4) – C (46) – C (47)	106.1 (3)
O (5) – C (48)	1.402 (8)	O (5) – C (47) – C (46)	111.0 (4)
O (5) – C (47)	1.433 (6)	O (5) – C (48) – C (53)	125.8 (5)
C (7) – C (8)	1.464 (7)	C (48) – C (53) – N (2)	128.0 (7)
C (46) – C (47)	1.504 (7)		

3.3 Variable temperature ^{1}H-NMR (500 MHz) experiments of the compound 7 in $CDCl_3$

Compound 7 was characterized by ^{1}H-NMR (200 MHz) spectroscopy at room temperature as shown in Figure 3.3. It can be proposed that the coalescence of cone and partial-cone of calix[4]arene has occurred. This assumption is drawn from the observation of various broad peaks and also three broad signals corresponding to *tert*-butyl protons. In order to confirm this assumption, variable temperature ^{1}H-NMR experiments were performed on a 500 MHz NMR spectrometer.

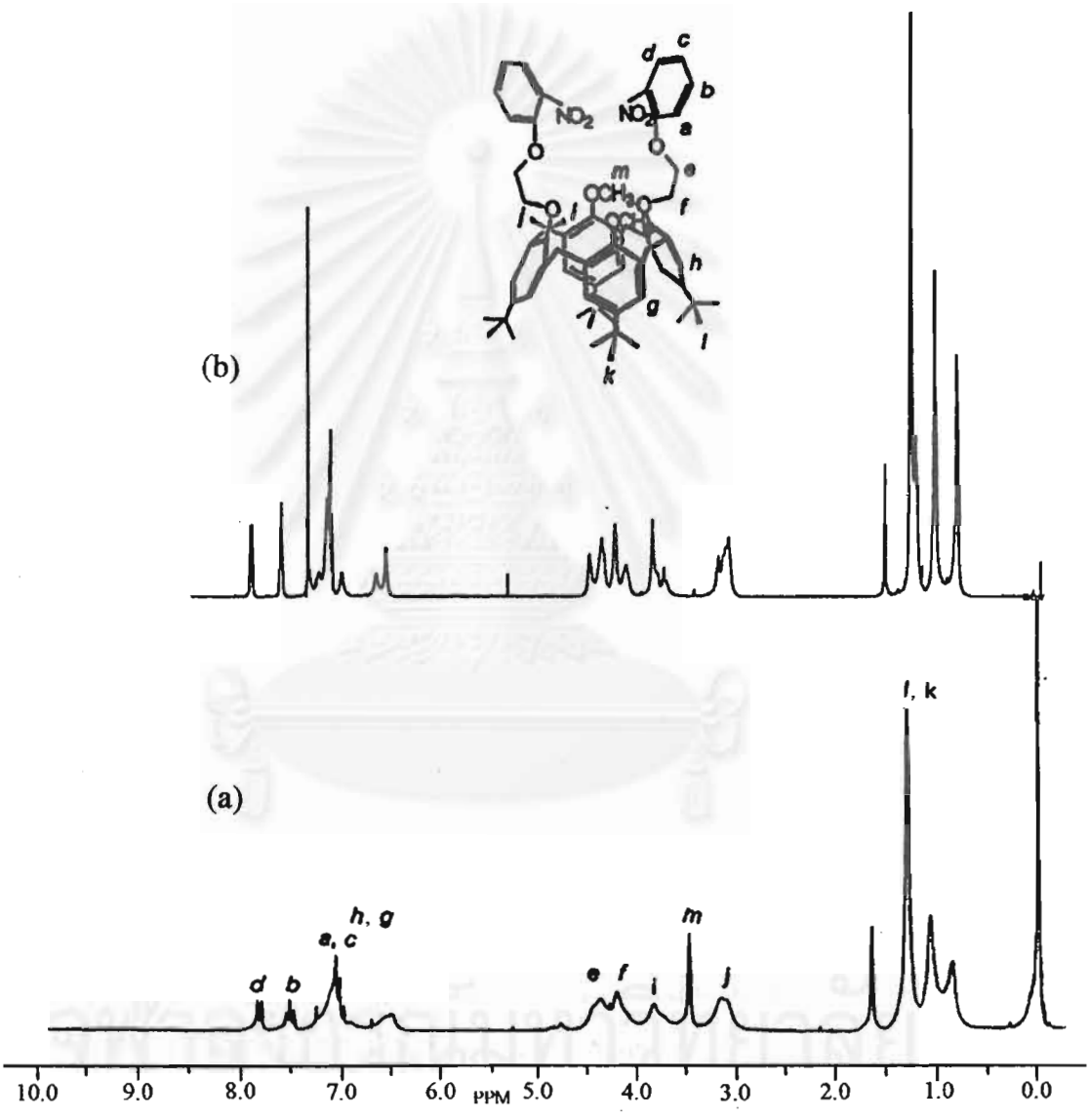


Figure 3.3 ^{1}H-NMR spectra of **7** at room temperature (a) 200 MHz (b) 500 MHz

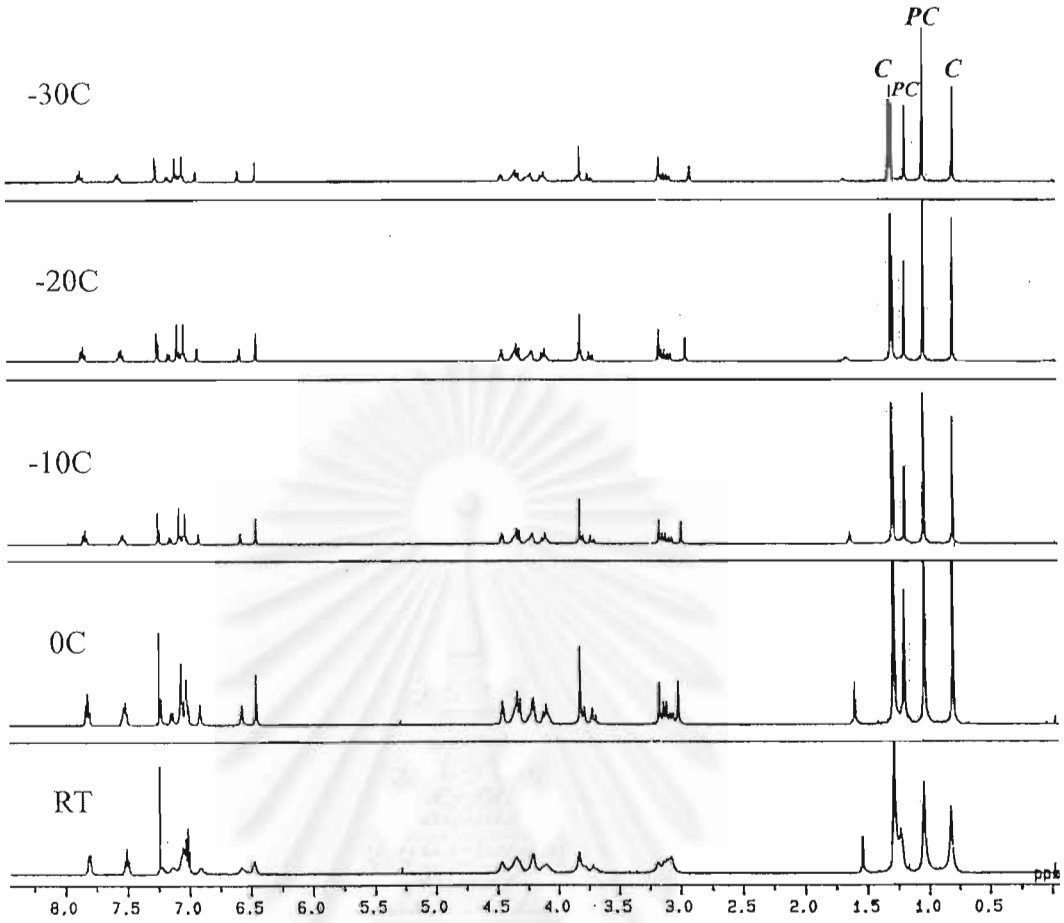


Figure 3.4 ^{1}H-NMR (500 MHz) spectrum of 7 in $CDCl_3$ at room temperature, 0, -10, -20 and –30 °C (***C***, ***PC*** denote respectively cone and partial conformation)

At room temperature, the spectrum contains broad peaks. The signals of the *tert*-butyl protons at 0.80-1.30 ppm appeared as a pair of seperated peaks and a group of unresolved peaks. When the temperatures were decreased to 0 °C, all the signals become sharper and the unresolved peaks split into two peaks at 1.23 and 1.28 ppm. Other regions of the spectrum change dramatically; the signals at 6.40-7.25 ppm corresponding to the aromatic protons and the signals at 2.80-4.50 ppm belonging to the ethereal and methylene protons are more resolved. When the temperature was further decreased to -30 °C. The singlet signal of *tert*-butyl protons at 1.28 ppm split into two singlet signals at 1.30 and 1.27 ppm showing now all five distinct lines belonging to *tert*-butyl protons of both cone and partial-cone conformations. The integral ratio 2:1:1:2:2 of *tert*-butyl protons also supports the existence of both the partial-cone and cone conformations in 7 at -30 °C.

3.4 The percentage of *cis*-isomer under the photostationary state of ligands 5 and 8

3.4.1 Photoisomerization of ligands 5 and 8

Upon exposure of **5** to the UV-light only 0.5 hour, the various ^{1}H-NMR signals of *cis*-**5** can be observed. The most characteristic signal was the singlet peak of hydroxy protons, confirmed by D_2O exchange, at 8.42 ppm compared to that of the *trans*-isomer at 7.67 ppm. The signals of ethereal and methylene protons of *cis*-isomer around respectively 4.2-4.4 and 3.3 ppm shifted seperately of those of the *trans*-isomer. The area integration of signals (Table C.1) provided the estimation of % cis-isomer. Ligand **5** reached the photostationary state after 24 hours and the ratio of *cis* : *trans* was calculated to be 36 : 64.

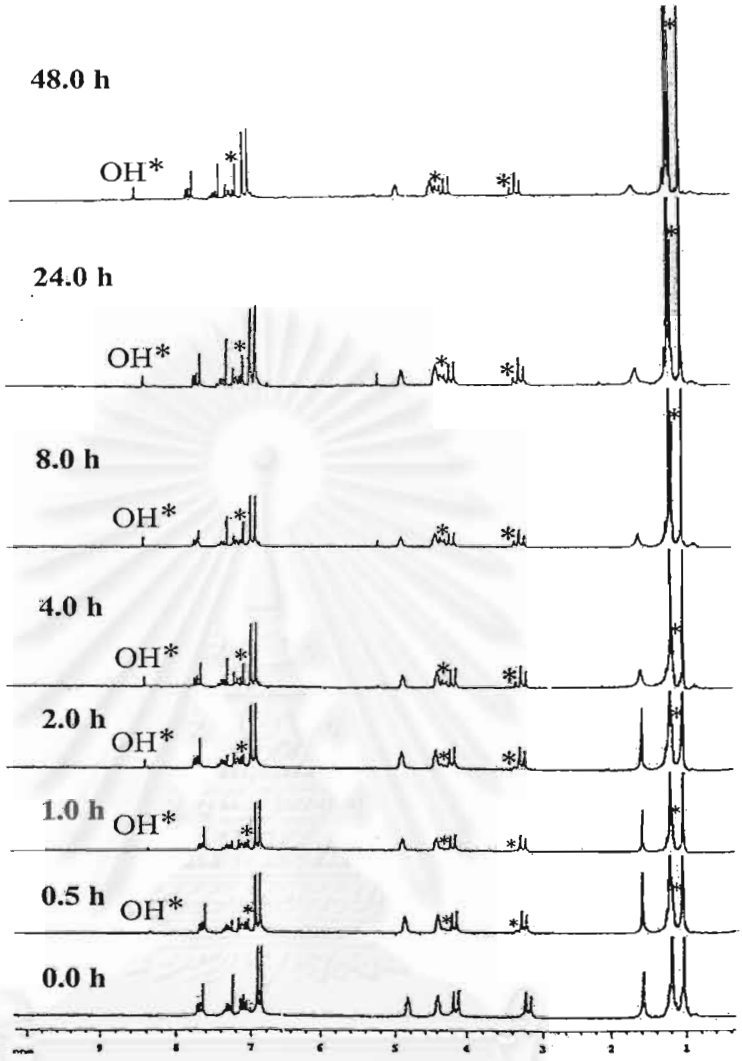


Figure 3.5 ^{1}H-NMR (200 MHz) spectra of irradiated ligand **5** under PSS at 0.0, 0.5, 1.0, 2.0, 4.0, 8.0, 24.0 and 48.0 hours (* denotes signal due to the *cis*-isomer).

The ^{1}H-NMR (200 MHz) spectra of ligand **8** also changed dramatically upon irradiation (Figure 3.6). The signals in the *tert*-butyl and methylene bridge regions became very complicated suggesting the existance of the various conformations of the calixarene unit. We have attempted to separate one of the conformers from the solution by crystallization but it was not successful. Nevertheless, the ^{1}H-NMR spectra of conpounds **5, 10, 11** and the compounds appeared in references 8(b), 11, 17(a) and 19 which possess *trans*-azobenzene groups show doublet signals of aromatic protons at ~7.6-7.8 ppm while ligand **8** , before and after irradiation, have no signal in this region. Moreover, the signals of aromatic protons of ligand **8** around 6.9-7.5 ppm are almost

identical with that observed in *cis*-azobenzene [8(b),11,17(a)]. We thus suggested that ligand **8** should be in the *cis*-form before irradiation.

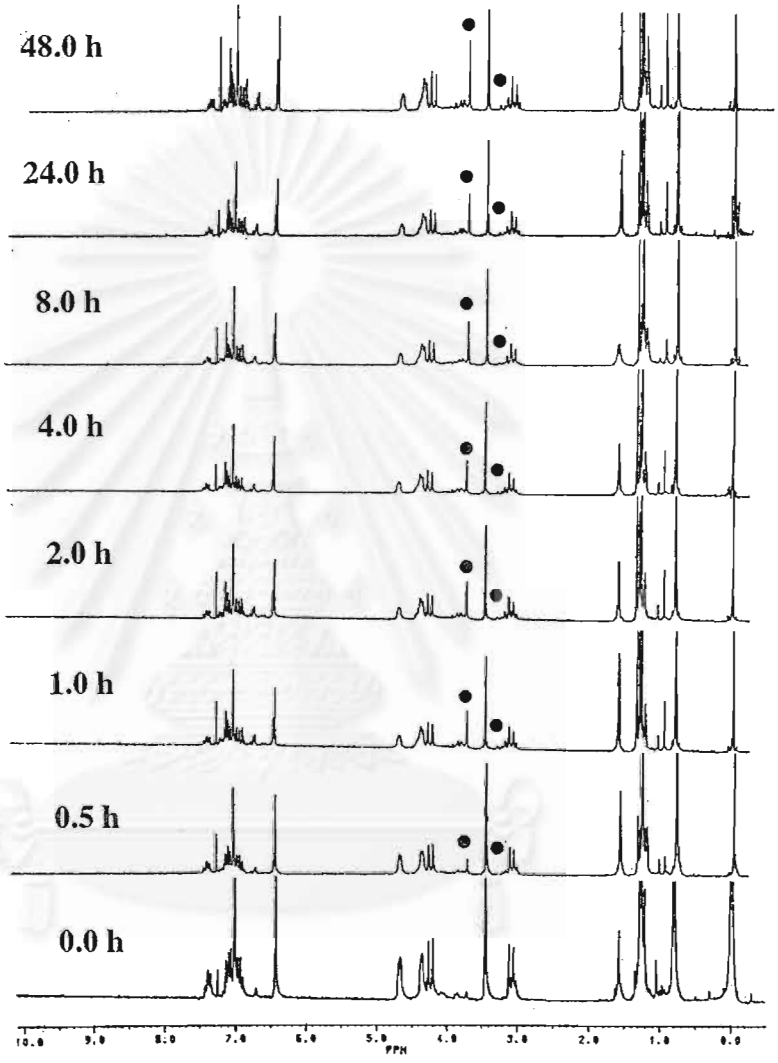


Figure 3.6 The ^{1}H-NMR (200 MHz) spectra of irradiated ligand **8** under PSS at 0.0, 0.5, 1.0, 2.0, 4.0, 8.0, 24.0 and 48.0 hours (• denotes signal due to the other conformer)

We are suspicious that ligand **8** still be in the *cis*-from and the change of the conformation of the calixarene unit occurs rather than *cis-trans* isomerization. These results may stem from the lack of intramolecular hydrogen bonding.

3.4.2 Isomerization of ligands 5 and 8 under the day light

The solution of ligand **5** was allowed to stand under the day light and followed by ^{1}H-NMR (200 MHz) spectroscopy for 8 days (Figure 3.7). The signals due to *cis*-**5** gradually appeared after 2 hours. The result showed that the isomerization from *trans* to *cis*-ligand **5** slowly occurred after standing under the day light. Ligand **5** reached the photostationary state after 6 days and the *cis* : *trans* ratio was calculated to be 33 : 67 (Table C.2). We can concluded that the isomerization standing under the day light condition gave the ratio of *cis* : *trans* closely to the isomerization by UV-irradiation.

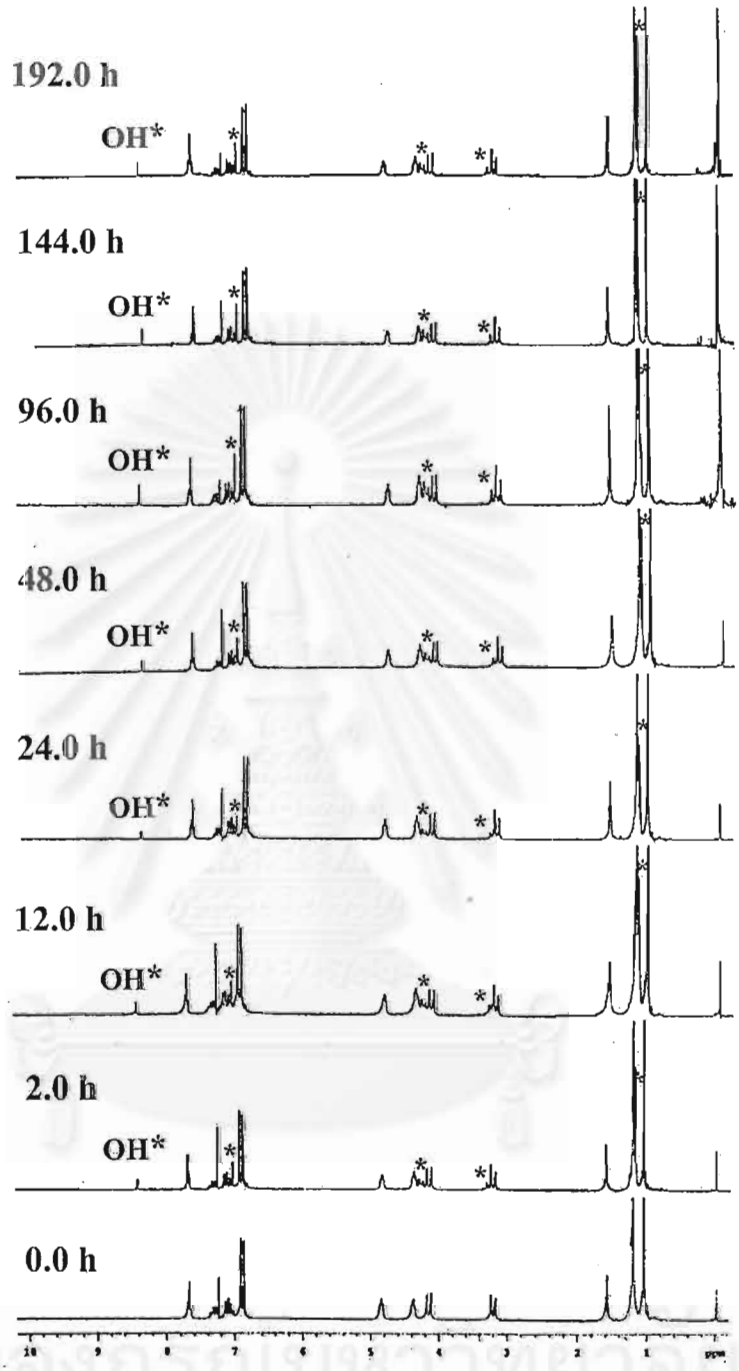


Figure 3.7 ^{1}H-NMR (200 MHz) spectra of ligand **5** upon standing under the day light for 0.0, 2.0, 12.0, 24.0, 48.0, 96.0, 144.0, and 192.0 hours (* denotes signals due to the *cis*-isomer)

The ^{1}H-NMR (400 MHz) spectrum of **5** was also obtained. The spectrum was more resolved and separated more distinctively than the 200 MHz spectrum and thus

allowed some assignments to be carried out. Signals belonging to both the *cis*-**5** and *trans*-**5** under PSS were presented in Table 3.4. We have tried to isolate the *cis*-form of **5**, however the attempts are not successful. The *trans*-form may be the thermodynamically more stable than the *cis*-form.

Table 3.4 The signal changes of ligand **5** from *trans*- to *cis*- isomer

Assignments	Chemical shift of *trans*-**5** (ppm)	Chemical shift of *cis*-**5** (ppm)
d	7.73-7.10	7.20-6.83
m	7.67	8.42
h, g	6.97, 6.93	7.06, 6.97
e	4.88	4.36 *
f	4.42	NA
i	4.20	4.27
j	3.24	3.31
k, l	1.24, 1.07	1.21, 1.19

^{1}H-NMR (400MHz) of ligand **5** in the presence of CH_3CN

Upon standing under the day light, ligand **8** gave almost the same results as that of exposing to the UV-light. For example, the singlet signal appeared at 3.74 ppm upon standing under day light for solely 10 minutes. From the ^{1}H-NMR 400 MHz spectra (Figure 3.8), some signals separated from the complicated peaks as compared to 200 MHz spectra. Two sets of doublet signals at 3.23 and 3.13 ppm corresponding to calixarene methylene protons of another conformer separated from the complicated peak around 3.07 ppm.. We cannot conclude that the isomerization has occurred because the crystal structure of **8** cannot be obtained. We thus proposed that ligand **8** existed in the *cis*-isomer and composed of a variety of conformations of calixarene.

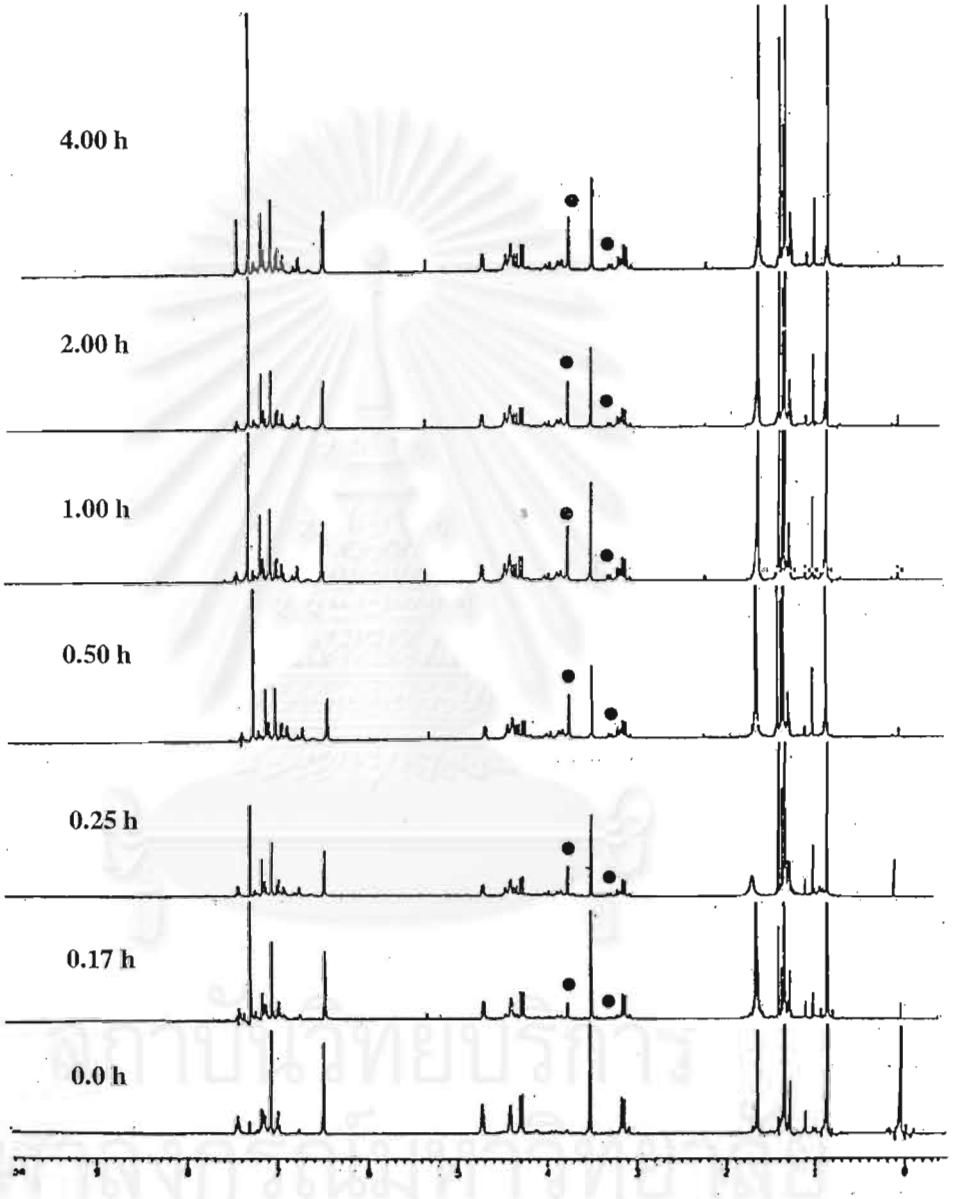


Figure 3.8 ^{1}H-NMR (400 MHz) spectra of day-light ligand **8** under PSS at 0.0, 0.17, 0.25, 0.50, 1.00, 2.00 and 4.00 hours (• denotes signal due to the other conformer)

Interestingly, when CH_3CN (10 μL) was added into the $CDCl_3$ solution of the ligand **5,** the spectrum changed significantly. Especially, the signals due to *tert*-butyl, aromatic, ethereal and hydroxy protons shifted dramatically. The spectrum of **5** in the presence of CH_3CN compared with the spectrum of ligand **5** are depicted in Figure 3.9. The chemical induced shifts of protons on *trans* and *cis*-**5** in the presence of CH_3CN are collected in Table 3.5. The results suggested that CH_3CN may include in the cavity of the upper rim of the calixarene. The cavity size may be enlarged by the movement of phenyl rings to accommodate CH_3CN and caused the signals to shift noticeably.

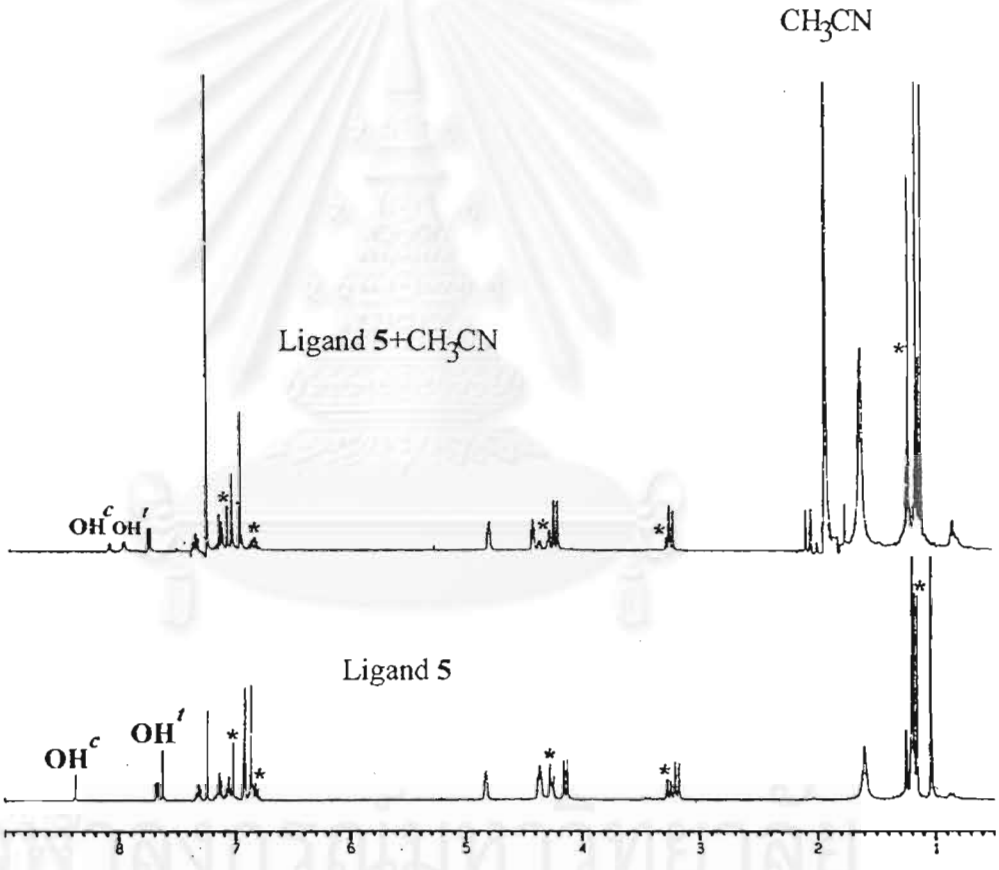


Figure 3.9. The comparison of ^{1}H-NMR spectrum of inclusion study between ligand **5** and CH_3CN

Table 3.5 The chemical induced shift (Hz)*of *trans*-and *cis*-5 in the presence of CH_3CN

Assignments	$\delta_{trans\ 5+MeCN}-\delta_{trans\ 5}$ (Hz)	$\delta_{cis\ 5+MeCN}-\delta_{cis\ 5}$ (Hz)
d	+24.37	NA
m	+128.38	+121.21
b	+9.18	NA
h, g	+41.98, +33.63	+18.21, +13.48
e	-18.18	-2.74
f	+14.85	NA
i	+26.11	-5.92
j	+15.35	-0.95
k, l	-13.92, +34.39	+21.60, -4.42

*(+) presents down field shift and (-) presents up field shift

3.5 Influence of alkali cations on the percentage of *cis*-isomer of ligands

3.5.1 Complexation studies of ligand **5** with Na^+ and K^+ picrates

The picrate salt is used to study the interaction with the ligand. The salt is not soluble in the $CDCl_3$ and was thus used as a solid and added directly into the solution of the investigated ligand in an NMR tube. The inclusion of cation into ligand can be signified by the appearing of a singlet signal of picrate aromatic protons around 8.6-8.9 ppm which is well separated from the signals of the ligands.

^{1}H-NMR spectra of the complexation of the ligand **5** with Na^+ and K^+picrates are shown in Figure 3.10.

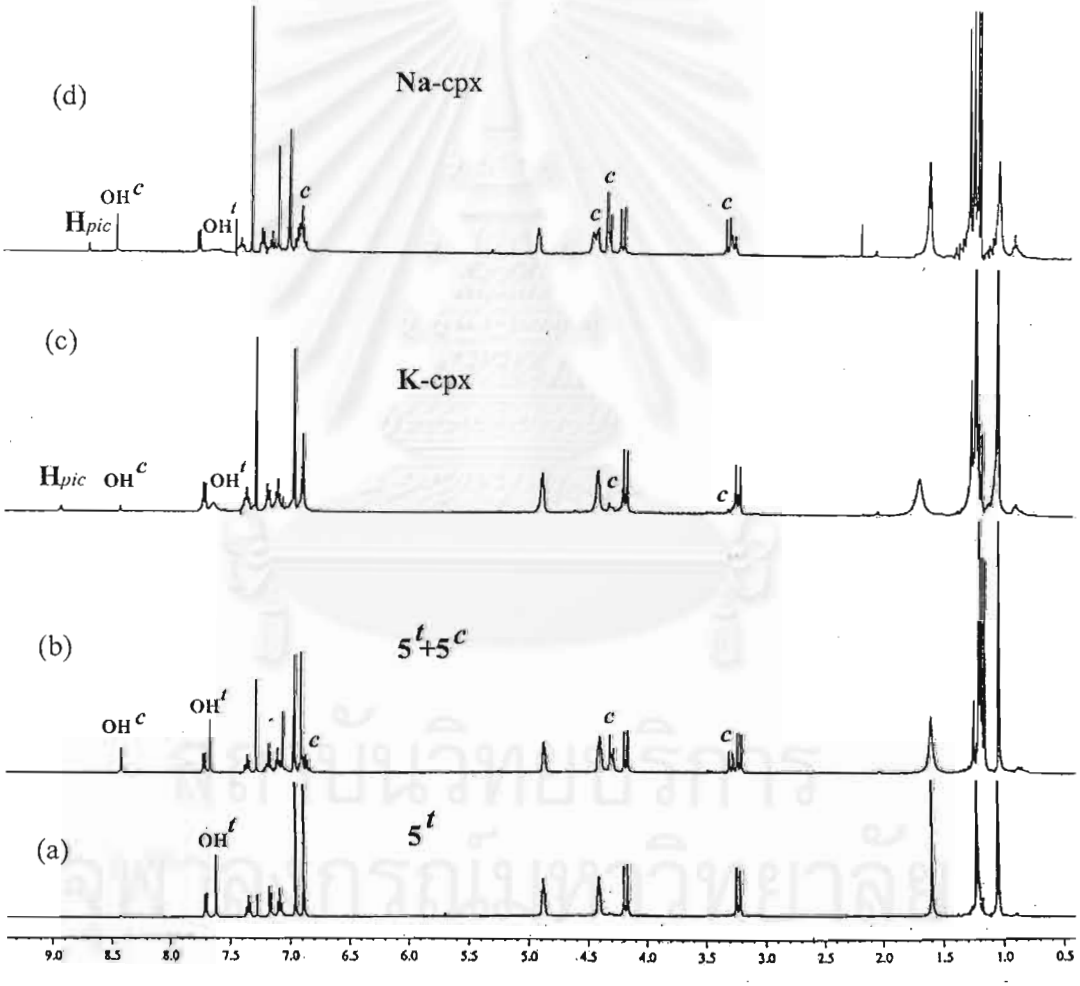


Figure 3.10 The ^{1}H-NMR (400 MHz) spectra of ligand **5** (*c, t* denote *cis*- and *trans*-isomer, respectively) (a) a fresh sample of **5** containing mostly *trans*-isomer

(b) the irradiated **5** showing both *cis*- and *trans*-isomer at PSS

(c) standing **5** days after an addition of K^+ picrates

(d) standing **5** days after an addition of Na^+ picrates

From ^{1}H-NMR results (Figure 3.10), the signals of ligand **5** in the presence of sodium picrate ion are different from those of ligand **5** in the presence of potassium picrate ion. The addition of sodium picrate into the deuterated chloroform solution of ligand **5** led to the appearance of a singlet signal of picrate proton at 8.64 ppm. The broad peak of the ethereal protons of *trans*-isomer at 4.44 ppm seperated from ones of *cis*-isomer at 4.40 ppm and the multiplet signals appeared around 6.82-6.93 ppm. Furthermore, doublet peaks of calixarene methylene bridge protons of both *trans*-from at 3.26 ppm and *cis*-form at 3.32 ppm shifted.

Contrarily, the addition of potassium picrate into the deuterated chloroform solution of ligand **5** led to an appearance of a singlet signal of picrate protons at 8.92 ppm. In addition, the intensity of the complicated peaks of the ethereal proton around 4.25-4.28 ppm became decreased. Conclusively, we suggest that sodium ion induces to the increase of the *cis*-form whereas potassium has an influence on the increase of *trans*-isomer.

We studied the ratio of *cis*:*trans* in the presence of alkali cation in two difference methods. The first method, the alkali picrate was added into the isomerized-**5**. We presumed that the *cis*-to *trans*- isomerization in the absence of a metal cation was at equilibrium, holding the *cis*:*trans* ratio at 36 : 64 for the isomerized-**5**. The other method, alkali picrate was added into the fresh -**5**. The *cis*:*trans* ratio at various times for the latter were virtually the same as those of the former method (Appendix C). The comparison of the percentages of *cis*-isomer for both methods is summarized in Table 3.6.

Table 3.6 The comparison of *cis*:*trans* ratio* of the isomerized **5** and the fresh **5** in the presence of Na^+, K^+ picrate

Time (days)	*cis*:*trans* ratio of the isomerized **5** + Na^+ picrate	*cis*:*trans* ratio of the fresh **5** + Na^+ picrate	*cis*:*trans* ratio of the isomerized **5** + K^+ picrate	*cis*:*trans* ratio of the fresh **5** + K^+ picrate
1	-	22:78	-	23:77
2	42:58	29:71	37:63	28:72
4	-	40:60	-	25:75
5	48:52	40:60	10:90	16:84
12	43:57	44:56	24:76	23:77
19	45:55	-	26:74	-
30	43:57	43:57	43:57	40:60

*The calculation is shown in Appendix C, - denotes no observation

The percentage of *cis*-**5** was virtually unaffected by the order of the addition of metal ions. For the complexation of the isomerized-**5** and Na^+ ion, the amount of *cis*-isomer was increased from 36% into the range of 42-47%. In the same way, the percentage of *cis*-isomer of the fresh **5** in the presence of Na^+ was slowly increased into the range of 40-44%. After standing several days, the amount of *cis*-form is still present in this extent. It is suggested that Na^+ suitable fit the cavity of *cis*-**5** better than with *trans*-**5**.

Contrarily, the results of the complexation of **5** with K^+ion were different from those of Na^+ ion. Upon standing for 5 days of both methods (Table 3.6), the percentage of *cis*-isomer was dramatically decreased into the range of 10-16%. Another word, *trans*-isomer was enhanced. Surprisingly, the amount of *cis*-form was gradually increased to 25% after standing for 19 days, and reached 42% in 30 days. We do not have a definite explanation for the re-increasing of percentages of *cis*-isomer. However, we think that K^+ may first form a complex with the *trans*- form of 5 and increases the percentage of the *trans*-form. Then, a *trans*- to *cis*-reisomerization resulted in increaseing percentage of *cis*-form. The result also suggests that the binding of ligand **5** with K^+ is not very strong. Nevertheless, both ^{1}H-NMR spectra of complexes of **5** possesses two doublet signals at 3.26 and 4.20 ppm (J~13 Hz) indicating that the ligand **5** maintains the cone conformation of calix[4]arene after its complexation with the metal ion.

3.5.2 Complexation studies of ligand **8** with Na^+ and K^+ picrates

^{1}H-NMR spectra of ligand **8** in the presence of metal picrates (Na^+ and K^+) are shown in Figure 3.11. The singlet signals of picrate aromatic protons of both sodium and potassium complexes were observed at the same position, 8.78 ppm.

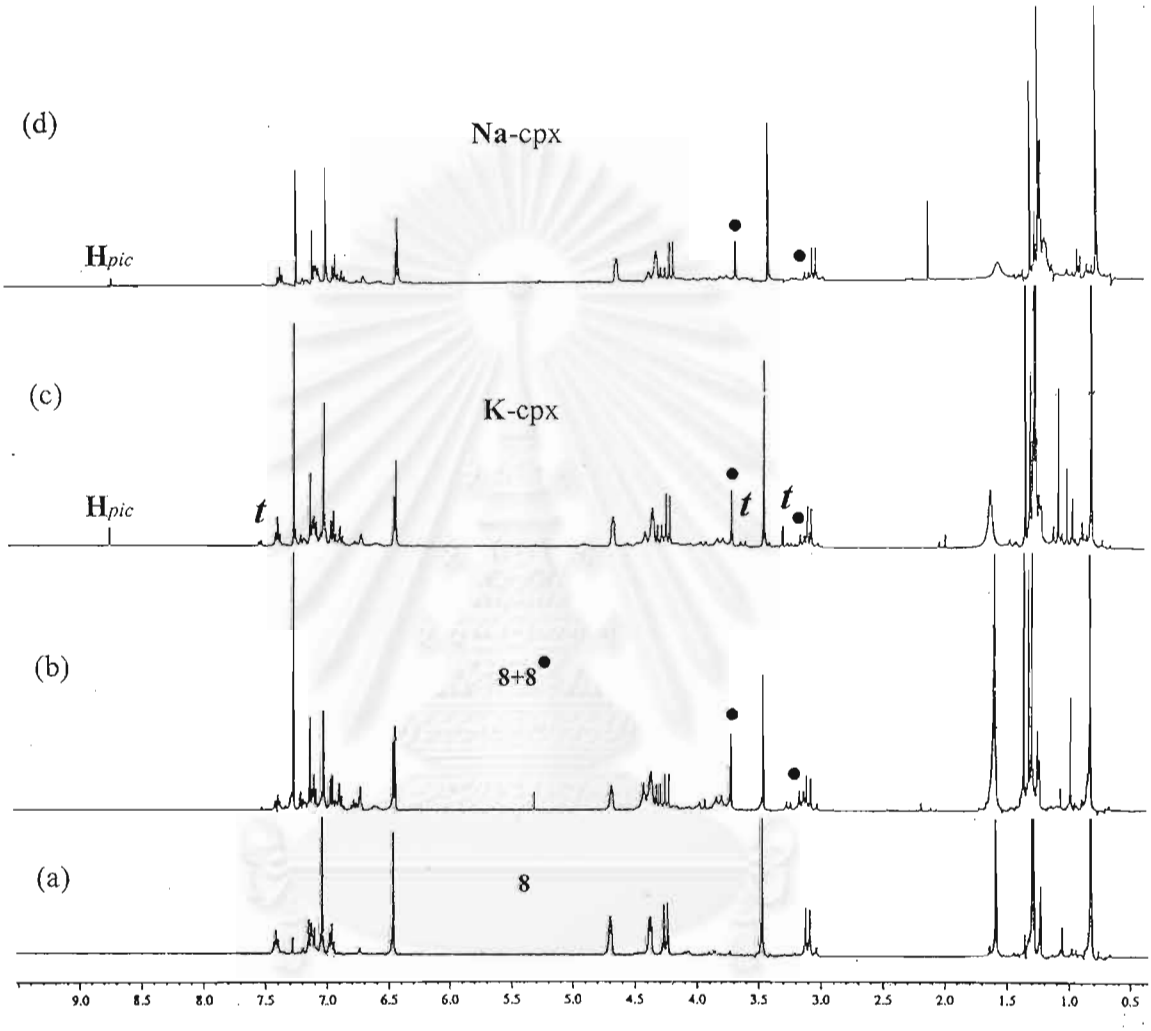


Figure3.11 The ^{1}H-NMR (400 MHz) spectra of ligand **8** (*t* and denote *trans*-isomer and other conformer, respectively) (a) a fresh sample of **8** containing mostly *cis* -isomer
(b) the irradiated **8** showing *cis*-isomer and another conformer at PSS
(c) standing **8** days after an addition of K^+ picrates
(d) standing **8** days after an addition of Na^+ picrates

Figures 11(b) and 11(d) show that, upon addition of Na^+, the spectrum of **8** does not change significantly. These evidences suggest that before isomerization **8** may exist in a *cis*-form. Surprisingly, doublet signal at 7.55 ppm and singlet peak at 3.33 ppm were

occurred upon the addition of potassium picrates into the solution of ligand **8** only 2 days. We assumed that K^+ ion induced some of the *cis*-form into *trans*-form. The complex between *trans*-form and K^+ may not be stable so the reversible process may be occurred to give the complex of *cis*-form.

3.6 UV Visible analysis

UV-Vis spectra of ligands **5** and **8** before and after irradiation in chloroform are depicted in Figure 3.12. The molar absorptivity at various wavelengths of ligands **5** and **8** are presented in Table 3.7.

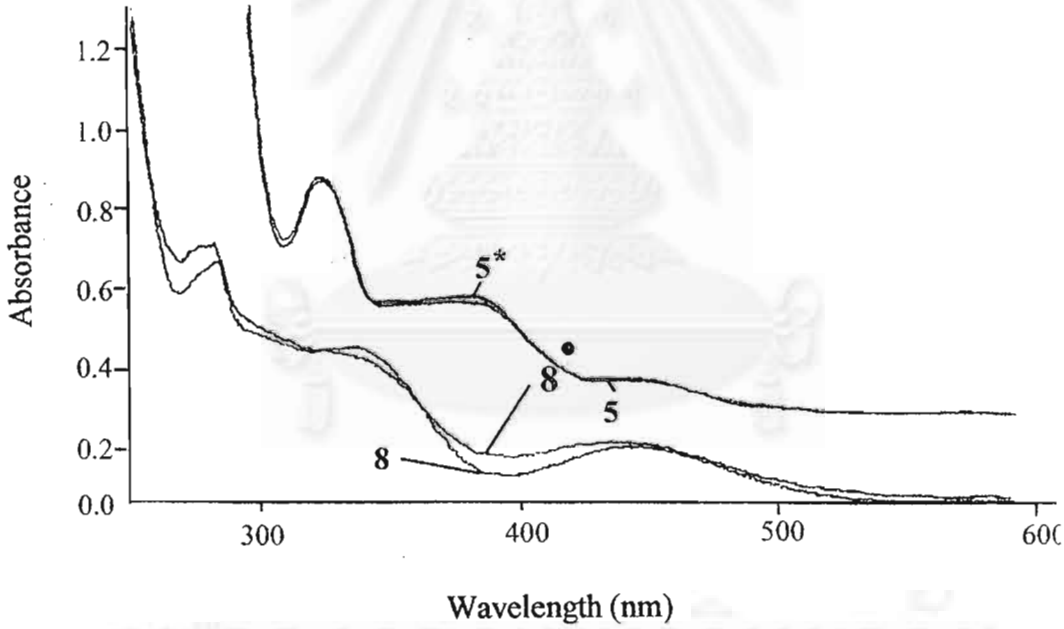


Figure 3.12 The UV-Vis spectra of ligand **5** and **8** both before and after irradiation

Table 3.7 The molar absorptivity at various wavelengths of ligands **5** and **8**

Ligand	$\lambda^{a}_{\pi\text{-}\pi^*}$ (nm) $\varepsilon_{\pi\text{-}\pi^*}$(L.mol^{-1}cm^{-1})	$\lambda^{a}_{n\text{-}\pi^*}$(nm) $\varepsilon_{n\text{-}\pi^*}$(L.mol^{-1}cm^{-1})	$\lambda^{b}_{\pi\text{-}\pi^*}$(nm) $\varepsilon_{\pi\text{-}\pi^*}$(L.mol^{-1}cm^{-1})	$\lambda^{b}_{n\text{-}\pi^*}$(nm) $\varepsilon_{n\text{-}\pi^*}$(L.mol^{-1}cm^{-1})
5	346 21496	426 7156	350 22999	420 8434
8	334 28184	442 11318	334 28745	440 14412

[a] Before irradiation, [b] After irradiation

The azobenzene chromophore contains two absorption bands, one in a UV region (π-π^* transition) with higher intensity and the other one in a visible region (n-π^* transition) with lower intensity[5, 8(b)]. Generally upon *trans*-to *cis*-isomerization, if the amount of *cis*-form occur distinctively more than that of *trans*-form, the molar absorptivity of n-π^* transition would increase because n-π^* transition of centro-symmetrical *trans*-isomer is forbidden. Moreover, the absorption band both at UV and visible regions of *cis*-form also shifted to short wavelength[5,8(b),20]. Before irradiation of **5**, the high intensity of absorption band appeared at 346 nm and the low intensity of absorption band appeared at 426 nm. Upon irradiation, the UV-Visible spectra of both **5** and **8** were not significantly altered. This results may be explained by two factors. First, the ratio of *cis* : *trans* is only 36 : 64 (from ^{1}H-NMR result) which the amount of *cis*-isomer is not so much to influence on the alteration of the intensity of absorption bands in the visible and UV regions. Second, the *trans*- isomer was not planar and the lack of center of symmetry due to the geometrical constraint of the calixarene platform. The distorted planar geometry of *trans*-**5** thus gives the similar UV-Vis spectrum to *cis*-**5** in both the molar absorptivity and the absorption wavelength. The UV-Vis analysis is therefore not suitable to characterize of the isomerization.

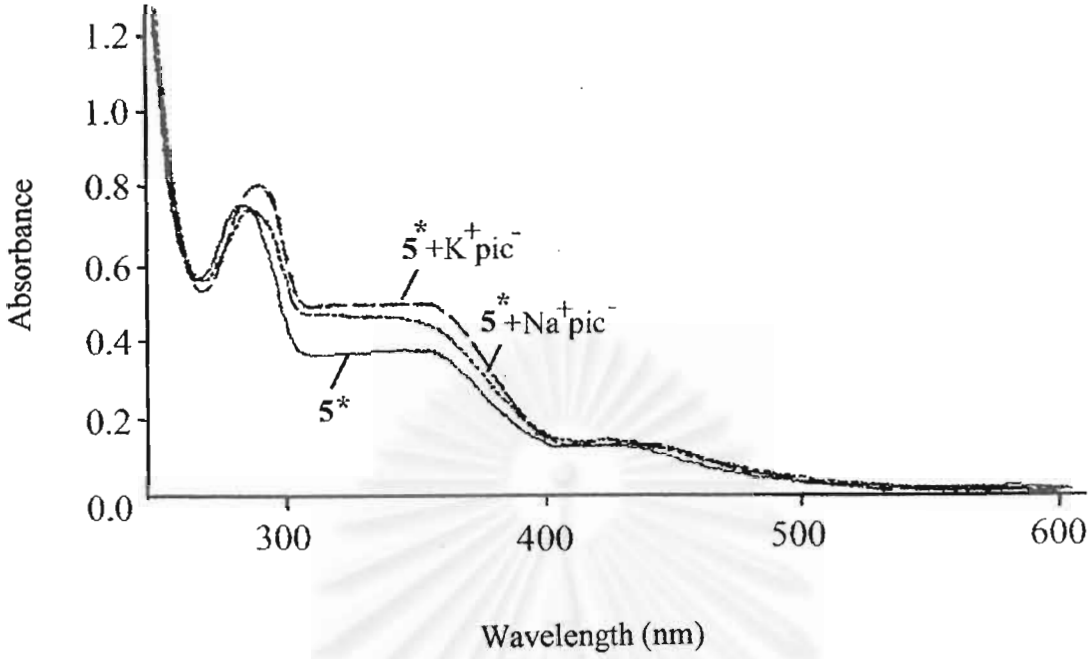


Figure 3.13 The UV-Vis spectra between the ligand **5** with Na^+ and K^+ions

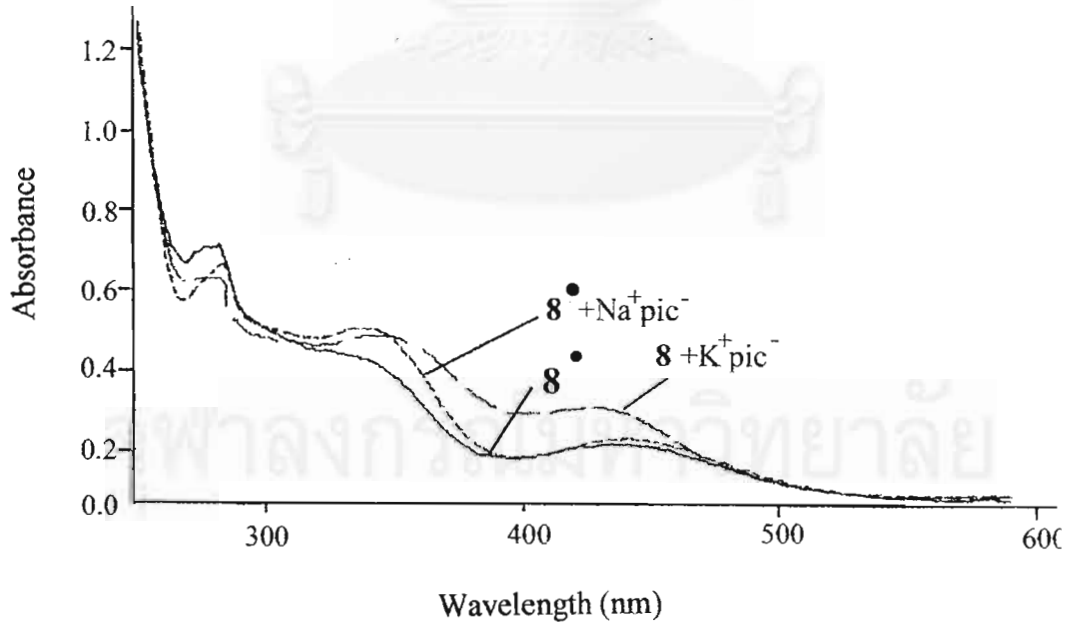


Figure 3.14 The UV-Vis spectra between the ligand **8** with Na^+ and K^+ions

Table 3.8 The molar absorptivity at various wavelengths of the complexes of **5** and **8**

Ligand	$\lambda^{e}_{\pi-\pi^*}$ $\varepsilon_{\pi-\pi^*}$	$\lambda^{e}_{n-\pi^*}$ $\varepsilon_{n-\pi^*}$	$\lambda^{f}_{\pi-\pi^*}$ $\varepsilon_{\pi-\pi^*}$	$\lambda^{f}_{n-\pi^*}$ $\varepsilon_{n-\pi^*}$
5	346 32276	420 13597	346 34499	430 10517
8	336 29803	438 11842	344 38932	426 16288

[e] in the presence of Na^+

[f] in the presence of K^+

CHAPTER IV

CONCLUSION

The ligands, azobenzene crown ether *p-tert*-butyl calix[4]arenes, **5** and **8**, have been synthesized in two pathways. The first pathway, the ligands **5** and **8** were prepared from alkylation of di-hidroxy groups on *p-tert*-butylcalix[4]arenes, **3** and **6**, respectively using 2-(2-bromoethoxy nitrobenzene), **1**, to give bis-nitrophenoxy crown *p-tert*-butylcalix[4]arene products, **4** and **7**, respectively. A reductive coupling of nitrobenzene product was then utilized to give the desired products, **5** (8 %) and **8** (12%). The other method, a reductive coupling of 2-(2hydroxoethoxy)nitrobenzene, **9** was carried out to afford ethoxy azobenzene, **10** and then it was converted to mesylate, **11** and attached to calix[4]arenes to give the required products, **5** and **8** in 5% and 8 %, respectively.

Compounds **7** and **8** showed interesting conformational behaviors. Due to the absence of intramolecular hydrogen bonding, the calix[4]arene unit in **7** was found to have a coalescence structure between cone and partial cone conformation in the solution ($CDCl_3$). Compound **8** which is a product from a reductive coupling reaction of **7** was formed to possess cone conformation of calix[4]arene. However, upon exposure to light the azobenzene unit in **8** underwent isomerization. This reduced the rigidity of the structure, caused the conformational interconversion to occur and resulted in a various conformation of calix[4]arene.

Compound **5** showed interesting photo-switchable properties. It was found to undergo a *trans*- to *cis*-isomerization of the azobenzene unit upon exposure to the UV-light and standing in the day light. The photostationary state of *cis*:*trans* ratios are calculated to be 36:64 when exposing **5** to the UV light and 33:67 under the day light. In the presence of Na^+, the amount of the *cis*-isomer increased and the *cis*:*trans* ratio changed to 44:56. This suggests that Na^+ induced the *trans*- to *cis*- isomerization or it may imply the *cis*-form is suitable to bind Na^+. However, **5** was found to give a complex isomerization process in the presence of K^+. During the first 5 days, the *trans*-form of **5** increased dramatically. Nevertheless, the *trans*-form gradually decreased and the *cis*-form subsequently increased. The *cis*:*trans* ratio is about 42:58. We proposed the K^+ first induced the *trans*-isomer to occur and it then underwent the *trans*- to *cis*-isomerization. The *cis*-form may be a thermodynamic product in this isomerization process. Besides

alkali ions, CH_3CN was able to be included in the calix[4]arene framework of **5** and caused the ^1H NMR signals to shift significantly.

Eventhough, the crystal structure of **8** has not been determined due to the loss of solvents of crystallization during the measurement. Evidences from ^1H NMR studies suggested the **8** existed in a solution as a *cis*-form before the isomerization taking place. The presence of K^+ in a solution of **8** also induced the occurrence of the *trans*-isomer. It can thus be concluded the Na^+ is suitable to form a complex with the *cis*-form of **5** and **8** while K^+ is appropriate for the *trans*-forms. The complexation properties of **5** and **8** suggests the both of them can be used as switchable-sensor of Na^+ and K^+ ions.

The suggestion for further works

The future works should be focused on

1. Synthesis another azobenzene derivatives crown ether calix[4]arene such as *m*-, *p*-subsituted azobenzene.

2. The alkali metal complexes of both ligands **5** and **8** should be separated and characterized by ESI-MS, single crystal X-ray crystallography and elemental analysis.

3. The crystal structure of **8** must be determined.

4. Complexation study of the synthesized ligands with alkali-earth cation such as Mg^{2+}, Ca^{2+} ions.

5. Rate constant for thermal isomerization should be studied.

6. Solvant extraction studies of these ligands with various alkali cation.

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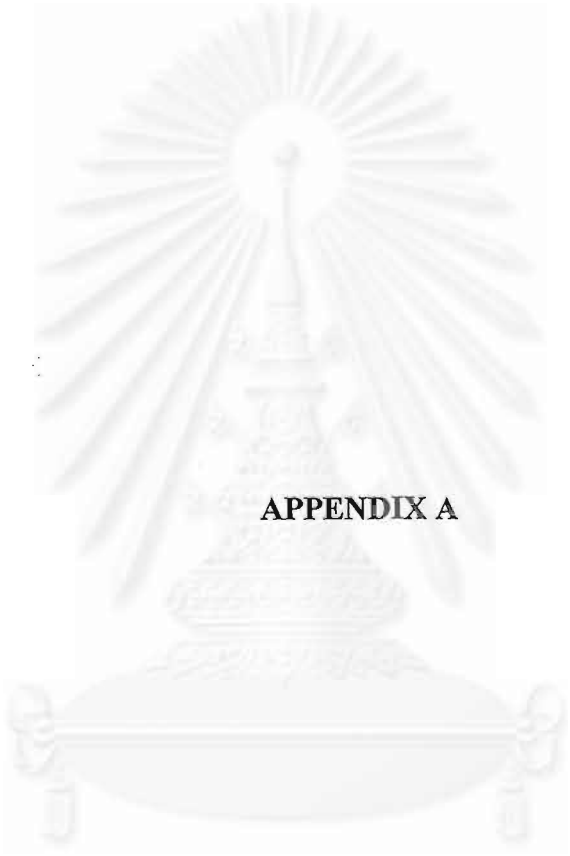


APPENDIX A

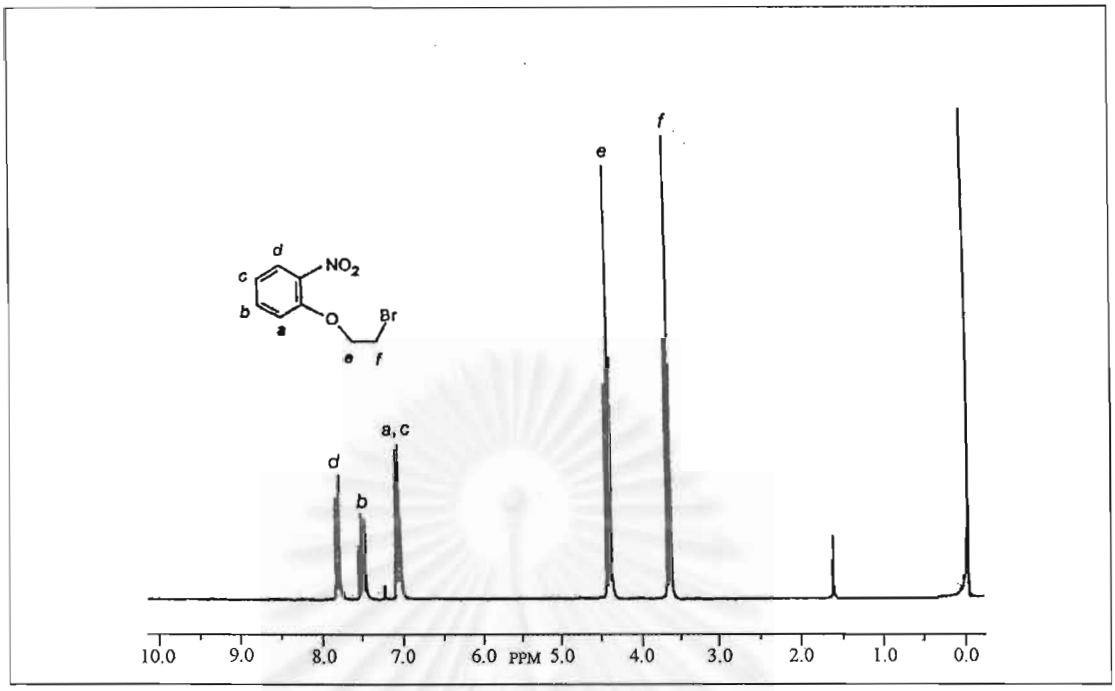


Figure A.1 The ^{1}H-NMR spectrum of 2-(2-bromoethoxy)nitrobenzene, **1**

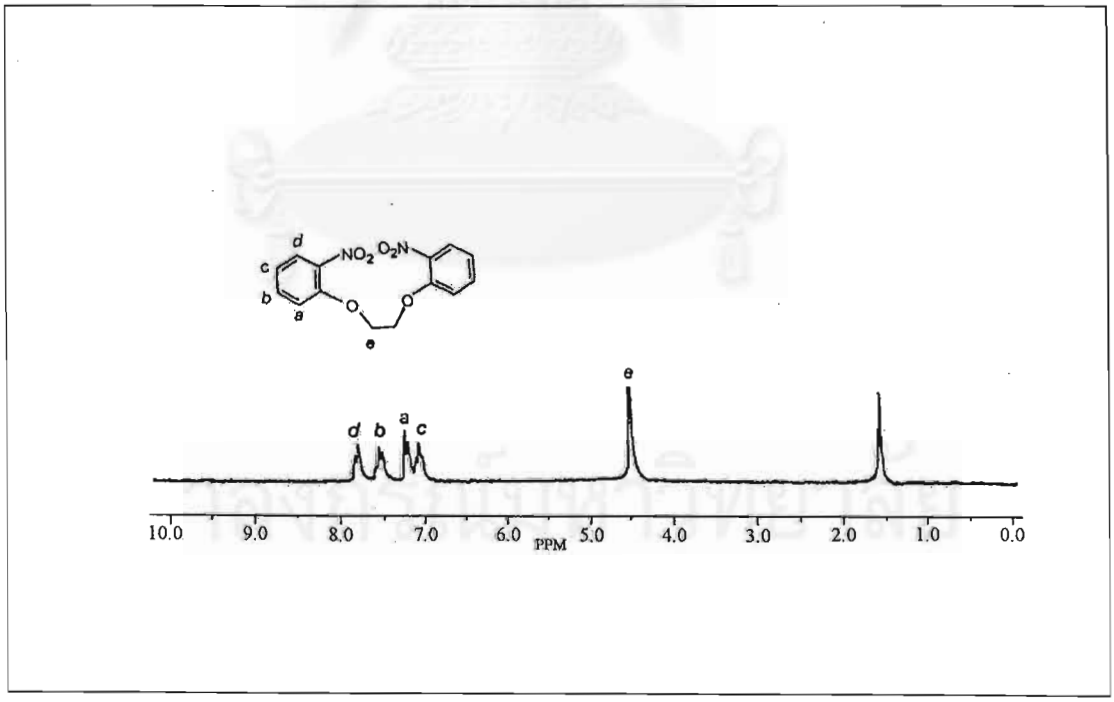


Figure A.2 The ^{1}H-NMR spectrum of 1,2-dinitrophenoxyethane, **2**

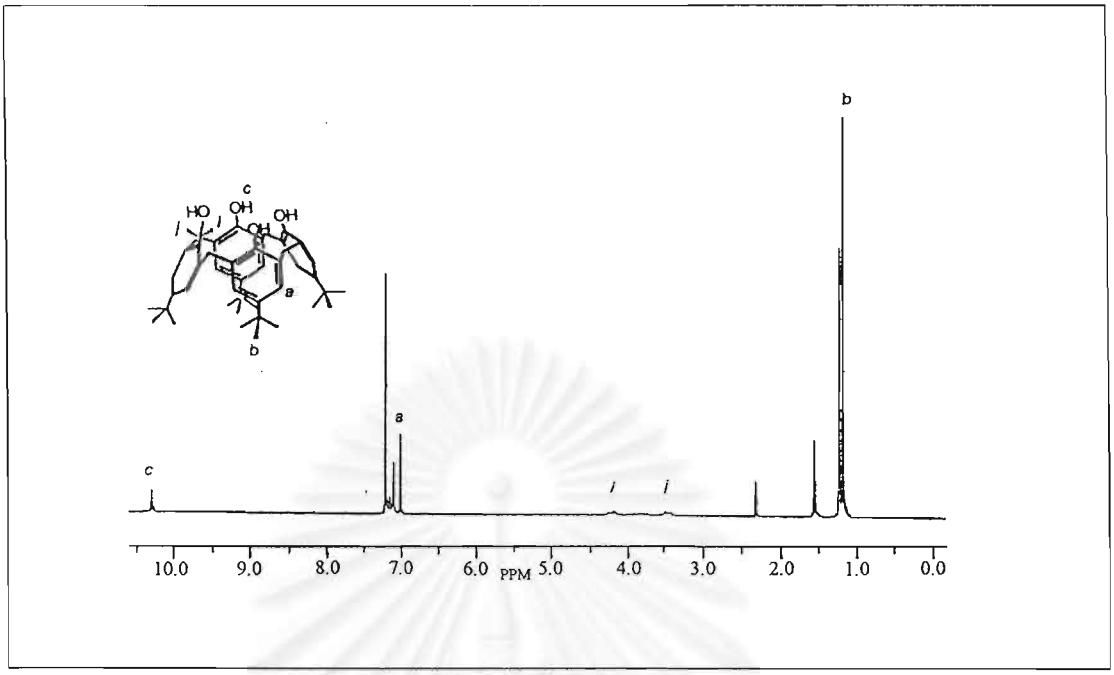


Figure A.3 The ^{1}H-NMR spectrum of *p-tert*-calix[4]arene, **3**

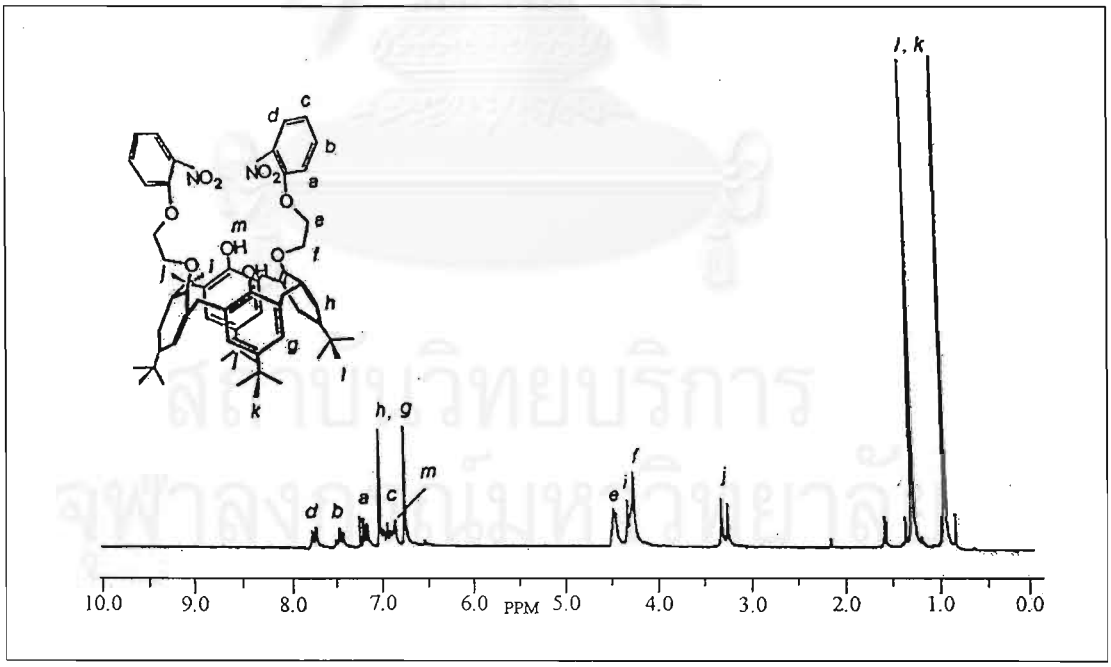


Figure A.4 The ^{1}H-NMR spectrum of 25, 27-bis-2-(2-nitropnenoxy)ethoxy-*p-tert*-butylcalix[4]arene, **4**

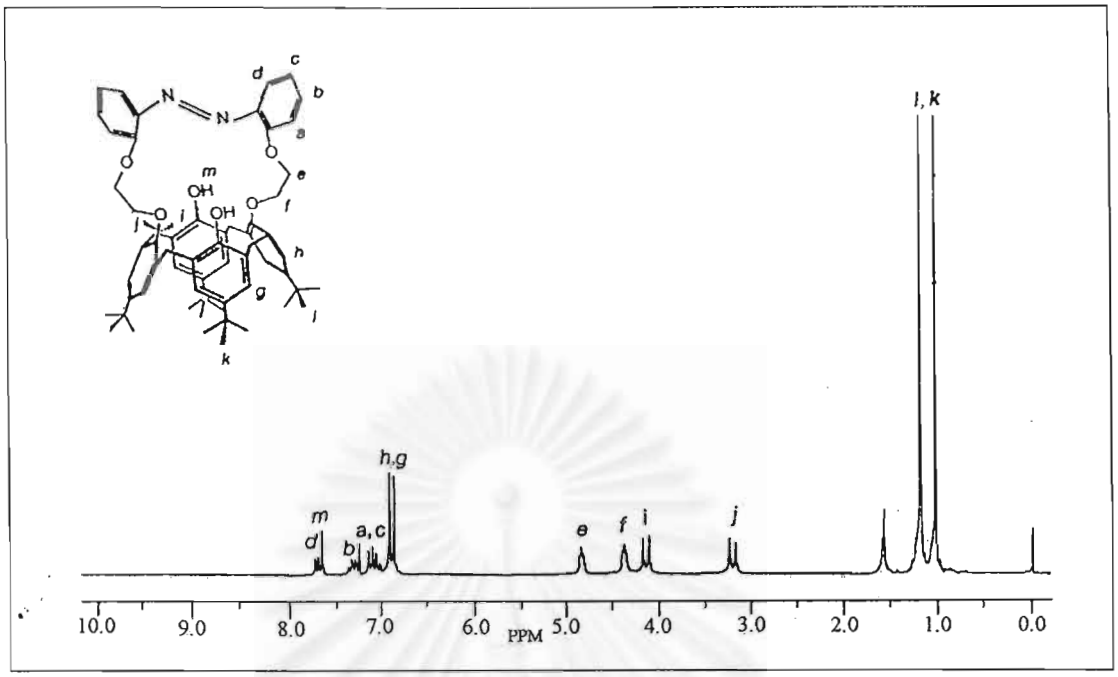


Figure A.5 The ^{1}H-NMR spectrum of azobenzene derivative of crown ether *p-tert*-butyl calix[4]arene, **5** (*trans*-isomer)

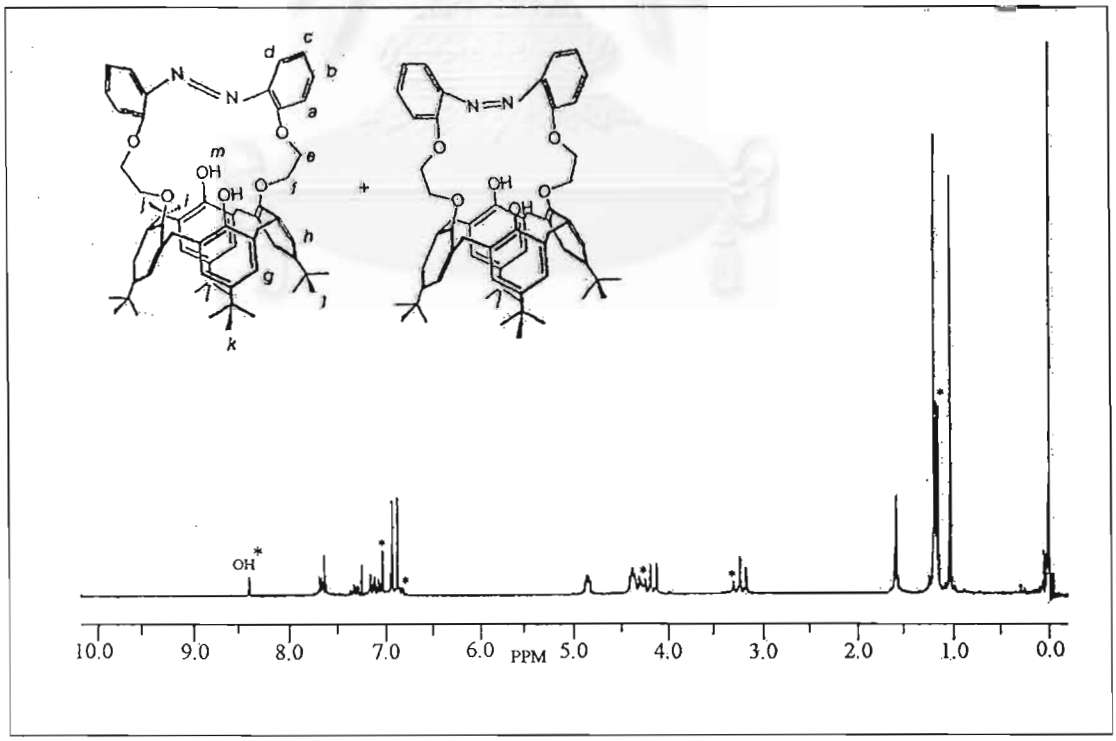


Figure A.5* The ^{1}H-NMR spectrum azobenzene derivative of crown ether *p-tert*-butyl calix[4]arene, **5** (*denotes *cis*-isomer)

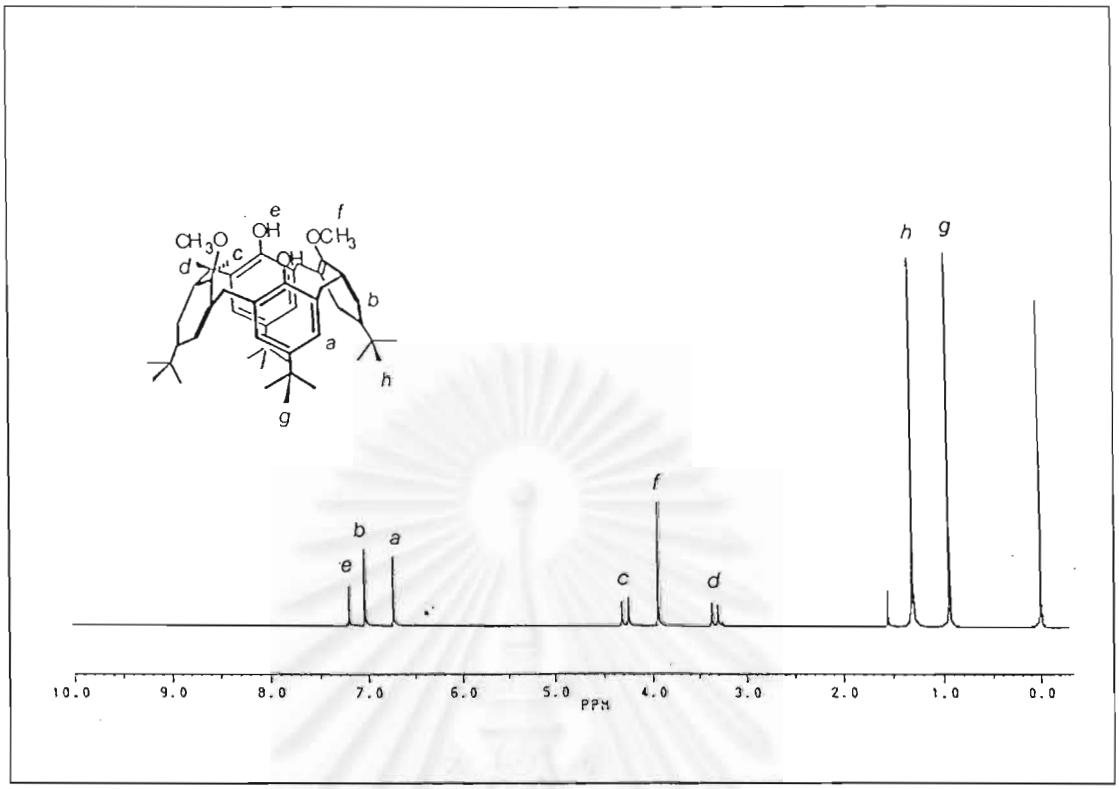


Figure A.6 The ^{1}H-NMR spectrum of 26, 28-dimethoxy-*p-tert*-butylcalix[4]arene, **6**

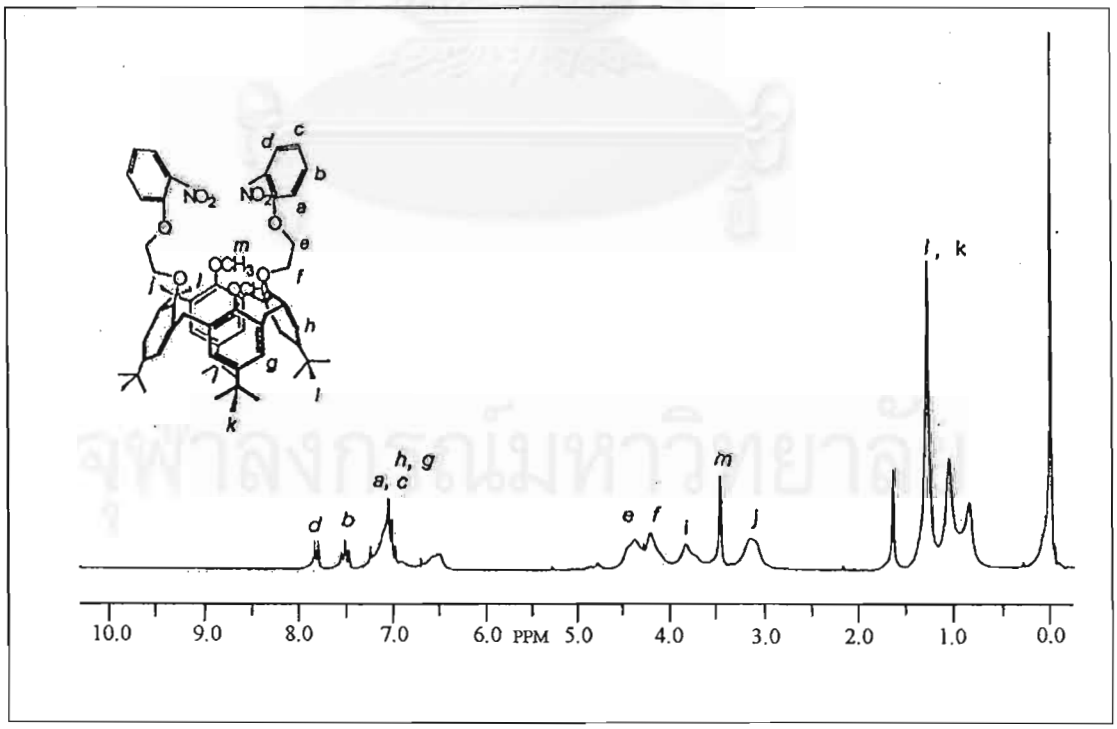


Figure A.7 The ^{1}H-NMR spectrum of 25, 27-bis-2-(2-nitrophenoxy)ethoxy-26, 28-dimethoxy-*p-tert*-butylcalix[4]arene, **7**

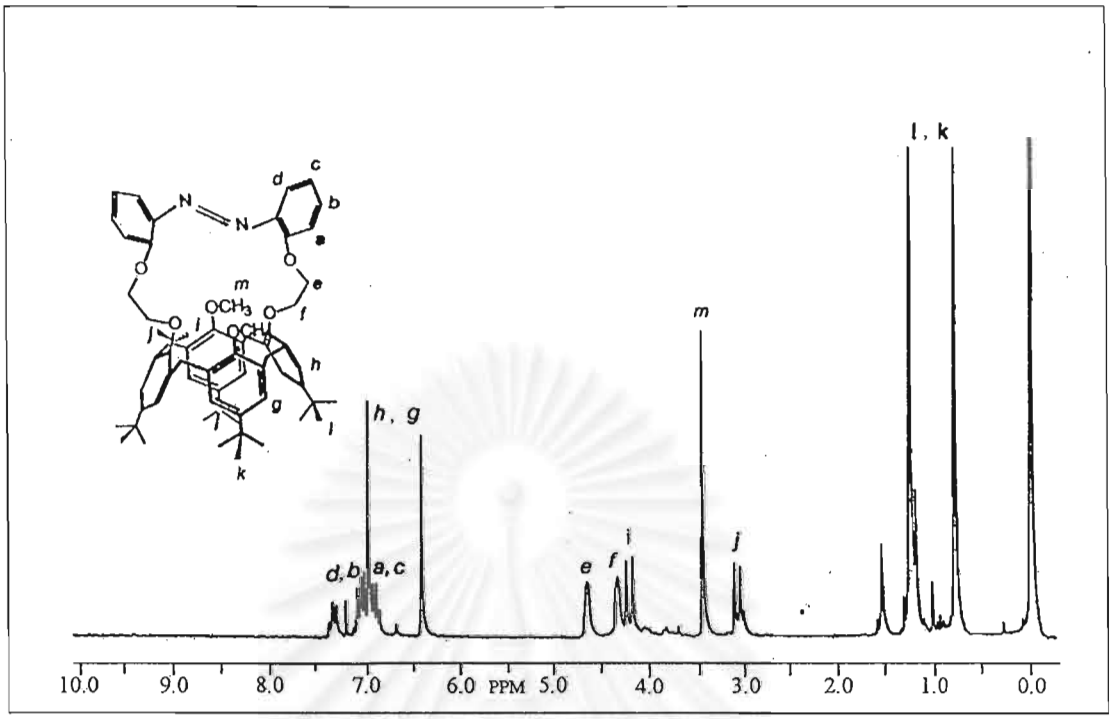


Figure A.8 The ^{1}H-NMR spectrum of azobenzene derivative of crown ether dimethoxy-*p-tert*-butylcalix[4]arene, **8**

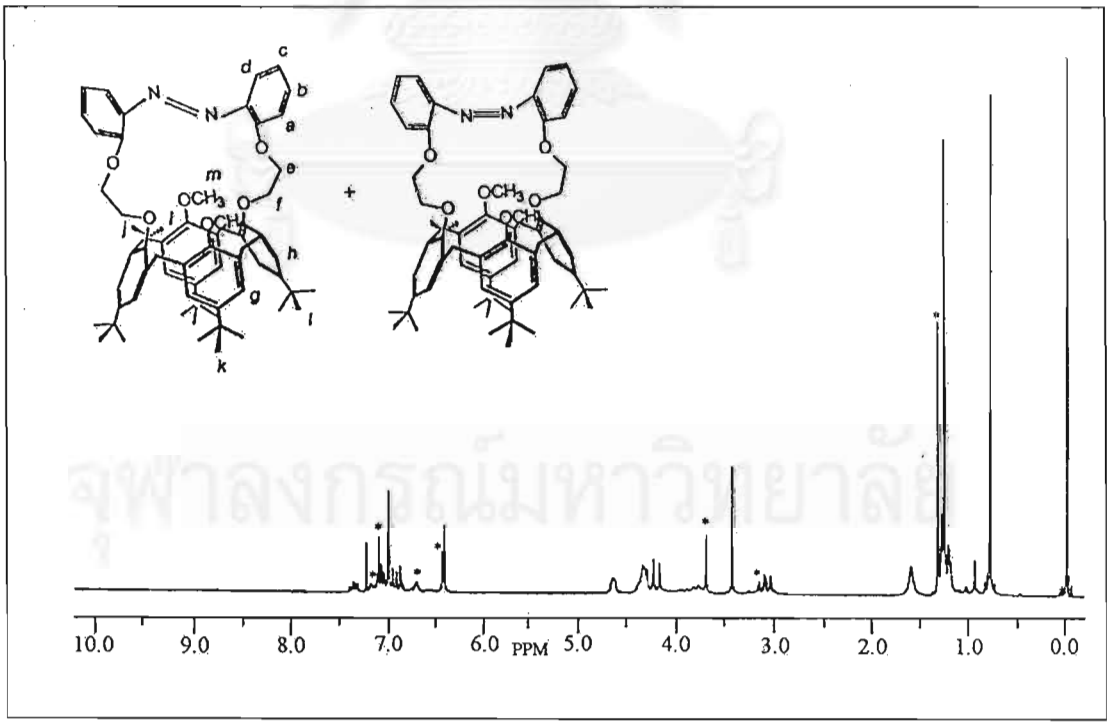


Figure A.8* The ^{1}H-NMR spectrum of azobenzene derivative of crown ether dimethoxy-*p-tert*-butylcalix[4]arene, **8** (* denotes another conformer)

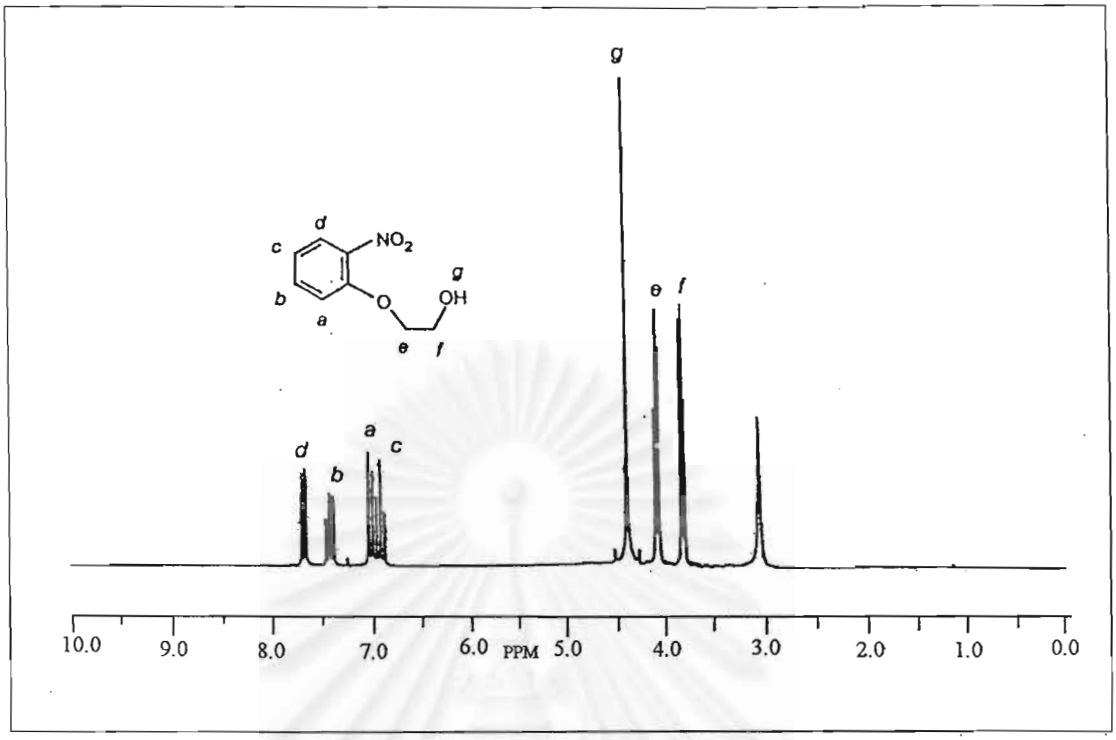


Figure A.9 The ^{1}H-NMR spectrum of 2-(2-hydroxoethoxy)nitrobenzene, **9**

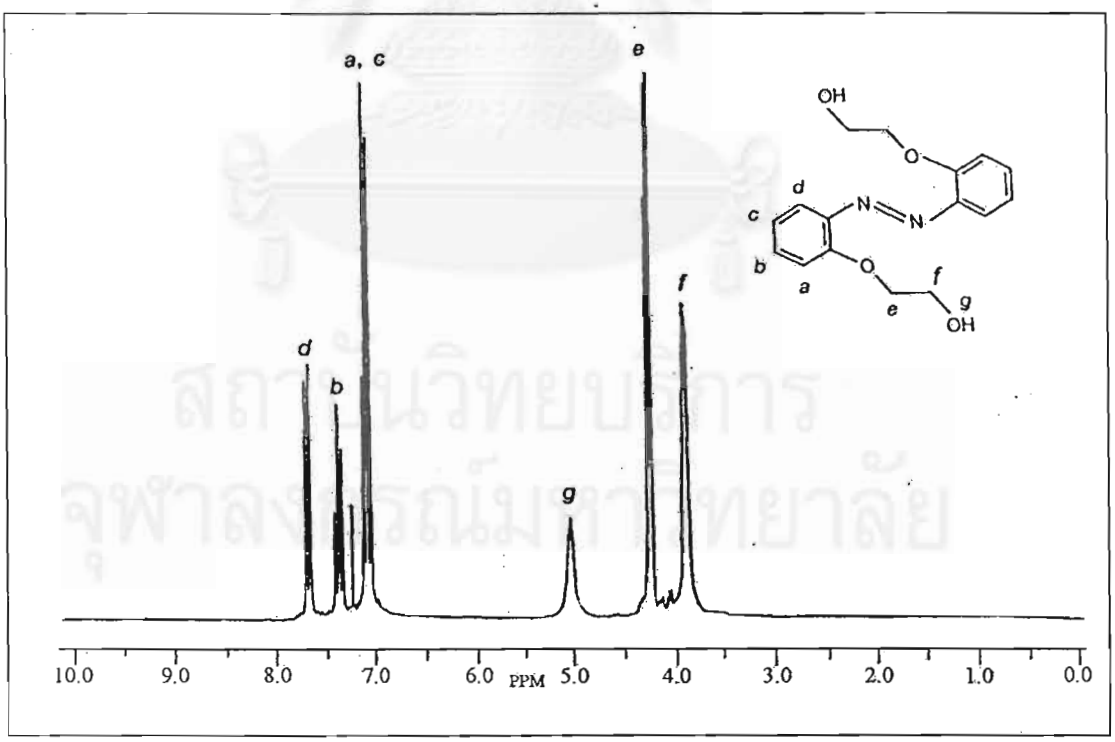


Figure A.10 The ^{1}H-NMR spectrum of bis-2-(2′-hydroxoethoxy)azobenzene, **10**

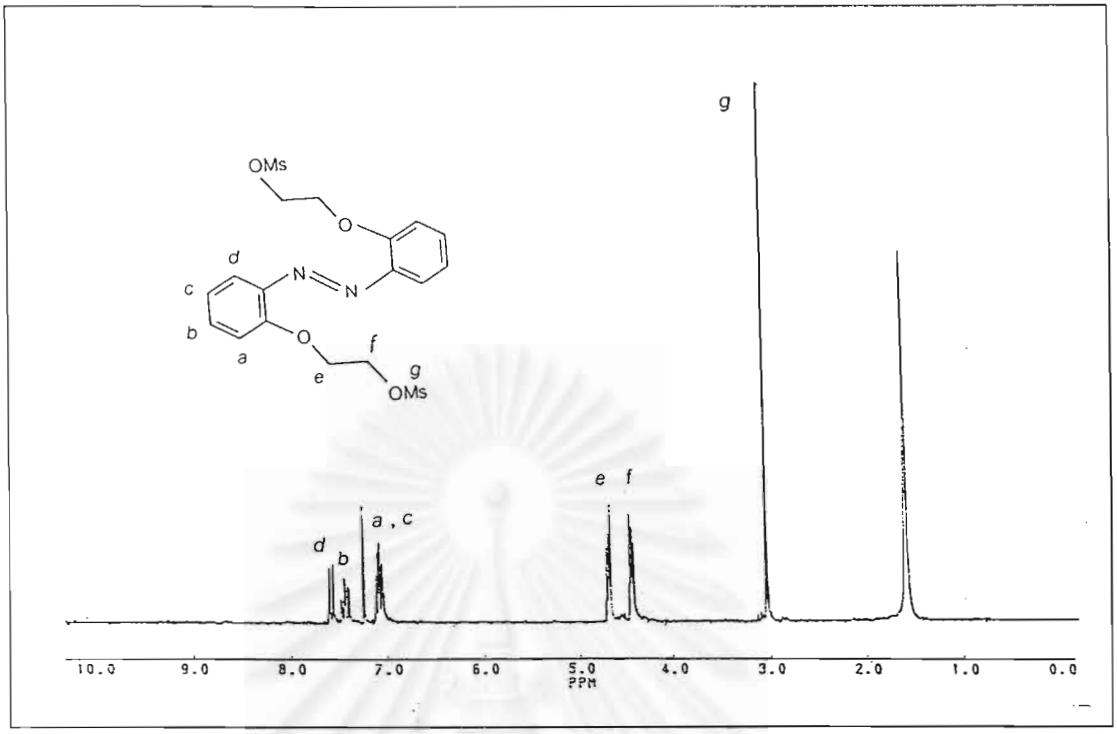


Figure A.11 The ^{1}H-NMR spectrum of bis-2-(2′-mesyloxyethoxy)azobenzene, **11**

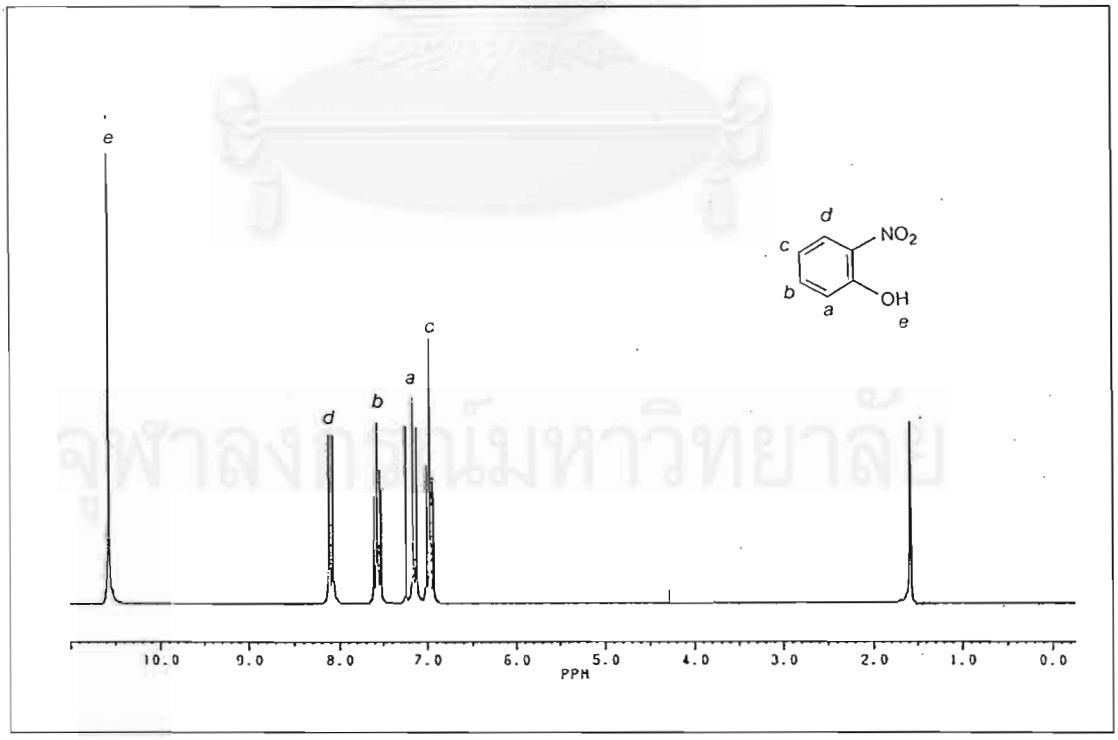


Figure A.12 The ^{1}H-NMR spectrum of *o*-nitrophenol

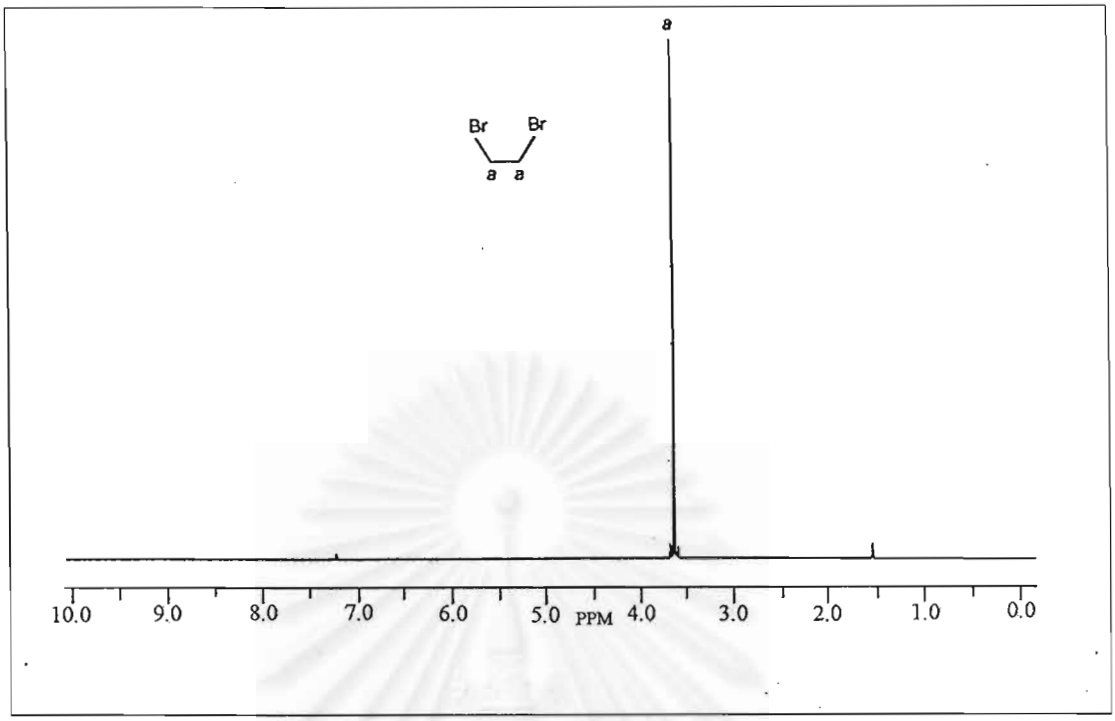


Figure A.13 The ^{1}H-NMR spectrum of 1,2-dibromoethane

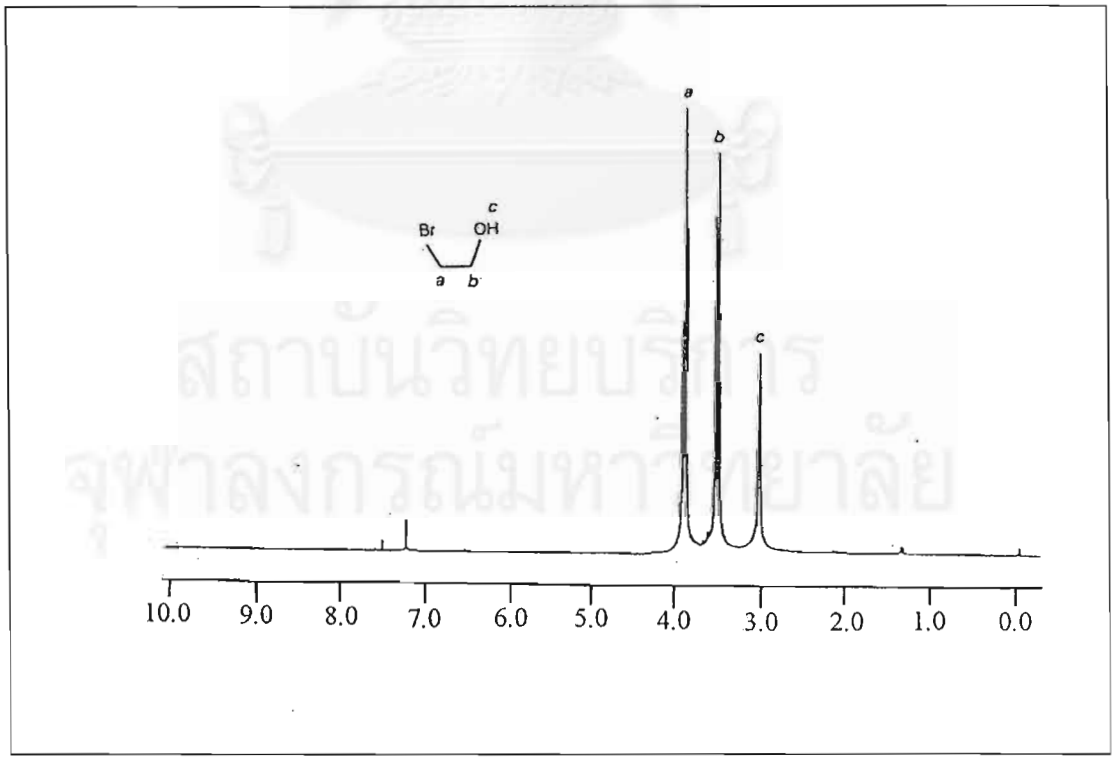


Figure A.14 The ^{1}H-NMR spectrum of 2-bromoethanol

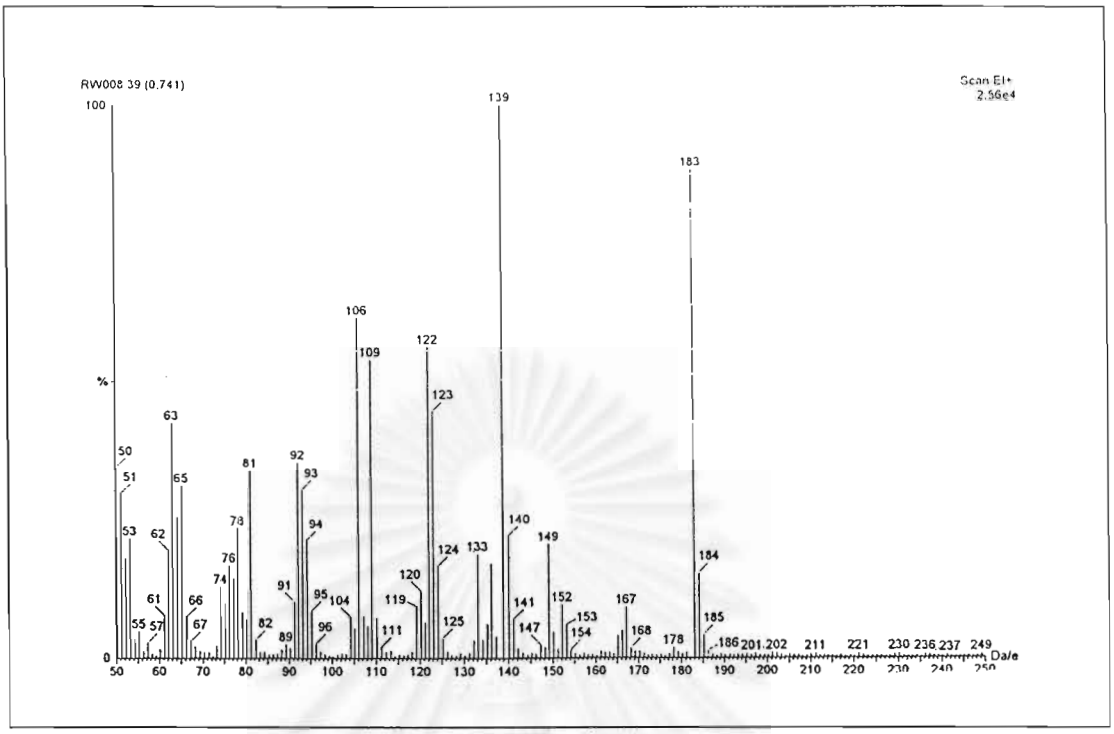


Figure A.15 The EI-MS spectrum of 2-(2-hydroxoethoxy)nitrobenzene, **9**

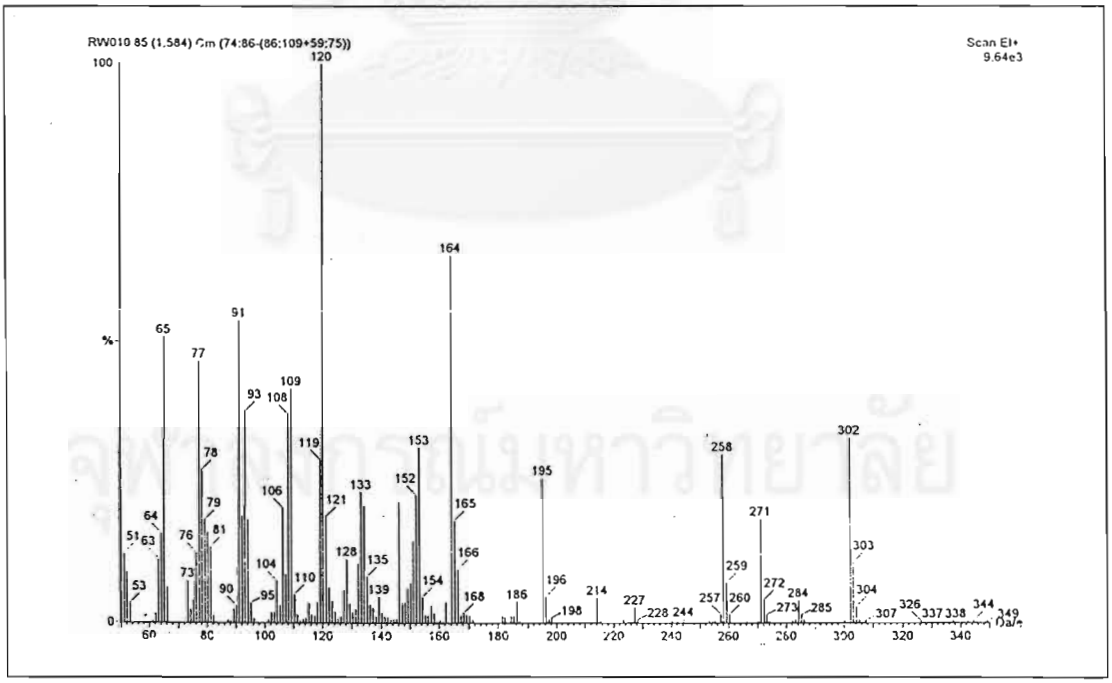


Figure A.16 The EI-MS spectrum of bis-2-(2-hydroxoethoxy)azobenzene, **10**

APPENDIX B

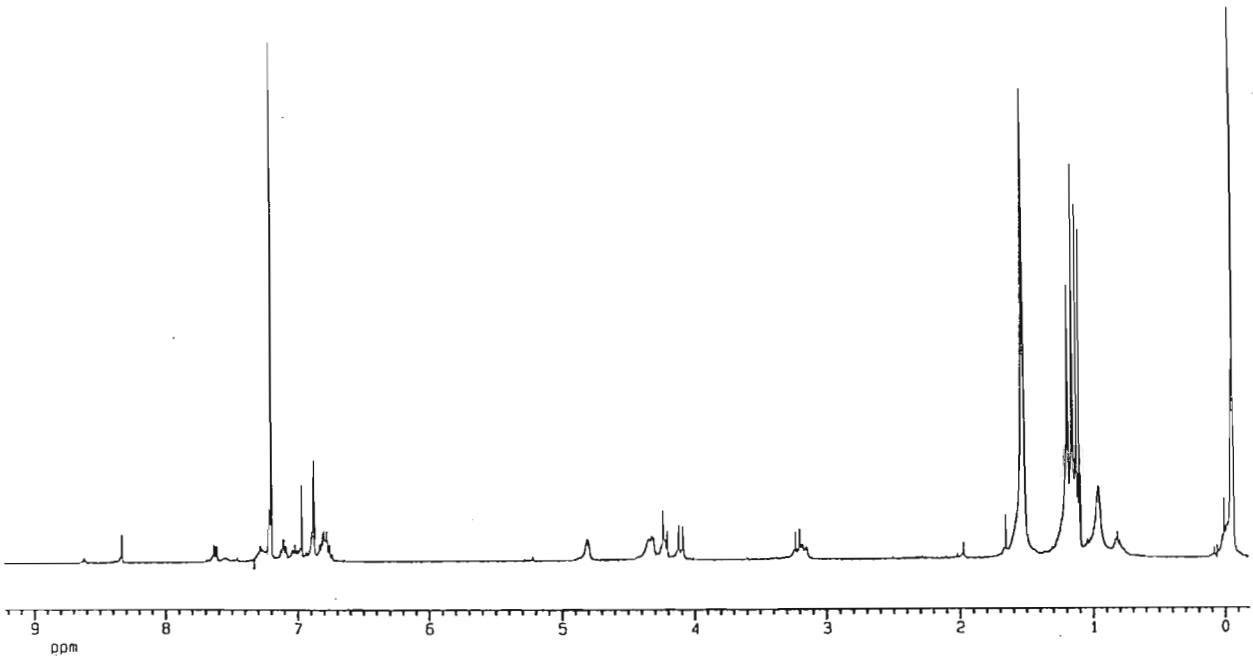


Figure B.1 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and sodium ion (standing for 2 days after an addition of sodium picrate)

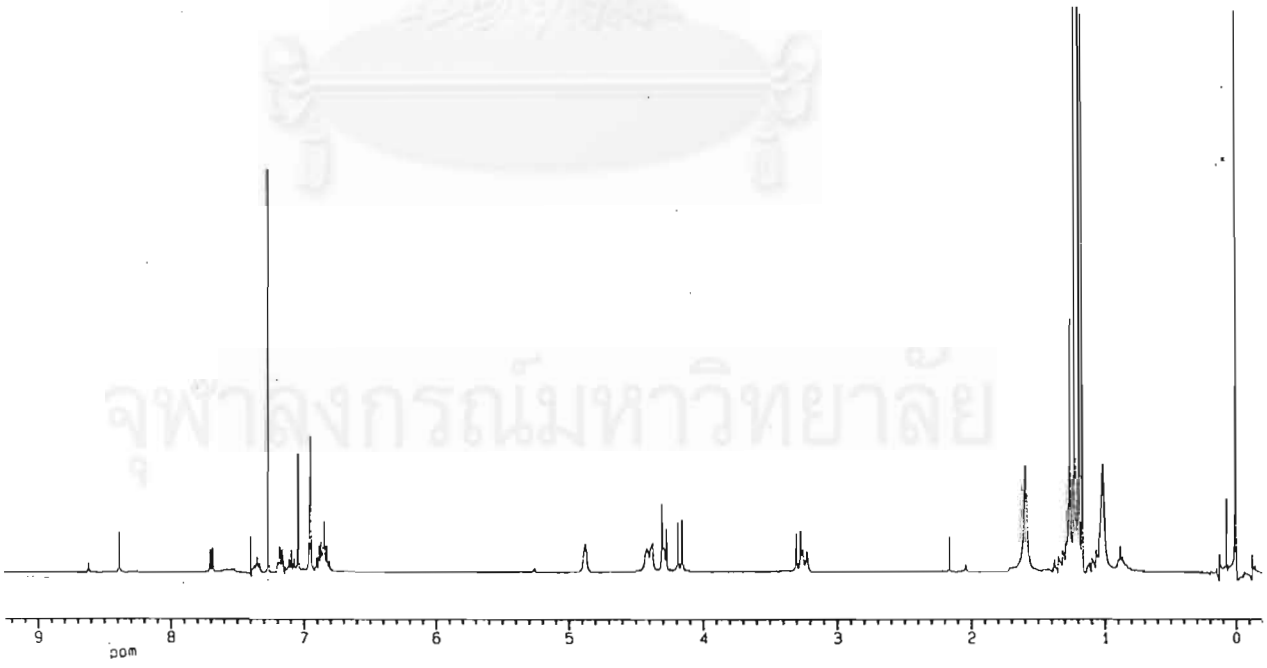


Figure B.2 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and sodium ion (standing for 5 days after an addition of sodium picrate)

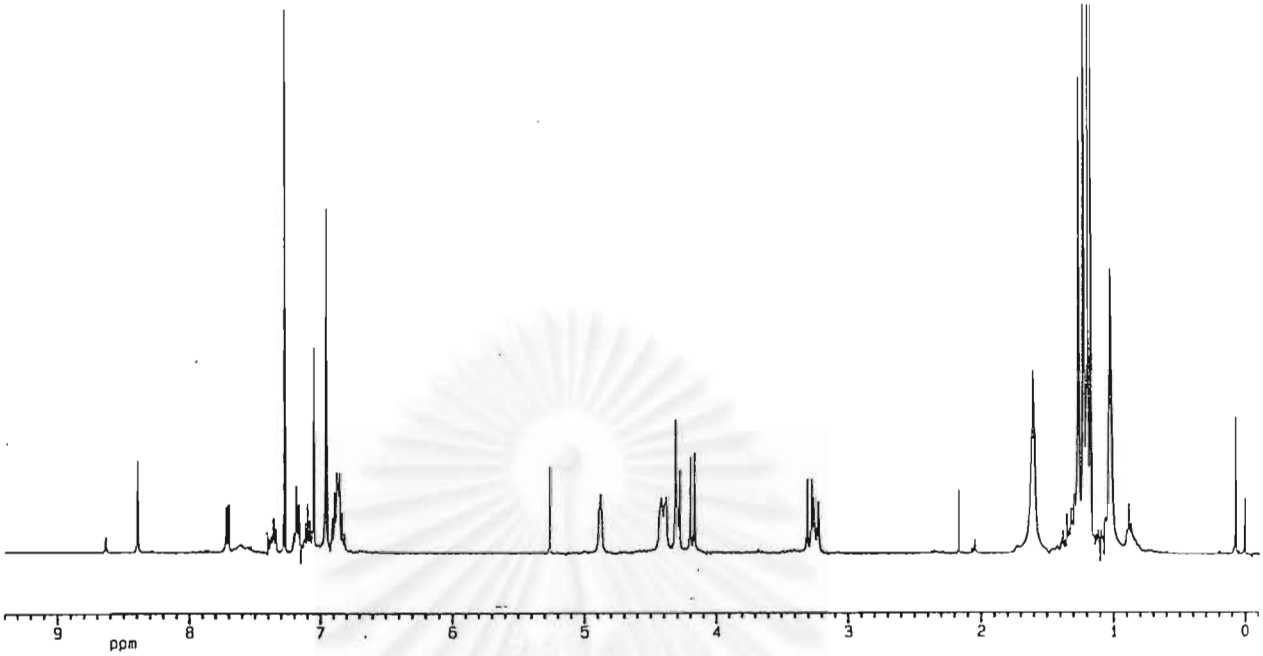


Figure B.3 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and sodium ion (standing for 12 days after an addition of sodium picrate)

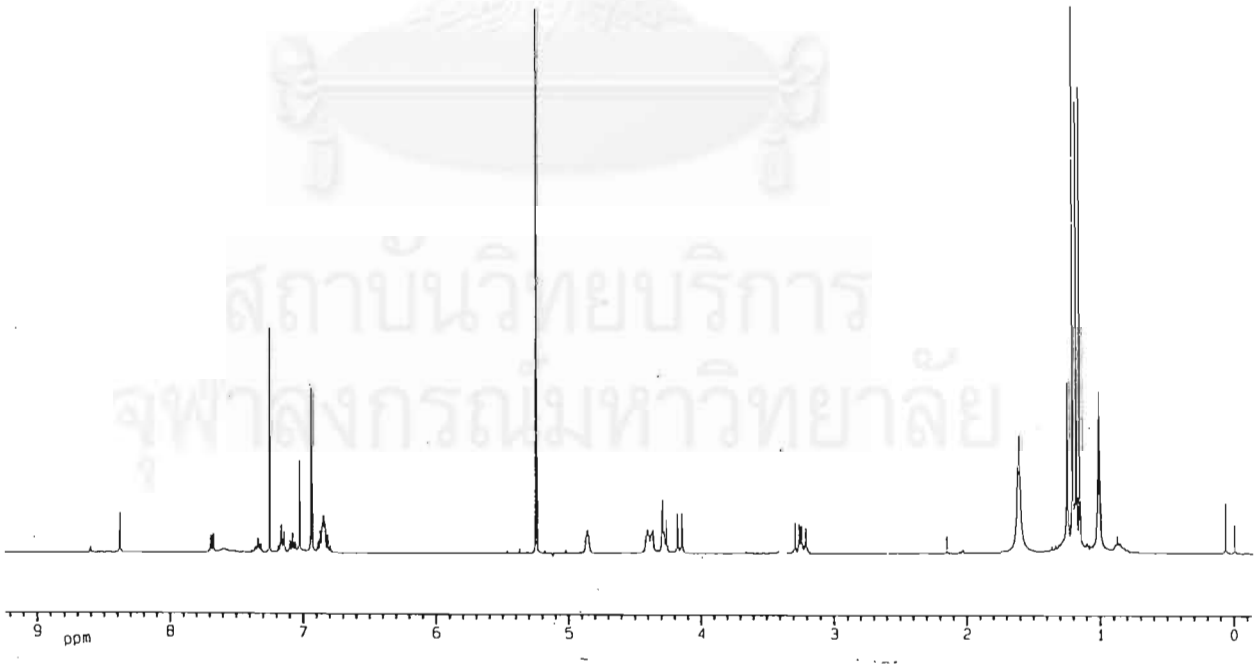


Figure B.4 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and sodium ion (standing for 19 days after an addition of sodium picrate)

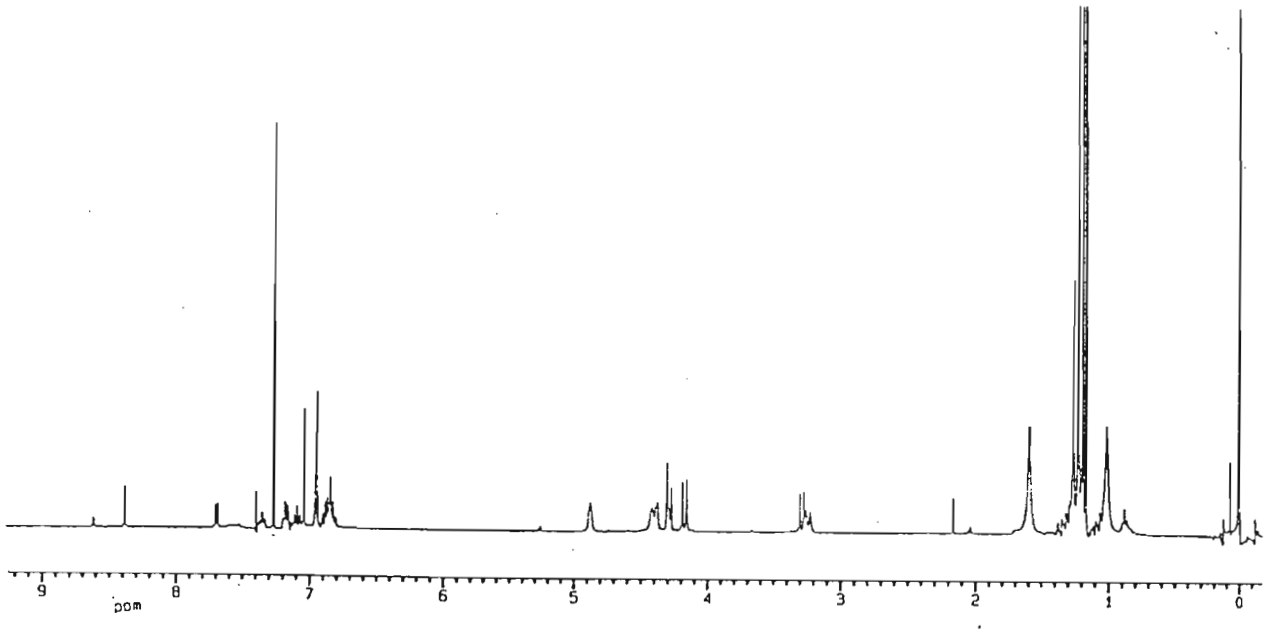


Figure B.5 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and sodium ion (standing for 30 days after an addition of sodium picrate)

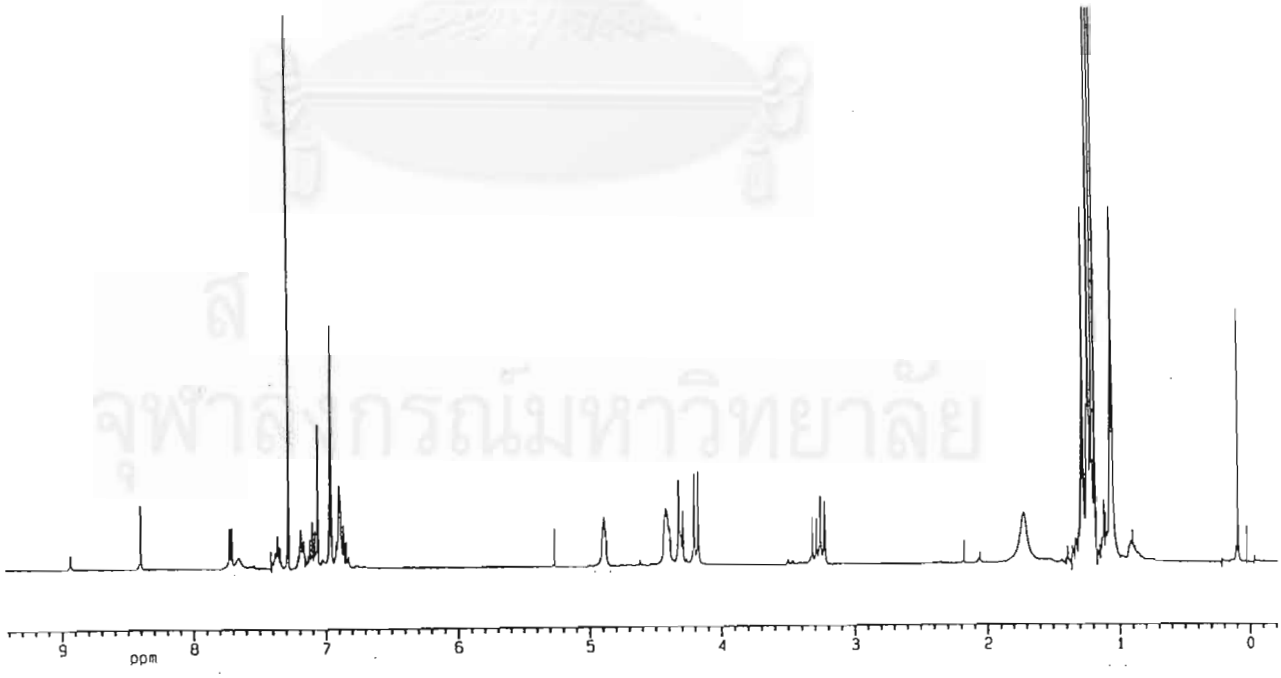


Figure B.6 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and potassium ion (standing for 2 days after an addition of potassium picrate)

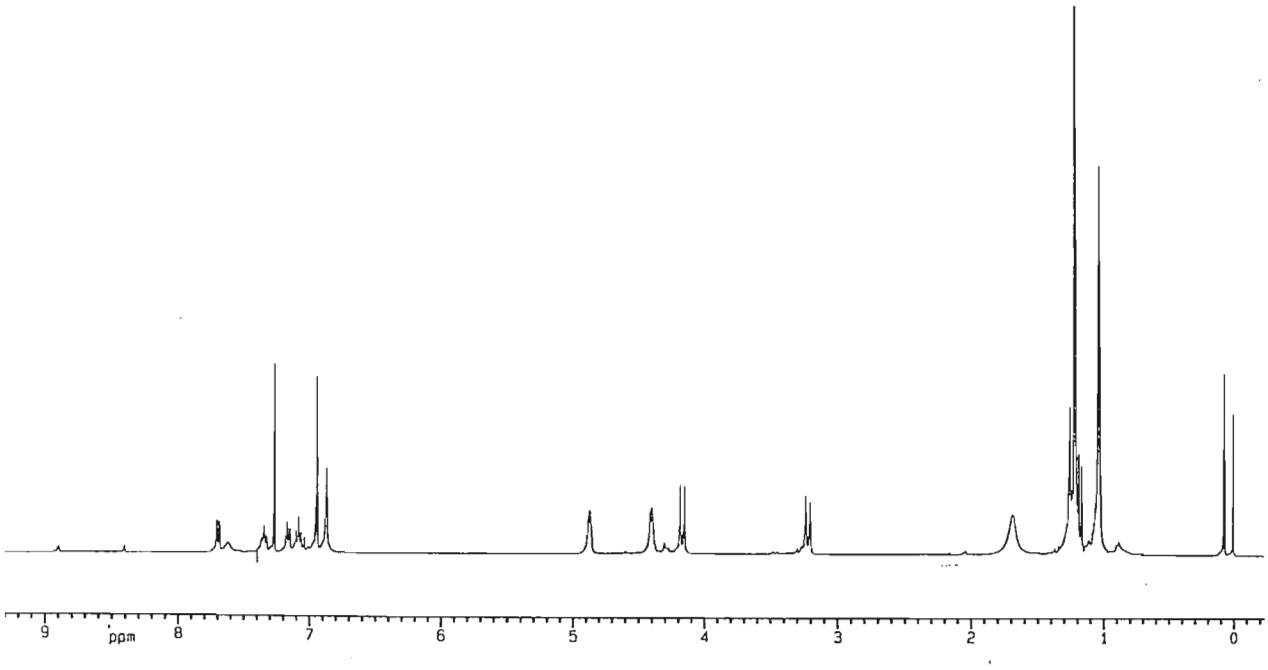


Figure B.7 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and potassium ion (standing for 5 days after an addition of potassium picrate)

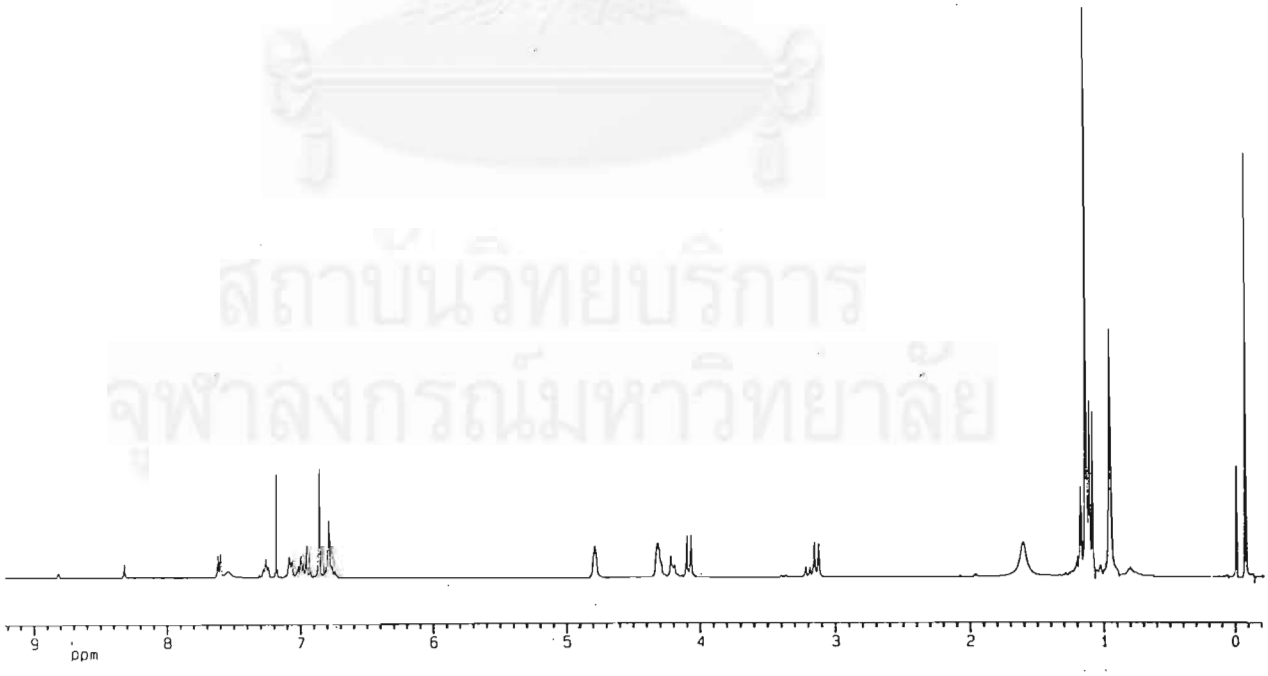


Figure B.8 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and potassium ion (standing for 12 days after an addition of potassium picrate)

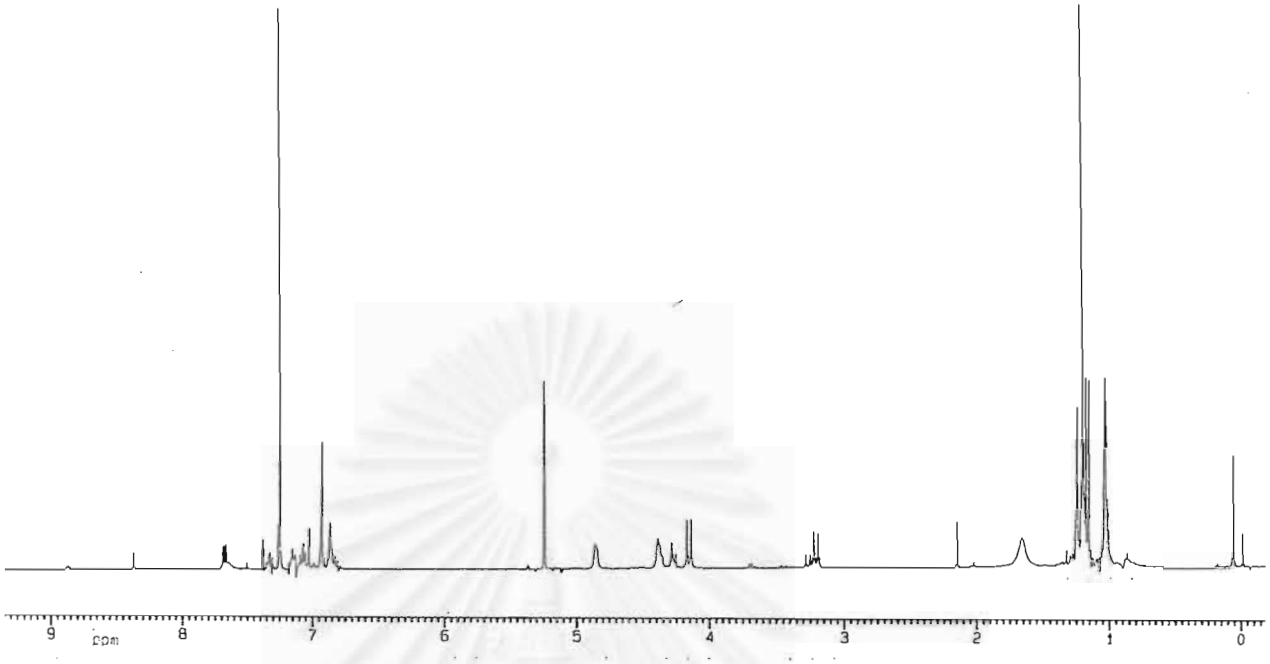


Figure B.9 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and potassium ion (standing for 19 days after an addition of potassium picrate)

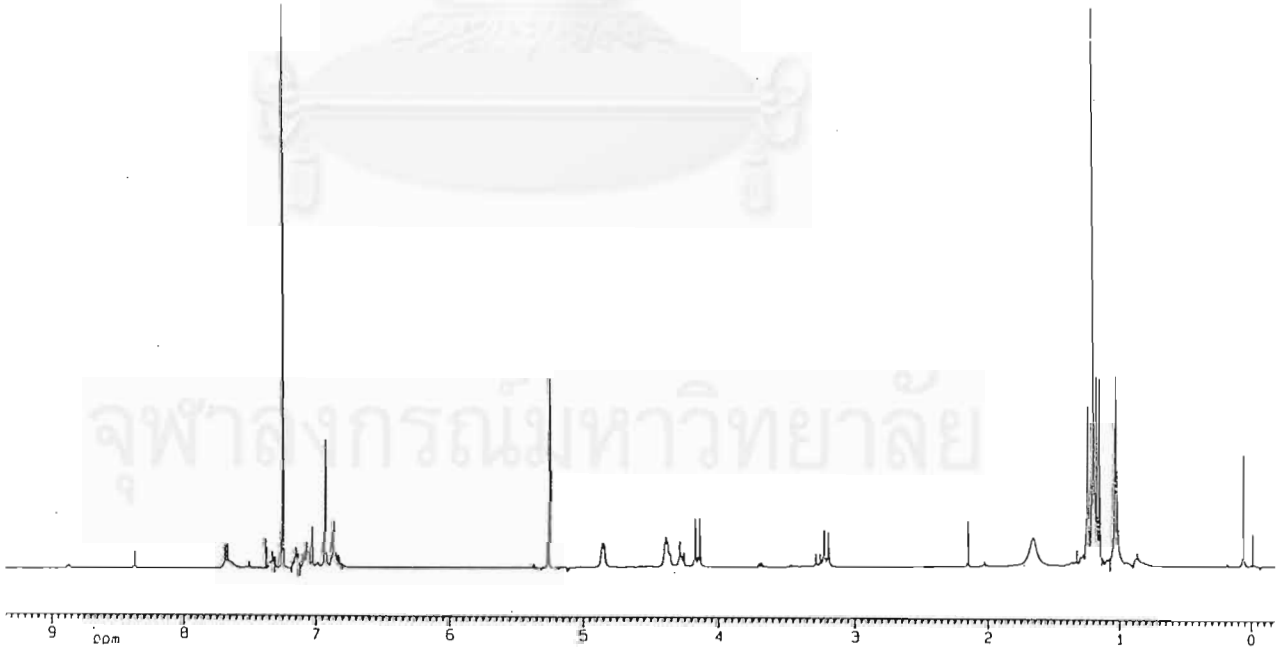


Figure B.10 The ^{1}H-NMR spectrum of the complex between the irradiated **5** and potassium ion (standing for 30 days after an addition of potassium picrate)

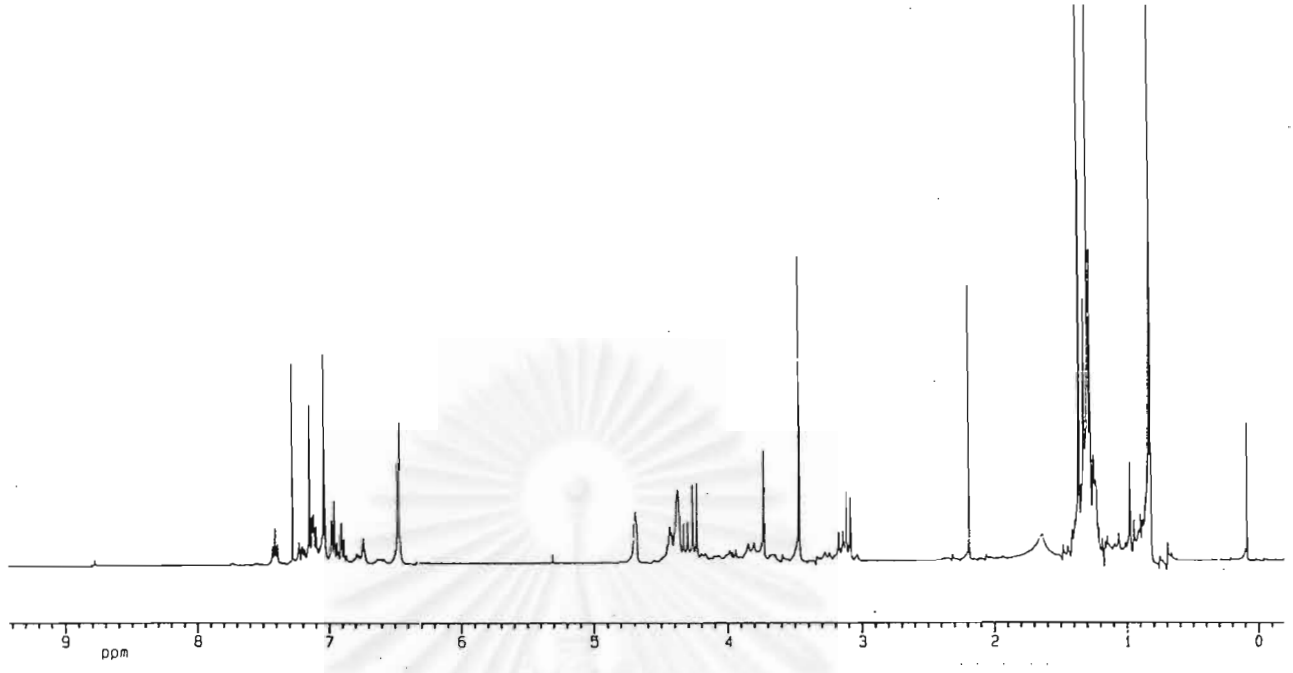


Figure B.11 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and sodium ion (standing for 2 days after an addition of sodium picrate)

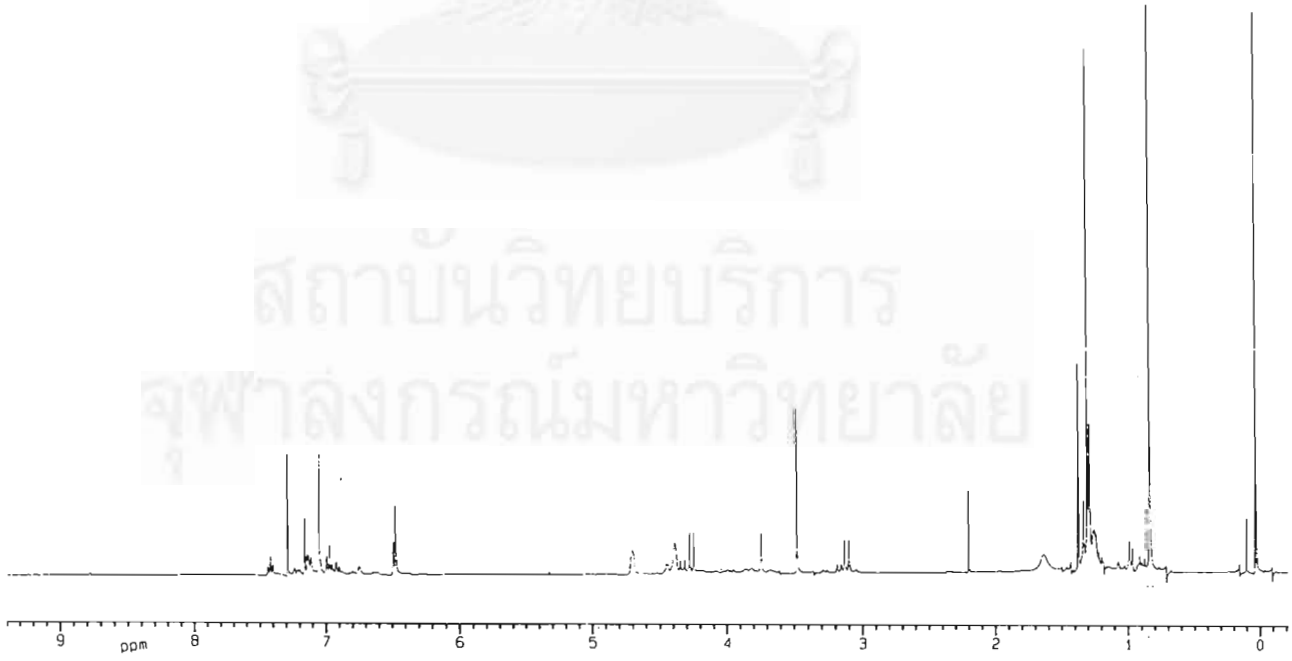


Figure B.12 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and sodium ion (standing for 5 days after an addition of sodium picrate)

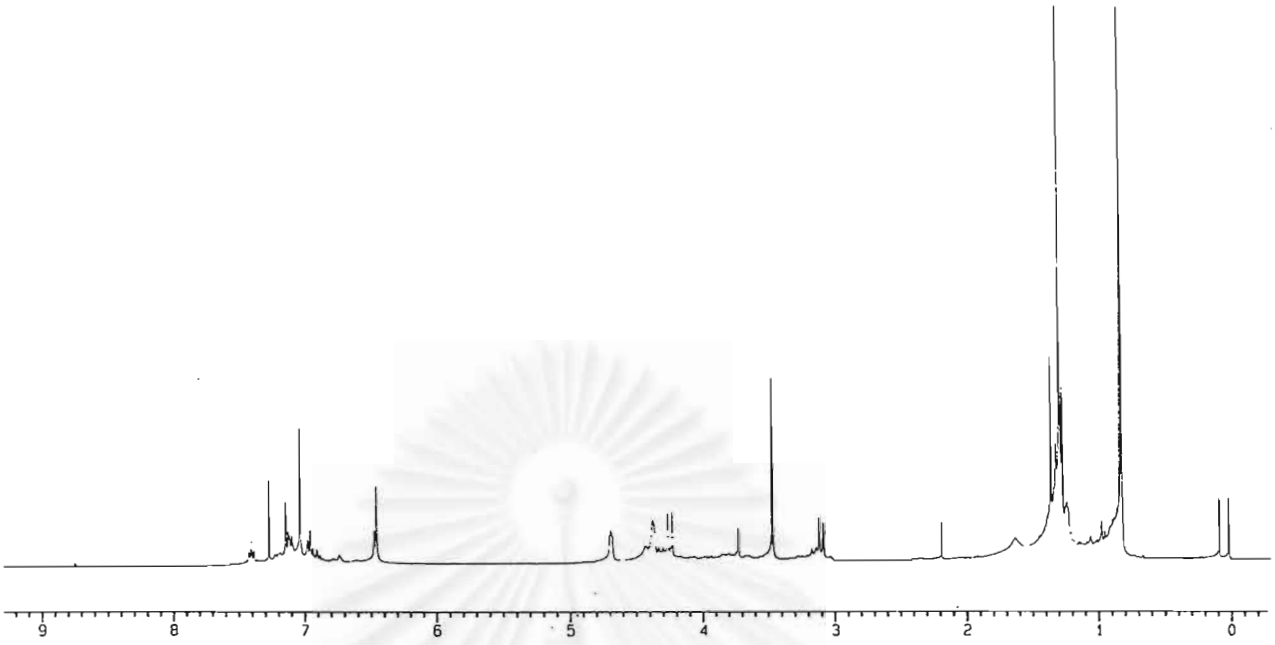


Figure B.13 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and sodium ion (standing for 12 days after an addition of sodium picrate)

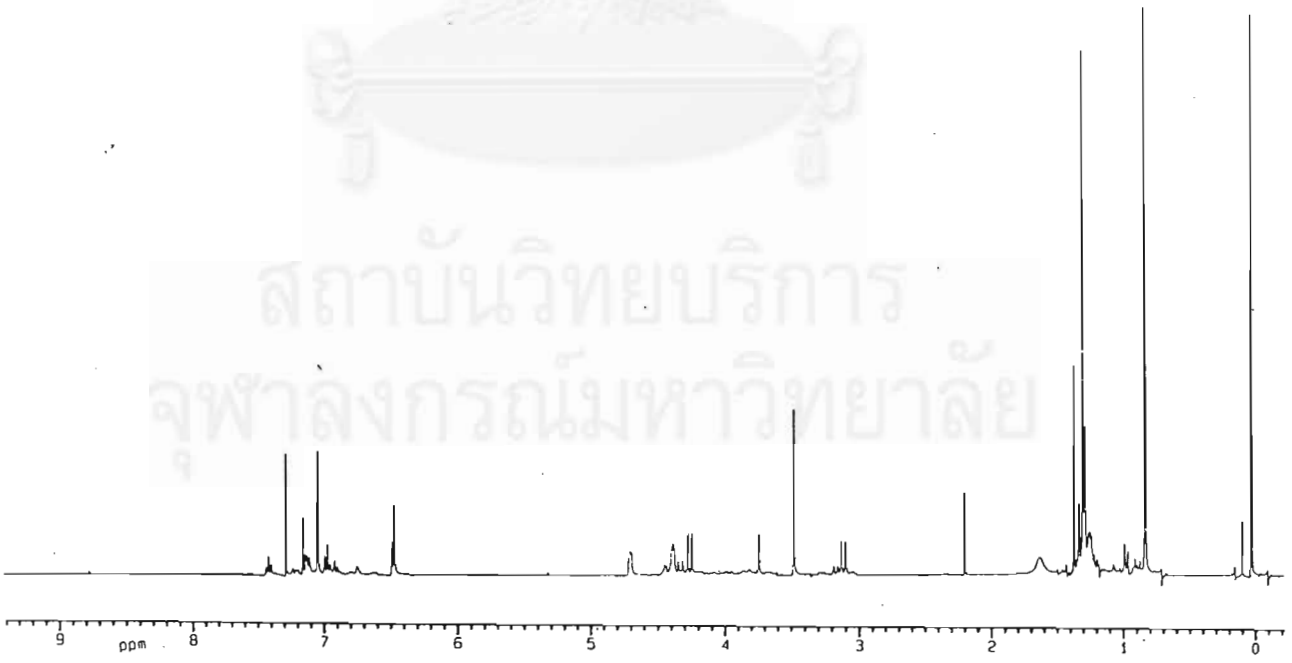


Figure B.14 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and sodium ion (standing for 19 days after an addition of sodium picrate)

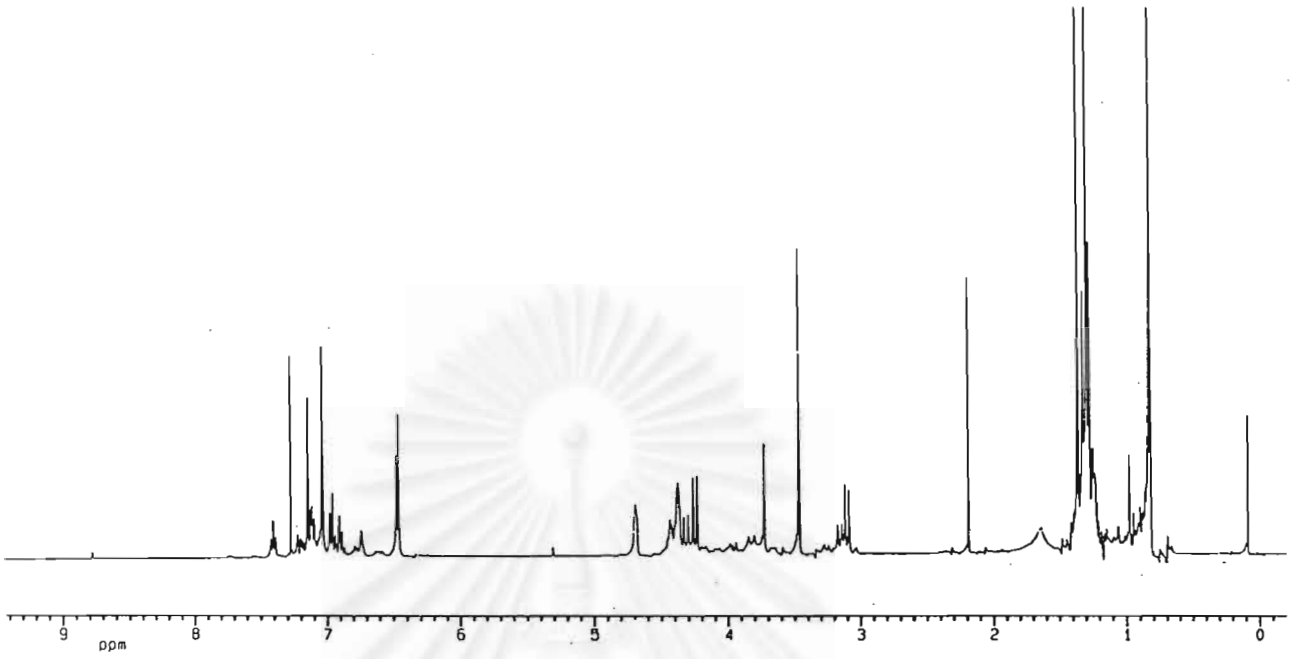


Figure B.15 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and sodium ion (standing for 30 days after an addition of sodium picrate)

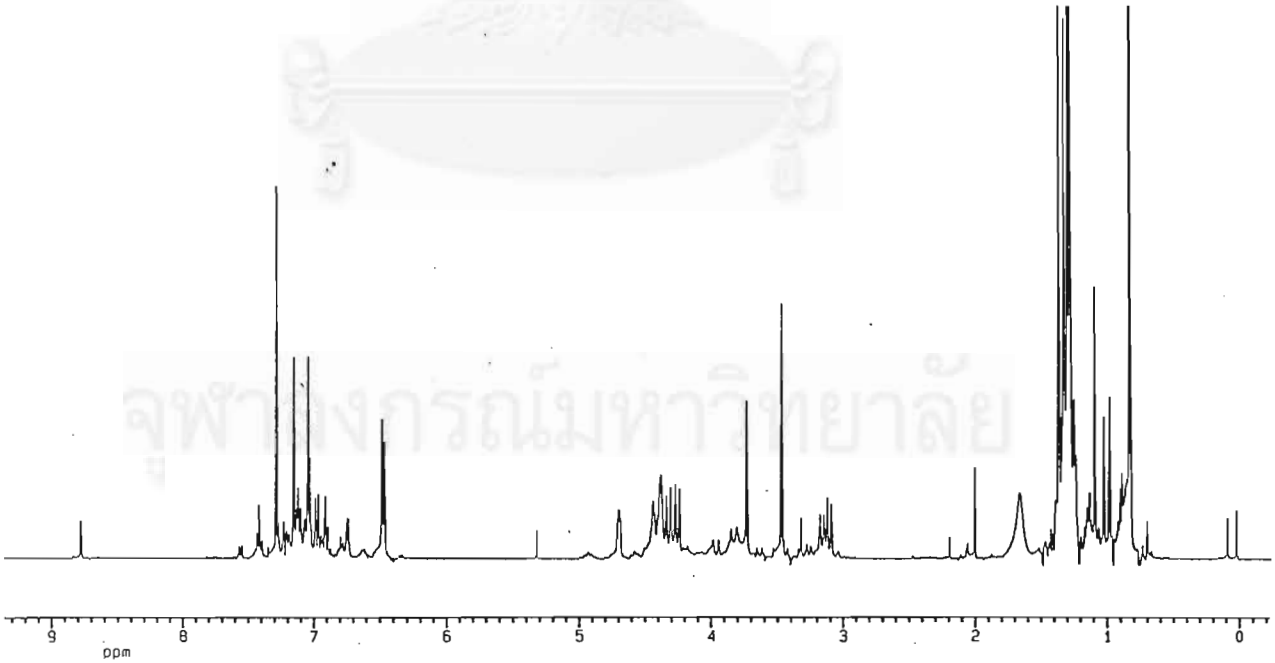


Figure B.16 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and potassium ion (standing for 2 days after an addition of potassium picrate)

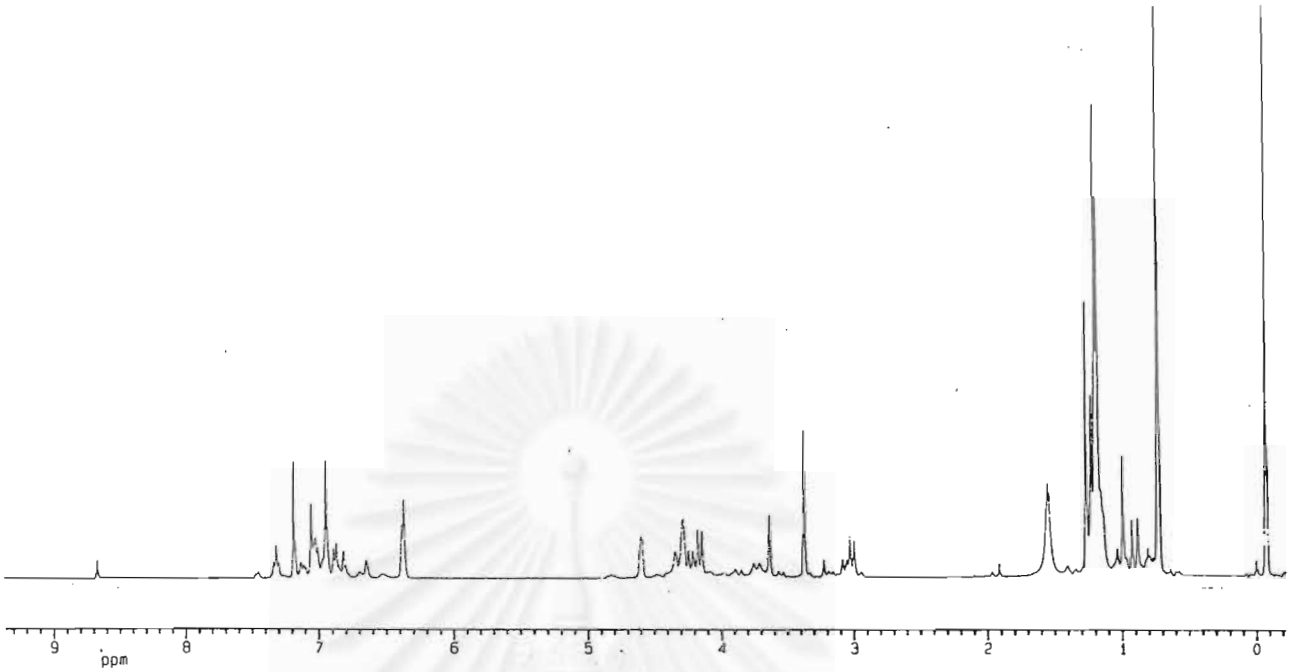


Figure B.17 The ^{1}H-NMR spectrum of the complex between the irradiated 8 and potassium ion (standing for 5 days after an addition of potassium picrate)

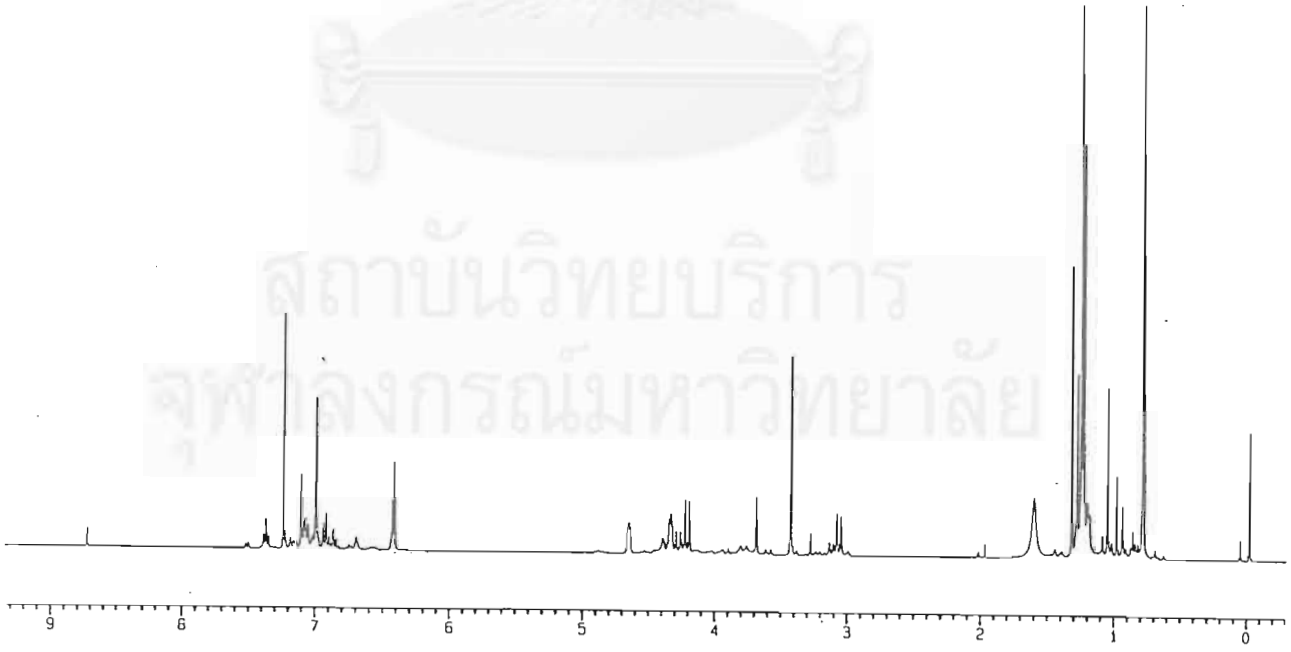


Figure B.18 The ^{1}H-NMR spectrum of the complex between the irradiated 8 and potassium ion (standing for 12 days after an addition of potassium picrate)

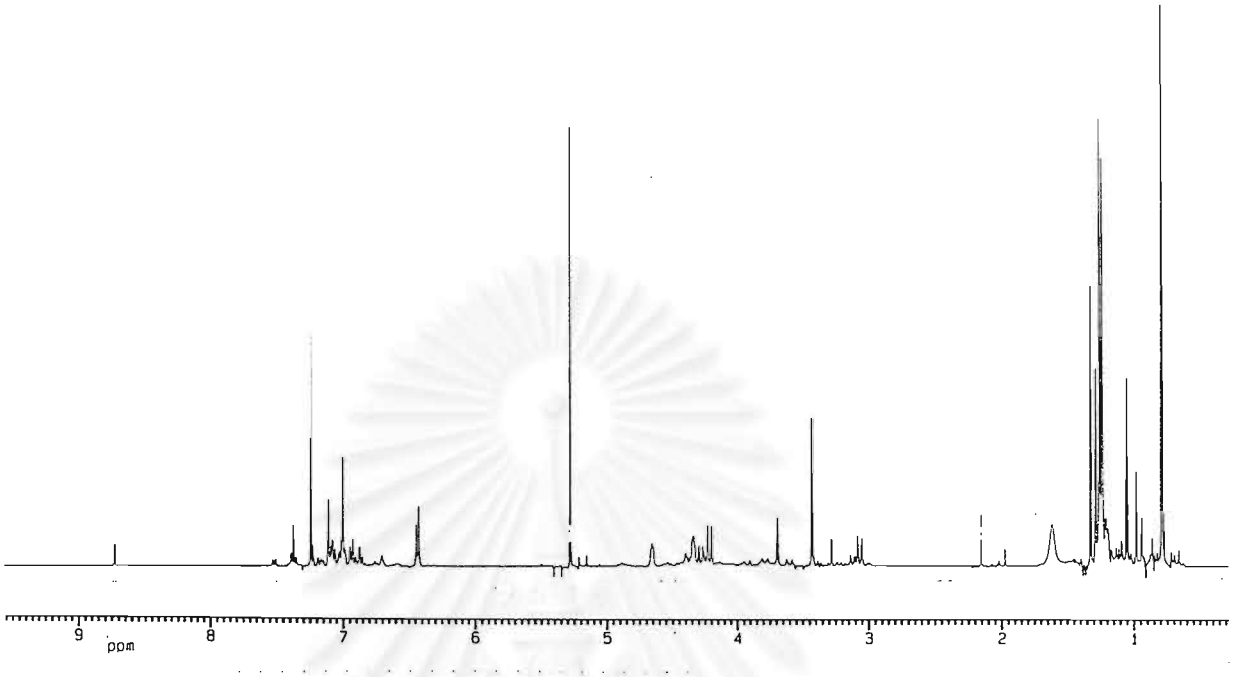


Figure B.19 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and potassium ion (standing for 19 days after an addition of potassium picrate)

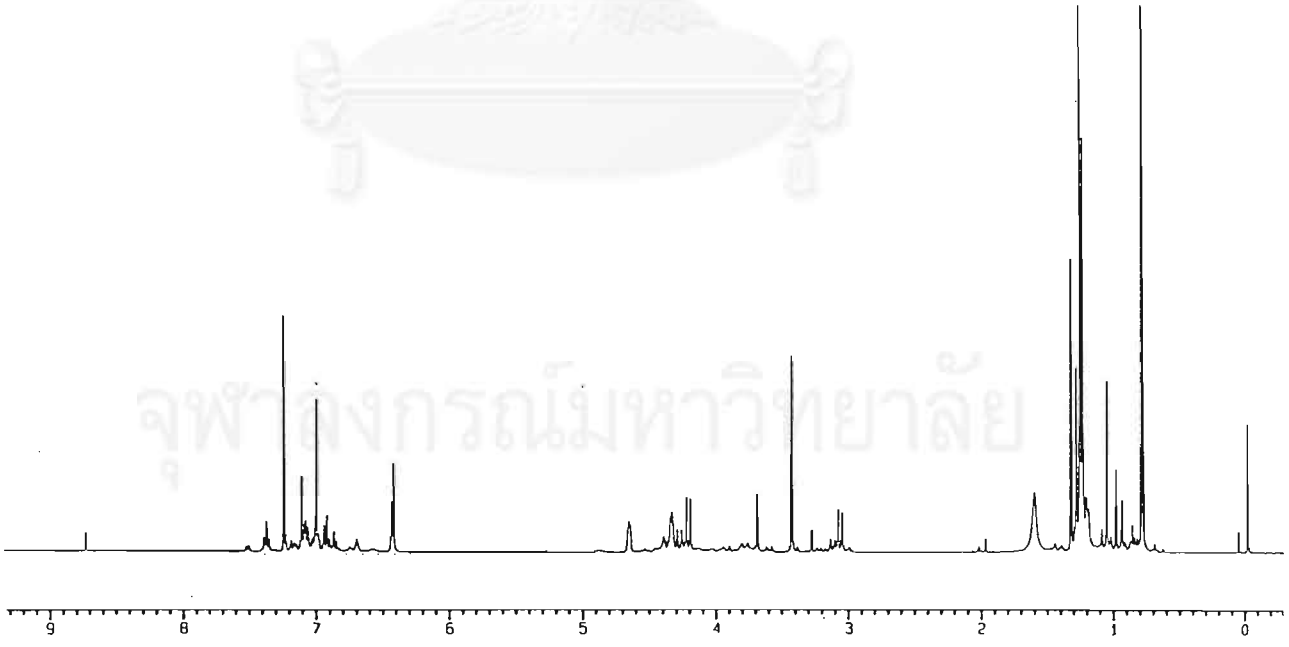
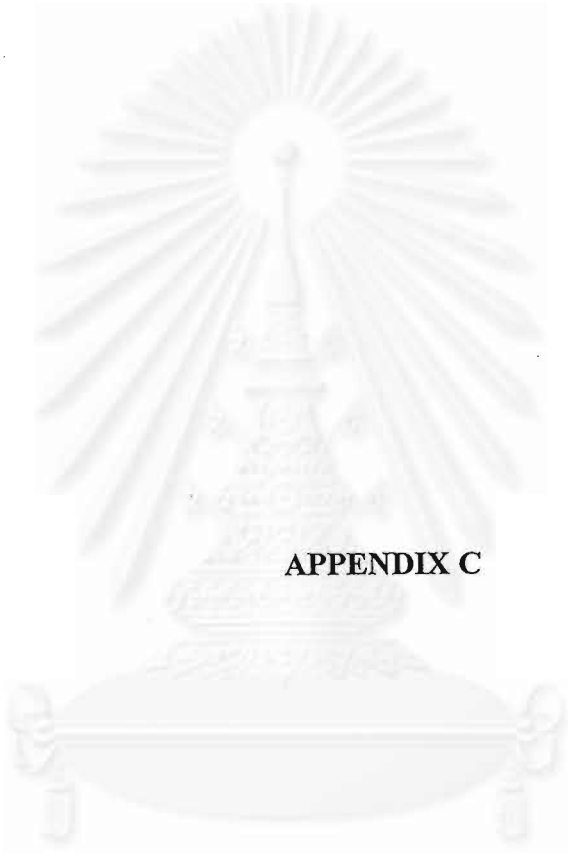


Figure B.20 The ^{1}H-NMR spectrum of the complex between the irradiated **8** and potassium ion (standing for 30 days after an addition of potassium picrate)



APPENDIX C

Table C.1 The percentage of *cis*-isomer[a] and various times for irradiated ligand **5**

Time (hrs)	The area integration of methylene protons of *cis*-**5**[b]	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
0.5	1.2	4.00	30.0
1.0	1.1	4.00	26.0
2.0	0.8	4.00	20.0
4.0	1.2	4.00	31.8
8.0	2.6	6.65	39.9
24.0	1.7	4.00	43.0
48.0	1.2	4.00	29.5

[a] % *cis*-isomer = $\frac{\text{The area integration of methylene protons of } cis\text{-}5}{\text{The area integration of methylene protons of } cis\text{- and } trans\text{-}5} \times 100$

[b] The area integration of methylene protons of *cis*-**5** = The area integration of methylene protons of *cis*- and *trans*-**5** - The area integration of methylene protons of *trans*-**5**

Table C.2 The percentage of *cis*-isomer and times for day-light ligand **5**

Time (hrs)	The area integration of methylene protons of *cis*-**5**[b]	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
2.0	0.299	3.527	8.5
12.0	0.210	2.227	9.4
24.0	0.306	5.845	5.2
48.0	1.272	5.047	25.2
96.0	1.572	4.493	34.9
144.0	2.429	7.671	31.6
192.0	0.823	2.500	32.9

Table C.3 The percentage of *cis*-isomer of the irradiated ligand **5** in the presence of sodium picrate

Time (days)	The area integration of methylene protons of *cis*-**5**	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
2	0.728	1.758	42.1
5	2.318	4.853	47.7
12	0.942	2.178	43.2
19	1.516	3.371	44.9
30	0.739	1.739	42.5

Table C.4 The percentage of *cis*-isomer of the irradiated ligand **5** in the presence of potassium picrate

Time (days)	The area integration of methylene protons of *cis*-**5**	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
2	0.991	2.646	37.4
5	2.170	20.79	10.4
12	0.316	1.316	24.0
19	0.316	1.220	25.9
30	0.628	1.465	42.8

Table C.5 The percentage of *cis*-isomer of the fresh ligand **5** in the presence of sodium picrate

Time (days)	The area integration of methylene protons of *cis*-**5**	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
1	1.233	5.648	21.8
2	1.520	5.233	29.0
4	1.689	4.189	40.3
5	2.588	6.450	40.1
12	0.897	2.025	44.3
30	0.958	2.261	42.3

Table C.6 The percentage of *cis*-isomer of the fresh ligand **5** in the presence of potassium picrate

Time (days)	The area integration of methylene protons of *cis*-**5**	The area integration of calixarene methylene protons of *cis*-and *trans*-**5**	% *Cis*-isomer
1	0.892	3.890	22.9
2	1.972	6.992	28.2
4	1.586	6.249	25.3
5	2.710	16.834	16.1
12	0.965	4.208	22.9
30	2.403	5.961	40.3

CURRICULUM VITAE

Name : Miss Bongkot Pipoosananakaton

Born : January 7th, 1974 in Bangkok, Thailand

Education & Related work :

1977-1985 : Elementary School Certificate

1985-1991 : High School Certificate

1991-1995 : Bachelor's degree of Science (Chemistry), Chulalongkorn University, Bangkok, Thailand

1995-1997 : Manufacturing Engineer, PCB Center, Chonburi

1997-2000 : Master's degree study in Inorganic Chemistry at Department of Chemistry, Chulalongkorn University, Bangkok, Thailand