จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย

กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย

เรื่อง

การตรวจสอบความเป็นเบสและการหาโครงสร้างของสารประกอบโพลีเอซาคาลิกซารีนและความเสถียรของสารประกอบเชิงซ้อนกับโลหะแคตไอออน

โดย

วิทยา เรืองพรวิสุทธิ์

กุมภาพันธ์ 2543

Chulalongkorn University

Rachadapiseksompoj Research Fund

Research Report

Basicity Investigation and Structure Optimization of Polyaza-Calixarenes and Stabilities of Their Complexes with Metal Cations

by

Vithaya Ruangpornvisuti

February 2000

รายงานความก้าวหน้าของโครงการวิจัย

เรื่อง

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เสนอ

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จุฬาลงกรณ์มหาวิทยาลัย

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กุมภาพันธ์ 2543

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ชื่อผู้วิจัย	รศ.ดร.วิทยา เรืองพรวิสุทธิ์
เดือนและปีที่ทำวิจัยเสร็จ	มกราคม 2543

บทคัดย่อ

การหาโครงสร้างที่เหมาะสมของ 25,26,27,28-เตตรา(2-เอททอกซีอะนิลีน)คาลิก[4]เอรีน โดยการคำนวณทางเคมีควอนตัมด้วยวิธี PM3 พบว่ามีโครงรูปเป็นชนิดโคน (**cL**) และ พาร์เชียลโคน (**pcL**) โดยโครงรูปชนิดโคนมีความเสถียรมากกว่าโครงรูปชนิดพาร์เชียลโคน ค่าพลังงานการรวมตัวกับโปรตอนบนอะตอมทั้งสี่ของไนโตรเจนชนิดอะนิลีนในลิแกนด์ทั้งสองโครงรูปได้รับการคำนวณพลังงานในระดับ 6-31 G กระบวนการรวมตัวกับโปรตอนบนโครงรูป **cL** และ **pcL** มีเส้นทางที่เป็นไปได้ทั้งหมดจำนวน 7 และ 24 เส้นทาง ตามลำดับ ค่าคงที่ของความเป็นเบสของโครง **pcL** หาค่าได้โดยวิธีโพเทนชิโอเมทริกไทเทรชันโดยมีค่าในเทอมลอการิทึมเป็น $\log K_1 = 11.87$, $\log K_2 = 5.59$, $\log K_3 = 4.62$ and $\log K_4 = 4.62$ สำหรับค่าคงที่ของความเป็นเบสของโครงรูป **cL** ไม่สามารถหาได้

Project Title	Basicity Investigation and Structure Optimization of Polyaza-Calixarenes and Stabilities of Their Complexes with Metal Cations
Name of investigator	Assoc.Prof. Dr.Vithaya Ruangpornvisuti
Year	February 2000

Abstract

The structure of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene of cone (**cL**) and partial cone (**pcL**) conformations were optimized by PM3 of quantum chemical method. It has been found that **cL** structure is more stable than **pcL** conformation. The stabilization energies of protonation on four aniline-nitrogen atoms of both conformations of the ligand at 6-31G energy level, were obtained. The protonations process on the **cL** and **pcL** being 7 and 24 possible pathways, respectively, were evaluated. The basicity constants of partial cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene obtained by potentiometric titration technique, expressed in term of logalithm are $\log K_1 = 11.87$, $\log K_2 = 5.59$, $\log K_3 = 4.62$ and $\log K_4 = 4.62$. For basicity constants of cone conformation was not successfully obained.

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CHAPTER I

INTRODUCTION

1.1 Review of supramolecular chemistry

Supramolecular chemistry has interested several groups of scientists [1-11]. It is the chemistry of molecular assemblies and of the intermolecular bonds which are non-covalent intermolecular forces such as van der Waals interaction, hydrogen bonding, electrostatic forces, donor-acceptor interactions, etc. The structures of molecules in supramolecular chemistry called supermolecules are defined by their conformational, thermodynamical, kinetical and dynamical properties. Supermolecules are distinguished by different degree of strength and directionality of intermolecular bonds such as metal ion coordinates, electrostatic forces, hydrogen bondings, van der Waals interactions, donor-acceptor interactions, etc. Bondings are classified in weak or moderate as in hydrogen bonds and strong or very strong interactions for metal ion coordination. In fact, intermolecular forces are weaker than covalent bonds. Due to the reson mentioned above, supermolecules are thermodynamically less stable, kinetically more labile and dynamically more flexible than classical molecules. Supramolecular chemistry is then concerned with soft bonds and represents a soft chemistry. Supramolecular chemistry can be divided into two general areas concerning:

(1) supermolecules as oligomolecules that are result of the intermolecular association of a few components such as receptor and its substrate(s) based on the principles of molecular recognition;

(2) supramolecular assemblies as polymolecules that result from the spontaneous association of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending on its nature such as films, layers, membranes, vesicles, micelles, mesomorphic phases, solid state structures, etc. It thus covers the rational, coherent approach to molecular associations, from the smallest, the dimer, to the largest, the organized phase, and to their designed manipulation.

1.2 Calix[4]arenes

Calix[n]arenes are oligophenols readily accessible by simple condensation of para-substituted phenols with formaldehyde under basic catalysts, Figure 1.1.

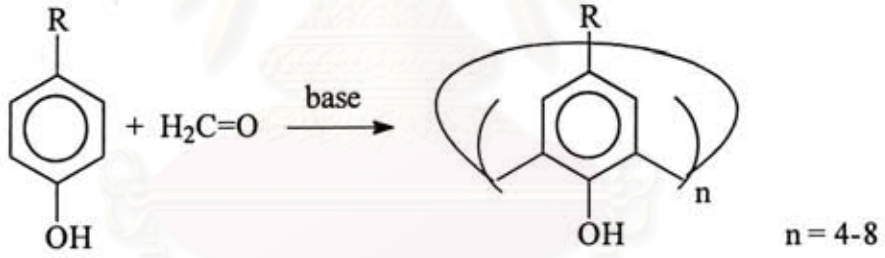


Figure 1.1 Preparation of calix[n]arenes.

The name "calixarene" has been given by Gutsche [1] because of the resemblance of the four-membered ring with a chalice (in Greek : calix). The suffix "arene" indicates the represent of aryl rings in the molecular framework.

Calix[n]arenes can be selectively prepared in different conditions. The calix[n]arene containing an even number of phenolic units such as calix[4]arene and calix[8]arene can be synthesized by simple techniques in satisfying yields. On the

other hand, calixarenes that contain an odd member of [n] are more difficult to prepare. Calix[n]arene and their derivatives can be used as host molecules to form complexes with target ions and/or neutral molecules. They can also be developed and modified for the construction of new types of molecular devices for various industrial applications. Calix[4]arene is surely the most significant member of the calix[n]arene family, and its chemistry is by far most advanced. This molecule represents a well-preorganized cavity, the shape of which is tunable by suitable substitution of hydroxy groups.

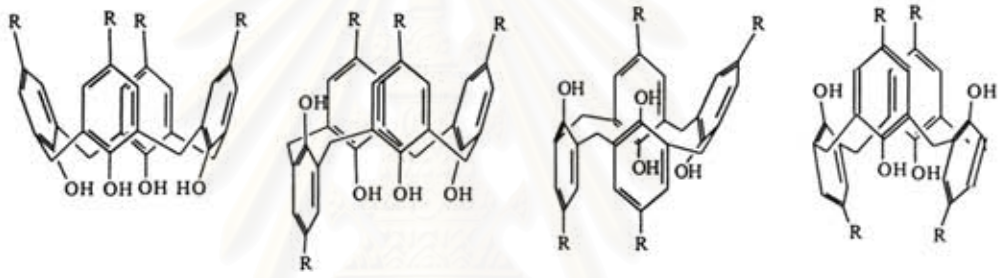


Figure 1.2 Possible conformations of calix[4]arene.

Figure 1.2 shows four basic conformations (isomers) which can be prepared from calix[4]arene: cone, partial cone, 1,2-alternate and 1,3-alternate. Each of them has its own specific properties and characteristic utilization in host-guest chemistry. This makes calix[4]arene a very attractive compound that can be used as a starting platform for designing more sophisticated structures for binding ions and neutral molecules.

1.3 Calix[4]arene complex with heavy metal ions

The complexation studies of heavy metals have attracted inorganic chemists for an extended period of time. The reason for this growing interest is the use of ligands as complexants for the selective extraction of metals in purification procedures. Among the most widely used ligands are chelates and macrocycles. These types of ligands are particularly attractive because they can be designed to have very high stability constants for particular metal ions due to judicious choices of ligating atoms and ring sizes.

Use of calixarenes as complexants for metal ions is a much more recent development. Calixarenes are akin to macrocycles in that they have a lower rim of oxygens in a cyclic arrangement that can be used to coordinate metal ions. Chemically modified calixarenes are used where both the lower rim oxygens and the functional groups appended as substituents coordinate to the metals. These chemically modified calixarenes can therefore be considered to have a combination of both a chelating and a macrocyclic portion.

Diaza-benzo crown ether-*p*-*tert*-butylcalix[4]arene [12,13] (Figure 1.3) were synthesized and studied complexation with Zn^{2+}, where the counter anions are Cl^-, Br^-, I^-, ClO_4^-, NO_3^- by ^1H NMR spectroscopy. This study showed that this ligand could bind Zn^{2+} to a different extent depending on the counter anions and the cavity size of the ligands. The stability of Zn^{2+} complexes of this ligand varied as follow : $NO_3^- > ClO_4^- > I^- > Br^- > Cl^-$. Recently, the protonation of this ligand and its complexation with $Zn(ClO_4)_2$ were studied by potentiometric and ultraviolet spectroscopy titrations [14].

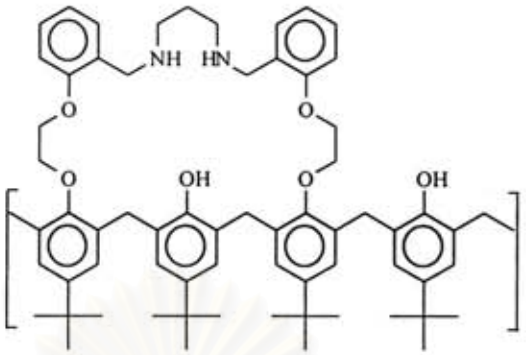


Figure 1.3 Diaza-benzo crown ether-*p-tert*-butylcalix[4]arene.

In 1994, Schiff base *p-tert*-butylcalix[4]arenes [15], (Figure 1.4) were synthesized. Alkali and alkaline earth cations were very poorly extracted by the ligands (I-III). However, the better extraction of Li^+ and Na^+ with ligand (III) may be explained by greater flexibility of its bridge which was due to an additional carbon that allows the chain to adopt a more suitable geometry for complexation. In the transition metal series, Fe^{2+} and Cu^{2+} were extracted more efficiently. Heavy metal cations were extracted with ligand (II) and (III), with higher preference for Pb^{2+}. For lanthanide series, there was an extraction selectivity for Nd^{3+} and Eu^{3+} with (II) and for Eu^{3+} with (III).

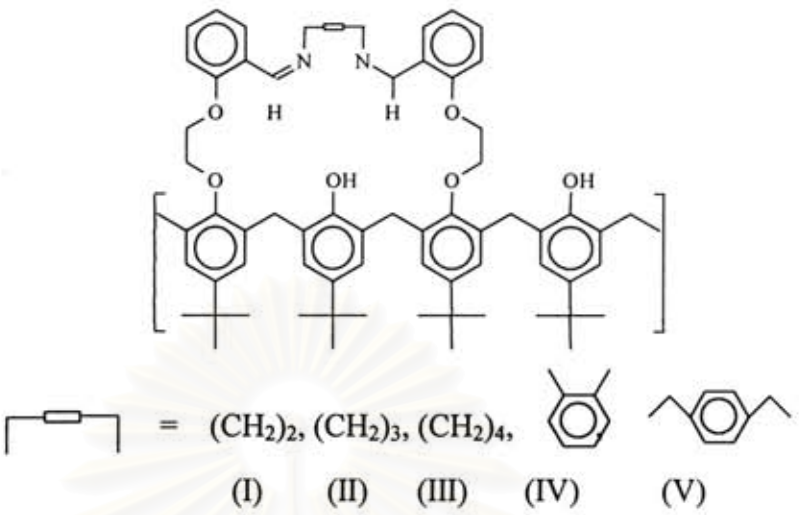
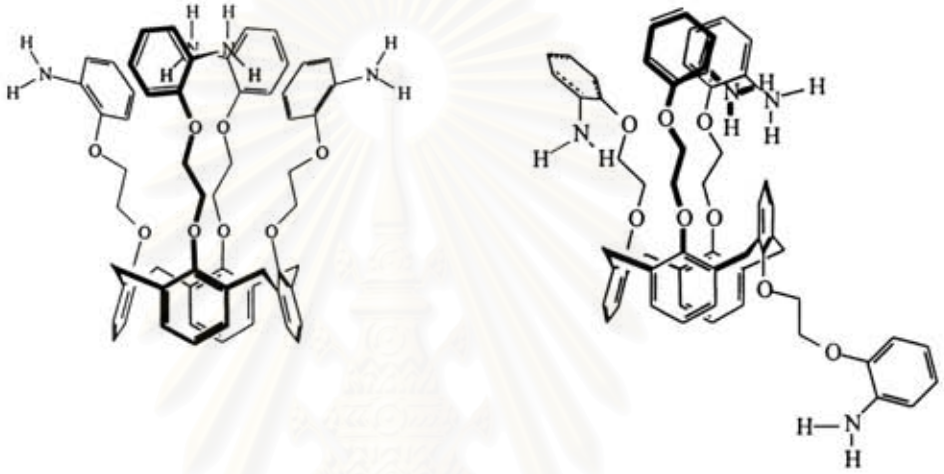


Figure 1.4 Schiff base *p-tert*-butylcalix[4]arenes.

The complexation work to date with calixarenes has primarily focused on metals of Group I or II, or on other oxophilic metal centers such as UO_2^{2+}. Calixarene based ligands with functionalities binding *via* their oxygen or nitrogen sites have been widely employed as selective complexants for both Group I and II metal ions. Nevertheless, little has been published on the preparation of calixarene derivatives which coordinate to the metal center *via* other heteroatoms. Such compounds are important if selective complexants for heavy metals are to be developed. Specific ligands need to be designed for these particular metals because they form stable complexes with "soft" rather than with "hard" donor ligands. For example, Cu^+, Ag^+, Au^+, Cd^{2+} and Hg^{2+} are soft acids which can show soft-soft interactions with soft bases such as R_2S, RSH or RS^-.

1.4 Structure of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene

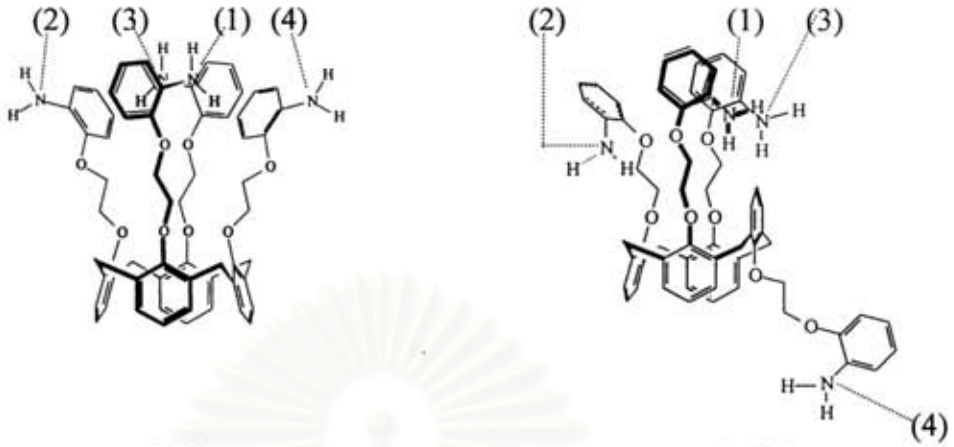
The structural conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] arene from the experiment of synthesis, the cone (**cL**) and partial cone (**pcL**) conformations have been discovered as shown in Figure 1.5.



(cL) **(pcL)**

Figure 1.5 Cone (**cL**) and partial cone (**pcL**) conformations found by the process of synthesis.

The four aniline-nitrogen atoms of cone (**cL**) and partial cone (**pcL**) conformations, assigned by the four number to identify the protonated structure of of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, has been labeled as shown in Figure 1.6.



(cL) **(pcL)**

Figure 1.6 Assignment of aniline-nitrogen atoms of cone (**cL**) and partial cone (**pcL**) conformations

1.4 Objective and Scope of the Research

To determine the structural conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene by quantum chemical calculations using semiempirical and ab initio methods. The stabilization energies of optimized protonated species will be evaluated by ab initio method with extended basis set. The most possible of protonation pathway of each conformation of 25,26,27,28-*tetra*(2-ethoxyaniline) calix[4]arene will be found out. The basicity constants of each conformation of the ligand will be determined by potentiometric titration technique. Complex formation of possible conformation to the transition metals will be investigated. The species distribution of the ligands and their complexes with heavy metal ions over the varied pH values will also be obtained. In addition, the knowledge of this research may lead to application of these ligands for heavy metal ion separation from environment in the future.

CHAPTER II

THEORY

2.1 Potentiometry and Equilibrium

2.1.1 Equilibrium Constant

2.1.1.1 Equilibrium Concentration Constant

An equilibrium constant is a quotient involving the concentrations or activities of reacting species in solution at equilibrium. Generally it is defined as the ratio of the product of the activities *a* of the reaction products, raised to appropriate power, to the products of the activities of the reactants, raised to appropriate power, illustrated by equation (2.1) where a, b, c and d are the stoichiometric coefficients of the solution species A, B, C and D respectively.

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{a_C^c \; a_D^d}{a_A^a \; a_B^b} \qquad (2.1)$$

The determination of the activities of complex ionic species at both infinite solution and in real solution is a complicated and time-consuming task. However concentrations are related to activities by the expression

$$a_X = [X]\,\gamma_X \qquad (2.2)$$

where a_X, [X] and γ_X are activity, concentration and activity coefficient of X respectively. Activity coefficients of reacting species are in general tedious and difficult to measure. They also depend very significantly on the nature and concentrations of other species present in solution so that it is not possible to build universal tables of activity coefficients. Theoretical attempts at calculating activity coefficients, based on the Debye-Huckel approach and its extensions, are at best of only limited accuracy. Substituting the activities from equation (2.2) in (2.1), then the equilibrium constant can be rewritten as follow.

$$K_{eq} = \frac{a_C^c \; a_D^d}{a_A^a \; a_B^b} = \frac{[C]^c \; [D]^d}{[A]^a \; [B]^b} \cdot \frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b} \qquad (2.3)$$

where[A] indicates molar concentrations. If now it is possible to ensure that the term $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ remains constant then the term $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \cdot K_{eq}$ is also a constant. Therefore, the equilibrium constant expressed in terms of the reacting species, called equilibrium concentration constant, K_c can be written as indicated by equation (2.4).

$$aA + bB \rightleftharpoons cC + dD \qquad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (2.4)$$

Equilibrium concentration constant, K_c is also known as the stoichiometric equilibrium constant which determined at constant ionic strength where as K_{eq} is indicated by equation (2.1) which is known as an equilibrium activity constant or thermodynamic equilibrium constant.

The term $\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$ in equation (2.3) may be maintained effectively constant by having a large excess of an inert background electrolyte present and using only low concentrations of the reacting ionic species so that any change in their concentrations as a result of their reaction together has an insignificant change on the overall ionic strength of the medium. It is generally possible to replace about 5% of the ions in the inert background electrolyte without appreciably altering the activity coefficients of the minor species present. However, in recording a stoichiometric equilibrium constant it is essential to record not only the concentration of the inert background electrolyte, but also its nature, since the activity coefficients depend on the electrolyte. Consequently, of course, in comparing stoichiometric equilibrium constants, only data obtained under very similar conditions should be used unless the differences between the equilibrium constants are large.

2.1.1.2 Acidity and Basicity Constants

The acid-base equilibria of the ligands can be treated by protonation and deprotonation constant. Protonation constant is the equilibrium constant for the addition the n^{th} proton to a charged or uncharged ligand. Protonation constant is known as basicity constant. The reciprocal of protonation constant is called

deprotonation constant and defined as the equilibrium constant for the splitting off n^{th} proton from a charged or uncharged ligand. Deprotonation constant is also known as acidity constant. The following equations define these constants and show their interrelation.

$$L + H \rightleftharpoons LH : K_1 = \frac{[LH]}{[L][H]} \quad (2.5)$$

$$LH + H \rightleftharpoons LH_2 : K_2 = \frac{[LH_2]}{[LH][H]} \quad (2.6)$$

$$LH_2 + H \rightleftharpoons LH_3 : K_3 = \frac{[LH_3]}{[LH_2][H]} \quad (2.7)$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$LH_{n-1} + H \rightleftharpoons LH_n : K_n = \frac{[LH_n]}{[LH_{n-1}][H]} \quad (2.8)$$

Another way of expressing the equilibria relations can be shown as follow:

$$L + H \rightleftharpoons LH : \beta_1 = \frac{[LH]}{[L][H]} \quad (2.9)$$

$$L + 2H \rightleftharpoons LH_2 : \beta_2 = \frac{[LH_2]}{[L][H]^2} \quad (2.10)$$

$$L + 3H \rightleftharpoons LH_3 : \beta_3 = \frac{[LH_3]}{[L][H]^3} \quad (2.11)$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$L + nH \rightleftharpoons LH_n : \beta_n = \frac{[LH_n]}{[L][H]^n} \quad (2.12)$$

The K_i's are called the stepwise protonation constants and the β_i's are called the overall or cumulative protonation constants.

2.2 Method of Calculations

2.2.1 Linear Method, Errors and Statistics

Stability constants are not directly measurable but must be calculated from an observed response function of a fixed, but experimentally adjustable, variable. Since the response data are subject to random error and indeed may be subject to systematic errors if we have not controlled the experiment well, the stability constants will be calculated with limited precision. However, it is important to estimate the precision of any calculated constants, as it will indicate the reliability of the value obtained and in turn the efficiency of the experiment. In addition we need to have a mathematical model for describing the data.

2.2.2 Model Building

Experiments attempts to find some functional form for the way quantities in nature are related. We try to build up a mathematical model which may be an assumed one, in which case we need to measure of how good the model is in describing our data, or it may be derived from first principles and then tested experimentally. The model could be an approximated one, which initially may be acceptable and then refined or modified in the further experimental observations. The typical experiment consists of fixing one group of known values variables called independent variables and then making observations of another dependent variables. In stability constant work, the independent variables might be temperature, ionic strength, or the concentration of one or more components and dependent variables might be e.m.f. or pH or absorbance of the solution. We then calculate or estimate the parameters of interest from the assumed function by relating the dependent to the independent variables.

The parameters for our model are calculated by fitting them to the experimental data. This may be done either graphically or by a mathematical procedure, such as least-squares. The latter calculates the values of the parameters which sum of the squares of the residuals is defined as the difference between the

observed and calculated data points at each fixed minimum value of the independent variable. In addition the method of least-squares allows us to obtain the estimated errors of the interested parameters and to estimate the 'goodness of fit' of the assumed model, that is, it allows us to test alternative hypotheses.

2.2.3 Random Errors

Random or observational errors are assumed to follow a Gaussian or normal distribution , expressed mathematically as

$$f(r_x) = \frac{1}{\sqrt{2}\sigma_x} e^{-r_x^2 / 2\sigma_x^2} \tag{2.13}$$

where r_x is the residual of x or observed value - true value , σ_x^2 is the variance of x and σ_x is the standard deviation.

The probability of observing the i th residual, P_i in the region r_{xi} to $r_{xi} + dr_{xi}$ is:

$$dP_i = \frac{1}{\sqrt{2}\sigma_x} e^{-r_{xi}^2 / 2\sigma_x^2} dr_{xi} \tag{2.14}$$

Now the probability for a given set of n observations, where P is the product of the probabilities of i th measurements is

$$dP = \prod_{i=1}^{i=n} dP_i = \prod_{i=1}^{i=n} \left(\frac{d\, r_{xi}}{\sqrt{2}\,\sigma_x} \right) e^{-\left(\frac{1}{2\sigma_x^2}\right)\sum r_{xi}^2} \tag{2.15}$$

Based on the statistical principle of maximum likelihood this probability becomes a maximum when the sum of the squares residuals is a minimum.

$$\sum_{i=1}^{n} r_{xi}^2 = \text{minimum} \tag{2.16}$$

Hence the origin of the term 'least squares ' is apparent.

The discussion so far has assumed that the measurements of x have all come from the same population distribution, that is, the variance of the residuals are equal. If this is not so, equation (2.14) should be rewritten as :

$$d P_i = \frac{1}{\sqrt{2}\sigma_{xi}} e^{-r_{xi}^2 / 2\sigma_{xi}^2} dr \tag{2.17}$$

and the equation (2.58) becomes

$$dP = \prod_{i=1}^{i=n} dp_i = \prod_{i=1}^{i=n} \left(\frac{d r_{xi}}{\sqrt{2}\ \sigma_{xi}} \right) e^{-\frac{1}{2}\sum\left(r_{xi}^2 / \sigma_{xi}^2\right)} \tag{2.18}$$

and the least-squares principle gives:

$$\sum_{i=1}^{i=n} \left(\frac{r_{xi}^2}{\sigma_{xi}^2} \right) = \text{minimum} \tag{2.19}$$

A quantity inversely proportional to the variance is termed the weight of an observation. Hence:

$$w_{xi} = \frac{\sigma_0^2}{\sigma_{xi}^2} \tag{2.20}$$

where σ_o^2 is known as the variance of an observation of unit weight. In practice σ_o^2 will often have the value of unity. The quantity now to be minimized is the sum of the weighted squares of the residuals.

$$\sum_{i=1}^{i=n} w_{xi} r_{xi}^2 = \text{minimum} \tag{2.21}$$

In practice we cannot know the true value of x , but the principle of least-squares attempts to adjust the estimate of x according to equation (2.21). Generally

the experimental data are function of the parameter x so that r_{xi} in equation (2.21) is defined as:

$$r_{xi} = \left[f(x_i) - f(\bar{x}) \right] \tag{2.22}$$

and $\bar{x}$ is the least-squares estimator of the true value of the parameter.

2.2.4 Systematic Errors

Systematic errors are caused by the limitations of the apparatus, or experimentalist, and introduce bias into the data resulting in inaccurate parameters. Thus it is possible to obtain high precision with poor accuracy, as indicated diagrammatically in Figure 2.1.

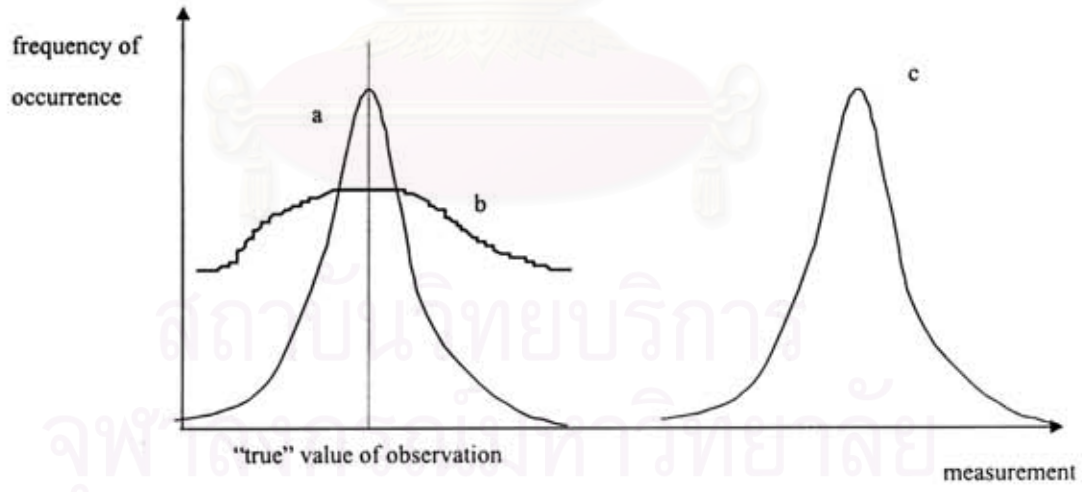


Figure 2.1 Diagrammatic representation types of experimental error : (a) high precision, high accuracy ; (b) low precision, high accuracy (due to large random errors); (c) high precision, poor accuracy (due to systematic errors).

2.2.5 Non-Linear Parameter Estimation

2.2.5.1 Least -squares-extension case

To extend least-squares theory to the non-linear case, that is the situation where the dependent variables are non-linear functions of the independent variables, we take equation and express the dependent variables (observables) as a function of the unknowns by a Taylor series expansion. Thus if the initial estimates of the parameter values are $\left(x_1^0\ x_2^0\ ...x_m^0\right)$ then the observables are expressed about this point in parameter space by:

$$o_i = f_i\left(x_1^o ... x_m^0\right) + \left(\frac{\partial f_i}{\partial x_i}\right)_0 \left(x_1 - x_1^o\right) + ... + \left(\frac{\partial f_i}{\partial x_m}\right)_0 \left(x_m - x_m^o\right) \qquad (2.23)$$

that is

$$o_i = f_i\left(x_1^o ... x_m^0\right) + \sum_{j=1}^{j=m}\left(\frac{\partial f_i}{\partial x_j}\right)_0 \Delta x_j \qquad (2.24)$$

where terms higher than first order have been neglected. Therefore the change in the observables Δo_i on making the corrections Δx_j are given by

$$\Delta o_i = o_i - f_i\left(x_1^o ... x_m^0\right) = \sum_{j=1}^{j=m}\left(\frac{\partial f_i}{\partial x_j}\right)_0 \Delta x_j \qquad (2.25)$$

2.2.5.2 Hypothesis testing

Another quantity which has been used in non-linear estimation situations is the Halmilton *R*-factor. In this procedure the *R*-factor defined by :

$$R = \left[\frac{\sum_{i=1}^{i=n} w_i \left(o_i^{calc} - o_i^{obs} \right)^2}{\sum_{i=1}^{i=n} w_i \left(o_i^{obs} \right)^2} \right]^{\frac{1}{2}} \qquad (2.26)$$

is compared with R_{lim} calculated from :

$$R_{lim} = \left[\frac{\sum_{i=1}^{i=n} w_i \ e_i^2}{\sum_{i=1}^{i=n} w_i \left(o_i^{obs} \right)^2} \right]^{\frac{1}{2}} \qquad (2.27)$$

where e_i is the residual in the i th equation calculated from the estimated errors in all the experimental quantities using error propagation rules, o_i^{calc} and o_i^{obs} are the calculated and the observed values of the response variable respectively, w_i are the appropriate weighting factors. A satisfactory fit is assumed if $R < R_{lim}$.

2.3 Calculation of Equilibrium Constants

The acidity and basicity constants were calculated by fitting the pH data to the SUPERQUAD program [16] which has been widely used to calculate the equilibrium constants of many ligands in solution. The formation constants are determined by minimization of an error-square sum based on measure electrode potentials. The SUPERQUAD program also permits refinement of any reactant concentration or standard electrode potential. The refinement is incorporated into new procedure which can be used for model selection. The assumptions for computation of formation constants by SUPERQUAD could be described as follows.

Assumptions : There are number of assumptions underlying the whole treatment, and each needs to be considered explicitly.

1. For each chemical species $A_aB_b...$ in the solution equilibria, there is a chemical constant, the formation constant, which is expressed as a concentration quotient in equation (2.28).

$$\beta_{ab}.... = \frac{[A_aB_b...]}{[A]^a[B]^b...} \qquad (2.28)$$

A, B... are the reactants (SUPERQUAD allows up to four of them) and [A], [B] are the concentrations of free reactant; electrical charges may be attached to any species, but they are omitted for sake of simplicity in this discussion. Since the thermodynamic definition of a formation constant is as an activity quotient, it is to be assumed that the quotient of the activity coefficients is constant, an assumption usually justified by performing the experiments with a medium of high ionic strength .

2. Each electrode present exhibits a pseudo-Nernstian behavior, equation (2.29), where [A] is the concentration of the electro-active ion,

$$E = E^\circ + S_L \log [A] \qquad (2.29)$$

E is the measured potential, and E^o is the standard electrode potential. The ideal value of the slope S_L is of course *RT/nF*, but we assume only that it is a constant for a given electrode. The value of E^o and S_L are usually obtained in a separate calibration experiment. Further there is a modified Nernst equation.

$$E = E^\circ + S_L \log [H^+] + r [H^+] + s [H^+]^{-1} \qquad (2.30)$$

This equation was first suggested as means of taking into account junction potentials in strongly acidic and strongly basic condition.

3. Systematic errors must be minimized by careful experimental work. Sources of systematic error include electrode calibration, sample weightings and dilutions, standardization of reagents (use of carbonate-free alkali in particular), temperature variation and water quality. The last-named factor is more significant today than it was in the past, as water may be contaminated by titrable species which

can pass through distillation columns by surface action. All statistical tests are based on the assumption that systematic errors are absent from the data.

4. The independent variable is not subject to error. Errors in the dependent variable are assumed to have a normal distribution. If these assumptions are true, use of the principle of least squares will yield a maximum likelihood result, and computed residuals should not show systematic trends.

5. There exits a model of the equilibrium system, which adequately accounts for the experimental observations. The model is specified by a set of coefficients a, b , ..., one for each species formed. All least-squares refinements are performed in terms of an assumed model. Examination of a sequence of models should yield a best model which is not significantly different from the true model. Choice of the best model is known as species selection.

2.4 Inert Background Electrolyte

To study acid-base characteristics of ligand and their complexation properties toward metal, ionic strength is controlled by inert background electrolyte present at a concentration far in excess that of the reacting ionic species under investigation. Inert background electrolyte is sometime called inert background solution or supporting electrolyte which is defined as electrolyte which does not react with any of reacting species such as metal ion, ligand or metal-ligand species in the equilibrium being studied. The main function of the inert background electrolyte is to keep the overall ionic strength and activity coefficient constant. Properties of the chosen inert background electrolyte must meet the following requirements

1. a strong and non reacting (inert) electrolyte,
2. no part of electrolyte involved in equilibrium under investigation,
3. its cation must not associate with the ligand and with the complex species,
4. its anion must not associate with the central metal ion and with the complex species,

5. redox reaction must not occur between the constituents of the inert electrolyte and the central ion or ligand,
6. its solubility has to be large enough,
7. its contribution to the measured physical or chemical property must be negligible.

Inert background electrolytes that are commonly used in aqueous solvent are sodium salts such as the perchlorate or nitrate e.g. sodium perchlorate ($NaClO_4$), sodium nitrate ($NaNO_3$), perchlorate is usually more suitable than any other ions. Sodium chloride (NaCl) has been used as an inert background electrolyte, but its use is less common than perchlorate or nitrate because chloride ions often form complexes with metal ions under study. Potassium salts such as potassium nitrate (KNO_3) and potassium chloride (KCl) have also been used occasionally, but potassium perchlorate ($KClO_4$) is unsuitable due to its low solubility in water [17].

In non-aqueous electrolyte such a methanolic and ethanolic solvents, quaternary ammonium salts [18-19] of perchlorate , chloride, nitrate or trifate such as tetraethylammonium perchlorate (EtN_4ClO_4), tetramethylammonium chloride (MeN_4Cl) and tetrabuthylammonium trifluoromethanesulfonate ($BuN_4CF_3SO_3$) are usually supplied. It is found that MeN_4Cl is not suitable for investigation of complex formation in the methanolic solution, because chloride can easily form complex(es) with many metal ions. The background electrolytes for basicity study of the ligands and their complexation in the ethanolic solution is the tetramethylammonium nitrate (MeN_4NO_3). For many equilibrium studies of the ligands and their complexes with metal ions in acetonitrile solution, the MeN_4ClO_4 and BuN_4ClO_4 are suitable background electrolytes. The $BuN_4CF_3SO_3$ was recently used in methanolic solution and introduced by reference 19. The $BuN_4CF_3SO_3$ was used by the reason of avoiding the explosive substance such as perchlorate salts.

2.5 Quantum Chemical Theory

2.5.1 Exact solutions to the Schrödinger equation

The Schrödinger equation can be solved exactly for only a few problems, such as a particle in a box, the harmonic oscillator, the particle on a ring, the particle on a sphere and the hydrogen atom, all of which are dealt with in introductory textbooks. A common feature of these problems is that it is necessary to impose certain requirements (often called boundary conditions) on possible solutions to the equation. Thus, for a particle in a box with infinitely high walls, the wavefunction is required to go to zero at the boundaries. For a particle on a ring the wavefunction must have a periodicity of 2π because it must repeat every traversal of the ring. An additional requirement on solutions to the Schrödinger equation is that the wavefunction at a point r when multiplied by its complex conjugate is the probability of finding the particle at the point (this is the Born interpretation of the wavefunction). The square of an electronic wavefunction thus gives the electron density at any given point. If we integrate the probability of finding the particle over all space, then the result must be one as the particle must be somewhere:

$$\int \Psi^* \Psi d\tau = 1 \qquad (2.31)$$

Indicates that the integration is over all space. Wavefunctions which satisfy this condition are said to be normalised. It is usual to require the solutions to the Schrödinger equation to be orthogonal:

$$\int \Psi_m^* \Psi_n d\tau = 0 \ (m \neq n) \qquad (2.32)$$

A convenient way to express both the orthogonality of different wavefunctions and the normalisation conditions uses the Kronecker delta:

$$\int \Psi_m^* \Psi_n d\tau = \delta_{mn} \qquad (2.33)$$

When used in this context, the Kronecker delta can be taken to have a value of one if m equals n and zero otherwise. Wavefunctions that are both orthogonal and normalised are said to be orthonormal.

2.5.2 The Born-Oppenheimer approximation

It was stated above that the Schrödinger equation can not be solved exactly for any molecular systems. However, it is possible to solve the equation exactly for the simplest molecular species, H_2^+ (and isotopically equivalent species such as HD^+), when the motion of the electrons is decoupled from the motion of the nuclei in accordance with the Born-Oppenheimer approximation. The masses of the nuclei are much greater than the masses of the electrons (the resting mass of the lightest nucleus, the proton, is 1836 times heavier than the resting mass of the electron). This means that the electrons can adjust almost instantaneously to any changes in the positions of the nuclei. The electronic wavefunction thus depends only on the positions of the nuclei and not on their momenta. Under the Born-Oppenheimer approximation the total wavefunction for the molecule can be written in the following form:

$$\Psi_{tot}(\text{nuclei,electrons}) = \Psi(\text{electrons})\,\Psi(\text{nuclei}) \qquad (2.34)$$

The total energy equals the sum of the nuclear energy (the electrostatic repulsion between the positively charged nuclei) and the electronic energy. The electronic energy comprises the kinetic and potential energy of the electrons moving in the electrostatic field of the nuclei, together with electron-electron repulsion: E_{tot} = E(electrons) + E(nuclei).

When the Born-Oppenheimer approximation is used we concentrate on the electronic motions; the nuclei are considered to be fixed. For each arrangement of the nuclei the Schrödinger equation is solved for the electrons alone in the field of the nuclei. If it is desired to change the nuclear positions then it is necessary to add the nuclear repulsion to the electronic energy in order to calculate the total energy of the configuration.

2.5.3 The Hartree-Fock equations

In our hydrogen molecule calculation the molecular orbitals were provided as input, but in most electronic structure calculations we are usually trying to

calculate the molecular orbitals. How do we go about this? We must remember that for many-body problems there is no "correct" solution; we therefore require some means to decide whether one proposed wavefunction is "better" than another. Fortunately, the *variation theorem* provides us with a mechanism for answering this question. The theorem states that the energy calculated from an approximation to the true wavefunction will always be greater than the true energy. Consequently, the better the wavefunction, the lower the energy. The "best" wayefunction is obtained when the energy is a minimum. At a minimum, the first derivative of the energy, δE will be zero. The Hartree-Fock equations are obtained by imposing this condition on the expression for the energy, subject to the constraint that the molecular orbitals remain orthonormal. The orthonormality corfdition written in terms of the overlap *integral*, S_{ij}, between two orbitals i and j. Thus

$$S_{ij} = \int \chi_i \chi_j d\tau = \delta_{ij} \left(\delta_{ij} \text{ is the Kronecker delta}\right) \qquad (2.35)$$

This type of constrained minimisation problem can be tackled using the method of Lagrange multipliers. In this approach (see section a brief introduction to Lagrange multipliers) the derivative of the function to be minimised is added to the derivatives of the constraint(s) multiplied by a constant called a Lagrange multiplier. The sum is then set equal to zero. If the Lagrange multiplier for each of the orthonormality conditions is written λ_{ij}, then:

$$\delta E + \delta \sum_i \sum_j \lambda_{ij} S_{ij} = 0 \qquad (2.36)$$

In the Hartree-Fock equations the Lagrange multipliers are actually written $-2\varepsilon_{ij}$ to reflect the fact that they are related to the molecular orbital energies. The equation to be solved is thus:

$$\delta E - 2\delta \sum_i \sum_j \varepsilon_{ij} S_{ij} = 0 \qquad (2.37)$$

We will not describe in detail how this equation is solved, as it is rather complicated. However, a qualitative picture is possible. The major difference between polyelectronic systems and systems with single electrons is the presence of

interactions between the electrons, which as we have seen are expressed as Coulomb and exchange integrals. Suppose we are given the task of finding the "best" (i.e. lowest energy) wavefunction for a polyelectronic system. We wish to retain the orbital picture of the system, in which single electrons are assigned to individual spin orbitals. The problem is to find a solution which simultaneously enables all the electronic motions to be taken into account, as a change in the spin orbital for one electron will influence the behavior of an electron in another spin orbital due to the coupling of the electronic motions. We concentrate on a single electron in a spin orbital χ_i in the field of the nuclei and the other electrons in their (fixed) spin orbitals χ_j. The Hamiltonian operator for the electron in χ_i contains three terms appropriate to the three different contributions to the energy that were identified above (core, Coulomb, exchange). The result can be written as an integro-differential equation for χ_i that has the following form:

$$\left[-\frac{1}{2}\nabla_i^2-\sum_{A=1}^{M}\frac{Z_A}{r_{1A}}\right]\chi_1(1)+\sum_{j\neq 1}\left[\int d\tau_2\chi_j(2)\chi_j(2)\frac{1}{r_{12}}\right]\chi_i(1) -\sum_{j\neq 1}\left[\int d\tau_2\chi_j(2)\chi_i(2)\frac{1}{r_{12}}\right]\chi_i(1)=\sum_j\varepsilon_{ij}\chi_j(1) \tag{2.38}$$

This expression can be tidied up by introducing three operators that represent the contributions to the energy of the spin orbital Xi in the "frozen" system:

The core Hamiltonian operator, $H^{core}(l)$

$$H^{core}(1)=-\frac{1}{2}\nabla_i^2-\sum_{A=1}^{M}\frac{Z_A}{r_{1A}} \tag{2.39}$$

In the absence of any interelectronic interactions this would be the only operator present, corresponding to the motion of a single electron moving in the field of the bare nuclei.

The Coulomb operator, $J_j(l)$

$$J_j(1)=\int d\tau_2\chi(2)\frac{1}{r_{12}}\chi_j(2) \tag{2.40}$$

This operator corresponds to the average potential due to an electron in χ_j. The exchange operator $H_j(l)$

$$H_j(1)\chi_i(1)=\left[\int d\tau_2 \chi_j(2)\frac{1}{r_{12}}\chi_i(2)\right]\chi_j(1) \qquad (2.41)$$

The form of this operator is rather unusual, insofar as it must be defined in terms of its effect when acting on the spin orbital χ_i. Equation (2.38) can thus be written:

$$H^{core}(1)\chi_i(1)+\sum_{j\neq i}^{N}J_j(1)\chi_i(1)-\sum_{j=1}^{N}H_j(1)\chi_i(1)=\sum_j \varepsilon_{ij}\chi_j(1) \qquad (2.42)$$

Making use of the fact that $\{J_j(l)-H^{core}(1)\}\chi_i(1) = 0$ leads to the following form:

$$\left[H^{core}(1)+\sum_{j=1}^{N}\{J_j(1)-H_j(1)\}\right]\chi_i(1)=\sum_{j=1}^{N}\varepsilon_{ij}\chi_j(1) \qquad (2.43)$$

Or, more simply:

$$f_i\chi_i=\sum_j \varepsilon_{ij}\chi_j \qquad (2.44)$$

f_i is called the Fock operator:

$$f_i(1)=H^{core}(1)+\sum_{j=1}^{N}\{J_j(1)-H_j(1)\} \qquad (2.45)$$

For a closed-shell system, the Fock operator has the following form:

$$f_i(1)=H^{core}(1)+\sum_{j=1}^{N/2}\{2J_j(1)-H_j(1)\} \qquad (2.46)$$

The Fock operator is an effective one-electron Hamiltonian for the electron in the polyelectronic system. However, written in this form of equation (2.44), the Hartree-Fock equations do not seem to be particularly useful: on the left-hand side we have the Fock operator acting on the molecular orbital χ_i, but this returns not the molecular orbital multiplied by a constant as in a normal eigenvalue equation, but rather a series of orbitals χ_j' multiplied by some unknown constants ε_{ij}. This is because the solutions to the Hartree-Fock equations are not unique. We have already seen that the value of a determinant is unaffected when the multiple of any column is added to another

column. If such a transformation is performed on the Slater determinant, then a different set of constants ε_{ij}' would be obtained with the spin orbitals χ_i being linear combinations of the first set. Certain trans-formations give rise to localised orbitals which are particularly useful for understanding the chemical nature of the system. These localised orbitals are no more "correct" than a delocalised set. Fortunately, it is possible to manipulate the equations (2.44) mathematically so that the Lagrangian multipliers are zero unless the indices i and j are the same. The Hartree-Fock equations then take on the standard eigenvalue form:

$$f_i\chi_i = \varepsilon_i\chi_i \tag{2.47}$$

Recall that insetting up these equations, each electron has been assumed to move in a "fixed" field comprising the nuclei and the other electrons. This has important implications for the way in which we attempt to find a solution, for any solution that we might find by solving the equation for one electron will naturally affect the solutions for the other electrons in the system. The general strategy is called a self-consistent field (SCF) approach. One way to solve these equations is as follows. First, a set of trial solutions χ_i to the Hartree-Fock eigenvalue equations are obtained. These are used to calculate the Coulomb and exchange operators. The Hartree-Fock equations are solved, giving a second set of solutions χ_i, which are used in the next iteration. The SCF method thus gradually refines the individual electronic solutions that correspond to lower and lower total energies until the point is reached at which the results for all the electrons are unchanged, when they are said to be self-consistent.

2.5.3.1 Hartree-Fock calculations for atoms and Slater's rules

The Hartree-Fock equations are usually solved in different ways for atoms and for molecules. For atoms, the equations can be solved numerically if it is assumed that the electron distribution is spherically symmetrical. However, these numerical solutions are not particularly useful. Fortunately, analytical approximations to these solutions, which are very similar to those obtained for the hydrogen atom, can be used with considerable success. These approximate analytical functions thus have the form:

$$\psi = R_{nl}(r)\,Y_{lm}(\theta,\phi) \tag{2.48}$$

Y is a spherical harmonic (as for the hydrogen atom) and R is a radial function. The radial functions obtained for the hydrogen atom cannot be used directly for polyelectronic atoms due to the screening of the nuclear charge by the inner shell electrons, but the hydrogen atom functions are acceptable if the orbital exponent is adjusted to account for the screening effect. Even so, the hydrogen atom functions are not particularly convenient to use in molecular orbital calculations due to their complicated functional form. Slater [1930] suggested a simpler analytical form for the radial functions:

$$R_{nl}(r) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2}\, r^{n-1} e^{-\zeta r} \tag{2.49}$$

These functions are universally known as Slater-type orbitals (STOs) and are just the leading term in the appropriate Lagrange's polynomials. The first three Slater functions are as follows:

$$R_{1s}(r) = 2\zeta^{3/2} e^{-\zeta r} \tag{2.50}$$

$$R_{2s}(r) = R_{2p}(r) = \left(\frac{4\zeta^5}{3}\right)^{1/2} r e^{-\zeta r} \tag{2.51}$$

$$R_{3s}(r) = R_{3p}(r) = R_{3d}(r) = \left(\frac{8\zeta^7}{45}\right)^{1/2} r^2 e^{-\zeta r} \tag{2.52}$$

To obtain the whole orbital we must multiply R(r) by the appropriate angular part. For example, we would use the following expressions for the I s, 2s and 2p, orbitals:

$$\phi_{1s}(r) = \sqrt{(\zeta^3/\pi)}\exp(-\zeta r) \tag{2.53}$$

$$\phi_{2s}(r) = \sqrt{(\zeta^5/3\pi)}\, r \exp(-\zeta r) \tag{2.54}$$

$$\phi_{2p_z}(r) = \sqrt{(\zeta^5/\pi)}\exp(-\zeta r)\cos\theta \tag{2.55}$$

Slater provided a series of empirical rules for choosing the orbital exponents ζ, which are given by:

$$\zeta = \frac{Z - \sigma}{n^*} \qquad (2.56)$$

Z is the atomic number and a is a *shielding constant*, determined as below. n^* is an effective principal quantum number which takes the same value as the true principal quantum number for $n = 1$, 2 or 3, but for $n = 4$, 5, 6 has the values 3.7, 4.0, 4.2 respectively. The shielding constant is obtained as follows:

First divide the orbitals into the following groups:

(1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); (5s, 5p); (5d)

For a given orbital, a is obtained by adding together the following contributions:

(a) zero from an orbital further from the nucleus than those in the group;

(b) 0.35 from each other electron in the same group, but if the other orbital is the 1s then the contribution is 0.3;

(c) 1.0 for each electron in a group with a principal quantum number 2 or more fewer than the current orbital;

(d) for each electron with a principal quantum number 1 fewer than the current orbital: 1.0 if the current orbital is d or f; 0.85 if the current orbital is s or p.

The shielding constant for the valence electrons of silicon is obtained using Slater's rules as follows. The electronic configuration of Si is $(1s^2)(2S^2\ 2P^6)$ $(3S^2\ 3p^2)$. We therefore count 3 x 0.35 under rule (b), 2.0 under rule (c), and 8 x 0.85 under rule (d), giving a total of 9.85. When subtracted from the atomic number (14) this gives 4.15 for the value of $Z - \sigma$.

2.5.3.2 Linear combination of atomic orbitals (LCAO) in Hartree-Fock theory

Direct solution of the Hartree-Fock equations is not a practical proposition for molecules and so it is necessary to adopt an alternative approach. The most popular strategy is to write each spin orbital as a linear combination of single electron orbitals:

$$\psi_i = \sum_{\nu=1}^{K} c_{\nu i}\phi_\nu \qquad (2.57)$$

The one-electron orbitals ϕ_ν are commonly called basis functions and often correspond to the atomic orbitals. We will label the basis functions with the Greek letters μ, ν, λ and σ. In the case of equation (2.57) there are **K** basis functions and we should therefore expect to derive a total of **K** molecular orbitals (although not all of these will necessary be occupied by electrons). The smallest number of basis functions for a molecular system will be that which can just accommodate all the electrons in the molecule. More sophisticated calculations use more basis functions than a minimal set. At the Hartree-Fock limit the energy of the system can be reduced no further by the addition of any more basis functions; however, it may be possible to lower the energy below the Hartree-Fock limit by using a functional form of the wavefunction that is more extensive than the single Slater determinant.

In accordance with the variation theorem we require the set of coefficients c_{vi} that gives the lowest energy wavefunction, and some scheme for changing the coefficients to derive that wavefunction. For a given basis set and a given functional form of the wavefunction (i.e. a Slater determinant) the best set of coefficients is that for which the energy is a minimum, at which point

$$\frac{\partial E}{\partial c_{\nu i}} = 0$$

for all coefficients c_{vi}. The objective is thus to determine the set of coefficients that gives the lowest energy for the system.

2.5.3.3 Closed-shell systems and the Roothaan-Hall equations

We shall initially consider a closed-shell system with N electrons in N/2 orbitals. The derivation of the Hartree-Fock equations for such a system was first proposed by Roothaan [1951] and (independently) by Hall [1951]. The resulting equations are known as the Roothaan equations or the Roothaan- Hall equations. Unlike the integro-differential form of the Hartree-Fock equations, equation (2.38), Roothaan and Hall recast the equations in matrix form which can be solved using standard techniques and

can be applied to systems of any geometry. We shall identify the major steps in the Roothaan approach, starting with the expression for the Hartree-Fock energy for our closed-shell system, equation (2.58):

$$E = 2\sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\left(2J_{ij} - K_{ij}\right) \tag{2.58}$$

The corresponding Fock operator is (equation 2.46):

$$f_i(1) = H^{core}(1) + \sum_{j=1}^{N/2}\left\{2J_j(1) - H_j(1)\right\} \tag{2.59}$$

We now introduce the atomic orbital expansion for the orbitals ψ_i and substitute for the corresponding spin orbital χ_i into the Hartree-Fock equation, { }

$$f_i(1)\sum_{\nu=1}^{K} c_{\nu i}\phi_\nu(1) = \varepsilon_i \sum_{\nu=1}^{K} c_{\nu i}\phi_\nu(1) \tag{2.60}$$

Premultiplying each side by $\phi_\mu(1)$ (where ϕ_μ is also a basis function) and integrating gives the following matrix equation:

$$\sum_{\nu=1}^{K} c_{\nu i}\int d\nu_1 \phi_\mu(1) f_i(1)\phi_\nu(1) = \varepsilon_i \sum_{\nu=1}^{K} c_{\nu i}\int d\nu_1 \phi_\mu(1)\phi_\nu(1) \tag{2.61}$$

$\int d\nu_1 \phi_\mu(1)\phi_\nu(1)$ is the overlap integral between the basis functions μ and ν, written $S_{\mu\nu}$. Unlike the molecular orbitals which will be required to be orthonormal, the overlap between two basis functions is not necessarily zero (for example, they may be located on different atoms).

The elements of the Fock matrix are given by

$$F_{\mu\nu} = \int d\nu_1 \phi_\mu(1) f_i(1)\phi_\nu(1) \tag{2.62}$$

The Fock matrix elements for a closed-shell system can be expanded as follows by substituting the expression for the Fock operator:

$$\begin{aligned} F_{\mu\nu} = {} & \int d\nu_1 \phi_\mu(1) H^{core}(1)\phi_\nu(1) \\ & + \sum_{j=1}^{N/2}\int d\nu_1 \phi_\mu(1)\left[2J_j(1) - H_j(1)\right]\phi_\nu(1) \end{aligned} \tag{2.63}$$

The elements of the Fock matrix can thus be written as the sum of core, Coulomb and exchange contributions. The core contribution is:

$$\int dv_1 \phi_\mu(1) H^{core}(1) \phi_\nu(1)$$
$$= \int dv_1 \phi_\mu(1) \left[-\frac{1}{2}\nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{|r_1 - R_A|} \right] \phi_\nu(1) = H_{\mu\nu}^{core} \qquad (2.64)$$

The core contributions thus require the calculation of integrals that involve basis functions on up to two centers (depending upon whether ϕ_μ and ϕ_ν are centerd on the same nucleus or not). Each element $H_{\mu\nu}^{core}$ can in turn be obtained as the sum of a kinetic energy integral and a potential energy integral corresponding to the two terms in the one-electron Hamiltonian.

The Coulomb and exchange contributions to the Fock matrix element $F_{\mu\nu}$ are together given by:

$$\sum_{j=1}^{N/2} \int dv_1 \phi_\mu(1) [2J_j(1) - H_j(1)] \phi_\nu(1) \qquad (2.65)$$

Recall that the Coulomb operator $J_j(1)$ due to interaction with a spin orbital χ_j is given by

$$J_j(1) = \int d\tau_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \qquad (2.66)$$

We need to write each of the two occurrences of the spin orbital χ_j in this integral in terms of the appropriate linear combination of basis functions:

$$J_j(1) = \int d\tau_2 \sum_{\sigma=1}^{K} c_{\sigma j} \phi_\sigma(2) \frac{1}{r_{12}} \sum_{\lambda=1}^{K} c_{\lambda j} \phi_\lambda(2) \qquad (2.67)$$

We have used the indices σ and λ for the basis functions here. Similarly, the exchange contribution can be written:

$$H_j(1) \chi_i(1) = \left[\int d\tau_2 \sum_{\sigma=1}^{K} c_{\sigma j} \phi_\sigma(2) \frac{1}{r_{12}} \chi_i(2) \right] \sum_{\lambda=1}^{K} c_{\lambda j} \phi_\lambda(2) \qquad (2.68)$$

When the Coulomb and exchange operators are expressed in terms of the basis functions and the orbital expansion is substituted for χ_i, then their contributions to the Fock matrix element $F_{\mu\nu}$ take the following form:

$$\sum_{j=1}^{N/2} \int dv_1 \, \phi_\mu(1)\left[2J_i(1) - H_j(1)\right]\phi_\nu(1)$$

$$= \sum_{J=1}^{N/2}\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} C_{\lambda j} c_{\sigma j} \left[\begin{array}{l} 2\int dv_1 dv_2 \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2) \\ -\int dv_1 dv_2 \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2) \end{array} \right] \quad (2.69)$$

$$= \sum_{J=1}^{N/2}\sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} C_{\lambda j} c_{\sigma j} \left[2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)\right]$$

We have used the shorthand notation for the integrals in the final expression. Note that the two-electron integrals may involve up to four different basis functions (μ, ν, λ, σ), which may in turn be located at four different centers. This has important consequences for the way in which we try to solve the equations.

It is helpful to simplify equation (2.69) by introducing the *charge density matrix*, **P**, whose elements are defined as:

$$P_{\mu\nu} = 2\sum_{i=1}^{N/2} c_{\mu i} c_{\nu i} \quad \text{and} \quad P_{\lambda\sigma} = 2\sum_{i=1}^{N/2} c_{\lambda i} c_{\sigma i} \qquad (2.70)$$

Note that the summations are over the N/2 occupied orbitals. Other properties can be calculated from the density matrix; for example, the electronic energy is:

$$E = \frac{1}{2}\sum_{\mu=1}^{K}\sum_{\nu=1}^{K} P_{\mu\nu}\left(H_{\mu\nu}^{core} + F_{\mu\nu}\right) \qquad (2.71)$$

The electron density at a point **r** can also be expressed in terms of the density matrix:

$$\rho(r) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} P_{\mu\nu}\phi_\mu(r)\phi_\nu(r) \qquad (2.72)$$

The expression for each element $F_{\mu\nu}$ of the Fock matrix elements for a closed- shell system of N electrons then becomes:

$$F_{\mu\nu} = \mathrm{H}_{\mu\nu}^{core} + \sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} \mathrm{P}_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)\right] \tag{2.73}$$

This is the standard form for the expression for the Fock matrix in the Roothaan-Hall equations.

2.5.3.4 Solving the Roothaan-Hall equations

The Fock matrix is a K x K square matrix that is symmetric if real basis functions are used. The Roothaan-Hall equations (2.59) can be conveniently written as a matrix equation:

$$\mathbf{FC = SCE} \tag{2.74}$$

The elements of the K x K matrix C are the coefficients c_{vi} :

$$C = \begin{pmatrix} c_{1,1} & c_{1,2} & \cdots & c_{1,K} \\ c_{2,1} & c_{2,2} & \cdots & c_{2,K} \\ \vdots & \vdots & & \vdots \\ c_{K,1} & c_{K,2} & \cdots & c_{K,K} \end{pmatrix} \tag{2.75}$$

E is a diagonal matrix whose elements are the orbital energies:

$$E = \begin{pmatrix} \varepsilon_1 & 0 & \ldots & 0 \\ 0 & \varepsilon_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & \varepsilon_K \end{pmatrix} \tag{2.76}$$

Let us consider how we might solve the Roothaan-Hall equations and thereby obtain the molecular orbitals. The first point we must note is that the elements of the Fock matrix, which appear on the left hand side of equation (2.74), depend on the molecular orbital coefficients c_{vi}, which also appear on the right-hand side of the equation. Thus an iterative procedure is required to find a solution.

The one-electron contributions $H_{\mu\nu i}^{core}$ due to the electrons moving in the field of the bare nuclei do not depend on the basis set coefficients and remain unchanged throughout the calculation. However, the Coulomb and exchange contributions do depend on the coefficients and we would expect these to vary throughout the calculation. The individual two-electron integrals $(\mu\nu|\lambda\sigma)$ are, however, constant throughout the calculation. An obvious strategy is thus to calculate and store these integrals for later use.

Having written the Roothaan-Hall equations in matrix form we would obviously like to solve them using standard matrix eigenvalue. However, standard eigenvalue methods would require an equation of the form FC = CE. The Roothaan-Hall equations only adopt such a form if the overlap matrix, S, is equal to the unit matrix, I (in which all diagonal elements are equal to 1 and all off-diagonal elements are zero). The functions ϕ are usually normalised but they are not necessarily orthogonal (for example, because they are located on different atoms) and so there will invariably be non- zero off-diagonal elements of the overlap matrix. To solve the Roothaan-Hall equations using standard methods they must be transformed. This corresponds to transforming the basis functions so that they form an orthonorinal set. We seek a matrix X, such that $X^TSX = I$. X^T is the transpose of X, obtained by interchanging rows and columns. There are various ways in which X can be calculated; in symmetric orthogonalisation, the overlap matrix is diagonalised. Diagonalisation involves finding the matrix U such that

$$\mathbf{U}^{\mathbf{T}}\mathbf{S}\mathbf{U} = \boldsymbol{D} = diag(\lambda_1 \ldots \lambda_K) \qquad (2.77)$$

D is the diagonal matrix containing the eigenvalues λ_i of S, and U contains the eigenvectors of S. U^T is the transpose of the matrix U. (This expression is often written $U^{-1}SU = D$ since for real basis functions $U^{-1} = U^T$.) Then the matrix X is given by $X = UD^{-1/2}U^T$ where, $D^{-1/2}$ is formed from the inverse square roots of D. We shall write X as $S^{-1/2}$, as it can be considered to be the inverse square root of the overlap matrix: $S^{-1/2}SS^{-1/2} = I$.

The Roothaan-Hall equations can now be manipulated as follows. Both sides of equation (2.74) are pre-multiplied by the matrix $S^{-1/2}$:

$$S^{-1/2}FC = S^{-1/2} = SCE = S^{1/2}CE \qquad (2.78)$$

Inserting the unit matrix, in the form $S^{-1/2}S^{1/2}$ into the left-hand side gives:

$$S^{-1/2}F\left(S^{-1/2}S^{1/2}\right)C = S^{1/2}CE \qquad (2.79)$$

or

$$S^{-1/2}FS^{-1/2}\left(S^{1/2}C\right) = \left(S^{1/2}C\right)E \qquad (2.80)$$

Equation (2.80) can be written FC'=C'E, where $F' = S^{-1/2}FS^{-1/2}$ and $C' = S^{1/2}C$.

The matrix equation FC'=C'E can be solved using standard methods; a solution only exists if the determinant |F' - EI| equals zero. In simple cases this can be done by multiplying out the determinant to give a polynomial (the secular equation) whose roots are the eigenvalues ε_i, but for large matrices a much more practical approach involves the diagonalisation of F'. The matrix of coefficients, C', are the eigenvectors of F. The basis function coefficients C can then be obtained from C' using $C=S^{-1/2}C'$. A common scheme for solving the Roothaan-Hall equations is thus as follows:

1. Calculate the integrals to form the Fock matrix, F.
2. Calculate the overlap matrix, S.
3. Diagonalise S.
4. Form $S^{-1/2}$.
5. Guess, or otherwise calculate an initial density matrix, P.
6. Fomi the Fock matrix using the integrals and the density matrix P.
7. Form $F' = S^{-1/2}FS^{-1/2}$.
8. Solve the secular equation |F' – EI| = 0 to give the eigenvalues E and the eigenvectors C' by diagonalising F'.
9. Calculate the molecular orbital coefficients, C from $C= S^{-1/2}C'$.
10. Calculate a new density matrix, P, from the matrix C.
11. Cheek for convergence. If the calculation has converged, stop. Otherwise repeat from step 6 using the new density matrix P.

This procedure requires an initial guess of the density matrix, P. The simplest approach is to use the null matrix, which corresponds to ignoring all the electron- electron terms so that the electrons just experience the bare nuclei. This can sometimes lead to convergence problems which may be prevented if a lower level of theory (such as semi-empirical or extended Hückel) is used to provide the initial guess. Moreover, a better guess may enable the calculation to be performed more quickly. A variety of criteria can be used to establish whether the calculation has converged or not. For example, the density matrix can be compared with that from the previous iteration, and/or the change in energy can be monitored together with the basis set coefficients.

The result of a Hartree-Fock calculation is a set of K molecular orbitals where K is the number of basis functions in the calculation. The N electrons are then fed into these orbitals in accordance with the Aufbau principle, two electrons per orbital, starting with the lowest energy orbitals. The remaining orbitals do not contain any electrons; these are known as the virtual orbitals. Alternative electronic configurations can be generated by exciting electrons from the occupied orbitals to the virtual orbitals.

A Hartree-Fock calculation provides a set of orbital energies, Fi. What is the significance of these? The energy of an electron in a spin orbital is calculated by adding the core interaction $H_{\mu\nu}^{core}$ to the Coulomb and exchange interactions with the other electrons in the system:

$$\varepsilon_i = H_{ii}^{core} + \sum_{j=1}^{N/2} \left(2J_{ij} - K_{ij}\right) \qquad (2.81)$$

The total electronic energy of the ground state is given by equation (2.82):

$$E = 2\sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\left(2J_{ij} - K_{ij}\right) \qquad (2.82)$$

The total energy is therefore not equal to the sum of the individual orbital energies, but is related as follows:

$$E = \sum_{i=1}^{N} \varepsilon_i - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \left(2J_{ij} - K_{ij}\right) \tag{2.83}$$

The reason for the discrepancy is that the individual orbital energies include contributions from the interaction between that electron and all the nuclei and all other electrons in the system. The Coulomb and exchange interactions between pairs of electrons are therefore counted twice when summing the individual orbital energies.

2.5.3.5 A simple illustration of the Roothaan-Hall approach

We will illustrate the stages involved in the Roothaan-Hall approach using the helium hydrogen molecular ion, HeH^+ as an example. This is a two-electron system. Our objective here is to show how the Roothaan-Hall method can be used to derive the wavefunction, for a fixed internuclear distance of 1 A^o.We use HeH^+ rather than H_2 as our system as the lack of symmetry in HeH^+ makes the procedure more informative. There are two basis functions, ISA (centerd on the helium atom) and 1 s_B (on the hydrogen). The numerical values of the integrals that we shall use in our calculation were obtained using a Gaussian series approximation to the Slater. This detail need not concern us here. Each wavefunction is expressed as a linear combination of the two 1 s atomic orbitals centerd on the nuclei A and B:

$$\begin{aligned} \psi_1 &= c_{1A} 1s_A + c_{1B} 1s_B \\ \psi_2 &= c_{2A} 1s_A + c_{2B} 1s_B \end{aligned} \tag{2.84}$$

First, it is necessary to calculate the various one- and two-electron integrals and to formulate the Fock and overlap matrices, each of which will be a 2 x 2 symmetric matrix (as there are two orbitals in the basis set). The diagonal elements of the overlap matrix, 8, are equal to 1.0 as each basis function is normalised; the off-diagonal elements have smaller, but non-zero values that are equal to the overlap between $1S_A$ and $1s_B$ for the internuclear distance chosen. The matrix S is:

$$S = \begin{pmatrix} 1.0 & 0.392 \\ 0.392 & 1.0 \end{pmatrix} \tag{2.85}$$

The core contributions $H_{\mu\nu}^{core}$ can be calculated as the sum of three 2 x 2 matrices comprising the kinetic energy (T) and nuclear attraction terms for the two nuclei A and B (V_A and V_B). The elements of these three matrices are obtained by evaluating the following integrals:

$$\begin{aligned} T_{\mu o} &= \int dv_1 \phi_\mu(1)\left(-\frac{1}{2}\nabla^2\right)\phi_\nu(1) \\ V_{A,\mu\nu} &= \int dv_1 \phi_\mu(1)\left(-\frac{Z_A}{r_{1A}}\right)\phi_\nu(1) \\ V_{B,\mu\nu} &= \int dv_1 \phi_\mu(1)\left(-\frac{Z_B}{r_{1B}}\right)\phi_\nu(1) \end{aligned} \qquad (2.86)$$

The matrices are:

$$\begin{aligned} T &= \begin{pmatrix} 1.412 & 0.081 \\ 0.081 & 0.760 \end{pmatrix} \qquad V_A = \begin{pmatrix} -3.344 & -0.758 \\ -0.758 & -1.026 \end{pmatrix} \\ V_B &= \begin{pmatrix} -0.525 & -0.308 \\ -0.308 & -1.227 \end{pmatrix} \end{aligned} \qquad (2.87)$$

H^{core} is the sum of these three:

$$H^{core} = \begin{pmatrix} -2.457 & -0.985 \\ -0.985 & -1.493 \end{pmatrix} \qquad (2.88)$$

As far as the two-electron integrals are concerned, with two basis functions there are a total of 16 possible two-electron integrals. There are however only six unique two-electron integrals as the indices can be permuted as follows:

(i) $(1S_A1S_A|1S_A1S_A) = 1.056$

(ii) $(1S_A1S_A|1S_A1S_B) = (1S_A1S_A|1S_B1S_A) = (1S_A1S_B|1S_A1S_A)$
$= (1S_B1S_A|1S_A1S_A) = 0.303$

(iii) $(1S_A1S_B|1S_A1S_B) = (1S_A1S_B|1S_B1S_A) = (1S_B1S_A|1S_A1S_B)$
$= (1S_B1S_A|1S_B1S_A) = 0.1\ 12$

(iv) $(1S_A1S_A|1S_B1S_B) = (1S_B1S_B|1S_A1S_A) = 0.496$

(v) $(1S_A1S_B|1S_B1S_B) = (1S_B1S_A|1S_B1S_B) = (1S_B1S_B|1S_A1S_B)$
$= (1S_B1S_B|1S_B1S_A) = 0.244$

(vi) $(1S_B1S_B|1S_B1S_B) = 0.775$

To reiterate, these integrals are calculated as follows:

$$(\mu\nu|\lambda\sigma) = \iint dv_1 dv_2 \phi_\mu(1)\phi_\nu(1)\frac{1}{r_{12}}\phi_\lambda(2)\phi_\sigma(2) \qquad (2.89)$$

Having calculated the integrals, we are now ready to start the SCF calculation. To formulate the Fock matrix it is necessary to have an initial guess of the density matrix, P. The simplest approach is to use the null matrix in which all elements are zero. In this initial step the Fock matrix F is therefore equal to H^{core}.

The Fock matrix must next be transformed to F' by pre- and post-multiplying by $S^{-1/2}$:

$$S^{-1/2} = \begin{pmatrix} -1.065 & -0.217 \\ -0.217 & 1.065 \end{pmatrix} \qquad (2.90)$$

F' for this first iteration is thus:

$$F' = \begin{pmatrix} -2.401 & -0.249 \\ -0.249 & -1.353 \end{pmatrix} \qquad (2.91)$$

Diagonalisation of F' gives its eigenvalues and eigenvectors which are:

$$\mathrm{E} = \begin{pmatrix} -2.458 & 0.0 \\ 0.0 & -1.292 \end{pmatrix} \qquad C' = \begin{pmatrix} 0.975 & -0.220 \\ 0.220 & 0.975 \end{pmatrix} \qquad (2.91)$$

The coefficients C are obtained from $C=S^{-1/2}C'$ and are thus:

$$C = \begin{pmatrix} 0.991 & -0.446 \\ 0.220 & 1.087 \end{pmatrix} \qquad (2.93)$$

To formulate the density matrix P we need to identify the occupied orbital(s). With a two-electron system both electrons occupy the orbital with the lowest energy (i.e. the orbital with the lowest eigenvalue). At this stage the lowest energy orbital is:

$$\psi = 0.991\ 1s_A + 0.022\ 1s_B \qquad (2.94)$$

The orbital is composed largely of the s orbital on the helium nucleus; in the absence of any electron-electron repulsion the electrons tend to congregate near

the nucleus with the larger charge. The density matrix corresponding to this initial wavefunction is:

$$P = \begin{pmatrix} 1.964 & 0.044 \\ 0.044 & 0.001 \end{pmatrix} \tag{2.95}$$

The new Fock matrix is formed using P and the two-electron integrals together with H^{core}. For example, the element F_{11} is given by:

$$\begin{aligned} F_{11} = H_{11}^{core} &+ P_{11}\left[(1s_A 1s_A|1s_A 1s_A) - \frac{1}{2}(1s_A 1s_A|1s_A 1s_A)\right] \\ &+ P_{12}\left[(1s_A 1s_A|1s_A 1s_B) - \frac{1}{2}(1s_A 1s_A|1s_A 1s_B)\right] \\ &+ P_{21}\left[(1s_A 1s_A|1s_B 1s_B) - \frac{1}{2}(1s_A 1s_B|1s_A 1s_B)\right] \\ &+ P_{12}\left[(1s_A 1s_A|1s_B 1s_B) - \frac{1}{2}(1s_A 1s_B|1s_A 1s_B)\right] \end{aligned} \tag{2.96}$$

The complete Fock matrix is:

$$F = \begin{pmatrix} -1.406 & -0.690 \\ -0.690 & -0.618 \end{pmatrix} \tag{2.97}$$

The energy that corresponds to this Fock matrix calculated using equation (2.74) is -3.870 Hartrees. In the next iteration, the various matrices are as follows:

$$F' = \begin{pmatrix} -1.305 & -0.347 \\ -0.347 & -0.448 \end{pmatrix} \qquad E = \begin{pmatrix} -1.427 & 0.0 \\ 0.0 & -0.325 \end{pmatrix}$$

$$C' = \begin{pmatrix} 0.943 & -0.334 \\ 0.334 & 0.943 \end{pmatrix} \qquad C = \begin{pmatrix} 0.931 & -0.560 \\ 0.150 & 1.076 \end{pmatrix}$$

$$P = \begin{pmatrix} 1.735 & 0.280 \\ 0.280 & 0.045 \end{pmatrix} \qquad F = \begin{pmatrix} -1.436 & -0.738 \\ -0.738 & -0.644 \end{pmatrix}$$

$$\text{Energy} = -3.909 \text{ Hartrees} \tag{2.98}$$

The calculation proceeds as illustrated in Table 2.1, which shows the variation in the coefficients of the atomic orbitals in the lowest energy wayefunction and the energy for the first four SCF iterations. The energy is converged to six decimal places after six iterations and the charge density matrix after nine iterations.

Table 2.1 Variation in basis set coefficients and electronic energy for the HeH^+ molecule.

Iteration	$C(1S_A)$	$C(1S_B)$	Energy
1	0.991	0.022	-3.870
2	0.931	0.150	-3.909
3	0.915	0.181	-3.911
4	0.912	0.187	-3.911

The final wavefunction still contains a large proportion of the Is orbital on the helium atom, but less than was obtained without the two-electron integrals.

2.5.3.6 Application of the Hartree-Fock equations to molecular systems

We are now in a position to consider how the Hartree-Fock theory we have developed can be used to perform practical quantum mechanical calculations on molecular systems. This is an appropriate place in our discussion to distinguish the two major categories of quantum mechanical molecular orbital calculations: the ab-initio and the semi-empirical methods. Ab-initio strictly means "from the beginning", or "from first principles", which would imply that a calculation using such an approach would require as input only physical constants such as the speed of light, Planck's constant, the masses of elementary particles and so on. Ab-initio in fact usually refers to a calculation which uses the full Hadree-Fock/Roothaan-Hall equations, without ignoring or approximating any of the integrals or any of the terms in the Hamiltonian. The ab-initio methods do rely upon calibration calculations and this has led some quantum chemists, notably Dewar (who has played a large part in the development of semi-empirical methods), to claim that any real difference between the ab-initio and the semi-empirical methods is entirely pedagogical. By contrast, semi-empirical methods simplify the calculations, using parameters for some of the integrals and/or ignoring some of the terms in the Hamiltonian. First we shall consider ab-initio methods.

2.5.4 Basis Set Effects

A basis set is the mathematical description of the orbitals within a system (which in turn combine to approximate the total electronic wavefunction) used to perform the theoretical calculation. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space. In the true quantum mechanical picture, electrons have a finite probability of existing anywhere in space; this limit corresponds to the infinite basis set expansion in the chart we looked at previously. Standard basis sets for electronic structure calculations use linear combinations of gaussian functions to form the orbitals. Gaussain (program) offers a wide range of per-defined basis sets, which may be classified by the number and types of basis functions that they contain. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbitals. These basis functions themselves are composed of a linear combination of gaussian functions; such basis functions are referred to as contracted functions, and the component gaussian functions are referred to as primitives. A basis function consisting of a single gaussian function is termed uncontracted.

2.5.5 Minimal Basis Sets

Minimal basis sets contain the minimum number of basis functions needed for each atom, as in these examples:

H : 1s

C : 1s, 2s, $2p_x$, $2p_y$,$2p_z$

Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set [20] is a minimal basis set (although it is not the smallest possible basis set). It uses three gaussian primitives per basis function, which accounts for the "3G" in its name. "STO" stands for "Slater-type orbitals," and the STO-3 basis set approximates Slater orbitals with gaussian functions.

2.5.6 Split Valence Basis Sets

The first way that a basis set can be made larger is to increase the number of basis functions per atom. Split valence basis sets, such as 3-21G [21-26] and 6-31G [27-31], have two (or more) sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:

H : 1s, 1s'

C : 1s, 2s, 2s', $2p_x$, $2p_x$', $2p_y$, $2p_y$',$2p_z$,$2p_z$'

Where the primed and umprimed orbtals differ in size.

The double zeta basis sets, such as the Dunning-Huzinage basis set [32] (D95), form all molecular orbitals from linear combinations of two sizes of functions for each atomic orbital. Similarly, triple split valence basis sets, like 6-311G [33-40], use three sizes of contracted functions for each orbital-type.

2.5.7 Polarized Basis Sets

Split valence basis sets allow orbitals to change size, but not of change shape. Polarized basis sets remove this limitation by adding orbitals with angular momentum beyond what is required for the ground state to the description of each atom. For example, polarized basis sets add d functions to carbon atoms and f functions to transition metals, and some of them add p functions to hydrogen atoms. So far, the only polarized basis set we've used is 6-31G(d). Its name indicates that it is the 6-31G basis set with d functions added to heavy atoms. This basis set is becoming very common for calculations involving up to medium-sized systems. This basis set is also known as 6-31G*. Another popular polarized basis set is 6-31G(d,p), also known as 6-31G**, which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms.

2.5.8 Diffuse Functions

Diffuse functions are large-size versions of s- and p-type functions (as oppose to the standard valence-size functions). They allow orbitals to occupy a larger region of space. Basis sets with diffuse functions are important for systems where electrons are

relatively far from the nucleus: molecules with lone pairs, anions and other systems with significant negative charge, systems in their excited states, systems with low ionization potentials, descriptions of absolute acidities, and so on.

The 6-31+G(d) basis set is the 6-31G(d) basis set with diffuse functions added to heavy atoms. The double plus version, 6-31++G(d), adds diffuse functions to the hydrogen atoms as well. Diffuse functions on hydrogen atoms seldom make a significant difference in accuracy.

2.5.9 Practical considerations when performing ab inito calculations

Ab inito calculations can be extremely time-consuming, especially when using the higher levels of theory or when the nuclei are free to move, as in a minimisation calculation. Various "tricks" have been developed which can significantly reduce the computational effort involved. Many of these options are routinely available in the major software packages and are invoked by the specification of simple keywords. One common tactic is to combine different levels of theory for the various stages of a calculation. For example, a lower level of theory can be used to provide the initial guess for the density matrix prior to the first SCF iteration. Lower levels of theory can also be used in other ways. Suppose we wish to determine some of the electronic properties of a molecule in a minimum energy structure. Energy minimisation requires that the nuclei move, and is typically performed in a series of steps, at each of which the energy (and frequently the gradient of the energy) must be calculated. Minimisation is therefore a computationally expensive procedure, particularly when performed at the high level of theory. To reduce this computational burden a lower level of theory can be employed for the geometry optimisation. A "single point" calculation using a high level of theory is then performed at the geometry so obtained to give a wavefunction from which the properties are determined. The assumption here of course is that the geometry does not change much between the two levels of theory. Such calculations are denoted by slashes (/). For example, a calculation that is described as "6-31G*/STO-3G" indicates that the geometry was determined using the STO-3G basis set and the wavefunction was obtained using the 6-31G* basis set. Two slashes are used when each calculation is itself described using a slash, such as when

electron correlation methods are used. For example, "MP2/6-31G*//HF/6-31G*" indicates a geometry optimisation using a Hartree-Fock calculation with a 6-31G* basis set followed by a single-point calculation using the MP2 method for incorporating electron correlation, again using a 6-31G* basis set.

2.5.10 Convergence of self-consistent field calculations

In an SCF calculation the wavefunction is gradually refined until self-consistency is achieved. For closed-shell ground-state molecules this is usually quite straight-forward and the energy converges after a few cycles. However, in some cases convergence is a problem, and the energy may oscillate from one iteration to the next or even diverge rapidly. Various methods have been proposed to deal with such situation. A simple strategy is to use an average set of orbital coefficients rather than the set obtained from the immediately preceding iteration. The coefficients in this average set can be weighted according to the energies of zeach iteration. This tends to weed out those coefficients that give rise to higher energies.

The initial guess of the density matrix may influence the convergence of the SCF calculation; a null matrix is the simplest approach, but better results may be obtain by using a density matrix from a calculation performed at a lower level of theory. For example, the density matrix from a semi-empirical calculation may be used as the starting point for an ab initio calculation. Conversely, such an approach may itself lead to problems if there is significant difference between the density matrices for the lower and the higher levels of theory.

A more sophisticated method that has often been very successful is Pulay's direct inversion of the iterative subspace (DIIS) [41] [1980]. Here, the energy is assumed to vary as a quadratic function of the basis set coefficients. In DIIS the coefficients for the next iteration are calculated from their values in the previous steps. In essence, one is predicting where the minimum in the energy will lie form a knowledge of the points that have been visited and by assuming that the energy surface adopts a parabolic shape.

2.5.11 The direct SCF method

An ab inito calculation can be logically considered to involve two separate stages. First, the various one- and two-electron integrals are calculated. This is a computationally intensive task and considerable effort has been expended finding ways to make the calculation of the integrals as efficient as possible. In the second stage, the wavefunction is determined using the variation theorem. In a "traditional" SCF calculation all of the integrals are first calculated and stored on disk, to be retrieved later during the SCF calculation as required. The number of integrals to be stored may run into millions and this inevitably leads to delays in accessing the data, particularly as the retrieval of information from a disk requires physical movement of the read head and so is slow. Modern computers (both workstations and supercomputers) have much faster (and cheaper) processing units, and many of these machines also have a substantial amount of internal memory that can be accessed in a fraction of the time it takes to read data from the disk. In a direct SCF calculation, the integrals are not stored on the disk but are kept in memory or recalculated when required by Almlöf et al. [42] [1982].

A much-quoted "fact" is that ab initio calculations scale as the fourth power of the number of basis functions for ground-state, closed-shell systems. This scaling factor arises because each two-electron integral $(\mu\nu|\lambda\sigma)$ involves four basis functions, so the number of two-electron integrals would be expected to increase in proportion to the fourth power of the number of basis functions. In fact, the number of such integrals is not exactly equal to the fourth power of the number of basis functions because many of the integrals are related by symmetry. We can calculate exactly the number of two-electron integrals that are required in a Hartree-Fock ab initio calculation as follows. There are seven different types of two-electron integrals:

1. $(ab|cd) \equiv (ab|dc) \equiv (ba|cd) \equiv (ba|dc) \equiv (cd|ab) \equiv (cd|ba) \equiv (dc|ab) \equiv (dc|ba)$
2. $(aa|bc) \equiv (aa|cb) \equiv (bc|aa) \equiv (cb|aa)$
3. $(ab|ac) \equiv (ab|ca) \equiv (ba|ac) \equiv (ba|ca) \equiv (ac|ab) \equiv (ac|ba) \equiv (ca|ab) \equiv (ca|ba)$
4. $(aa|bb) \equiv (bb|aa)$
5. $(ab|ab) \equiv (ab|ba) \equiv (ba|ab) \equiv (ba|ba)$

6. (aa|ab) ≡ (aa|ba) ≡ (ab|aa) ≡ (ba|aa)
7. (aa|aa)

For a basis set with K basis functions, they are K(K – 1)(K – 2)(K – 3) integrals of type(ab|cd), but due to symmetry only one-eighth of these are unique as shown. Similarly, there are 2K(K – 1)(K – 2) of type (2); 4K(K –1)(K –2) of type (3); K(K – 1) of type (4); 2K(K – 1) of type (5); 4K(K – 1) of type (6) and K' of type 7. Thus, a basis set with 2000functions has a total of 202 015 050 unique two-electron integrals. For all but the smallest of basis sets most integrals are of type (1) which is why an ab initio problem is often considered to scale as $K^4/8$ ($200^4/8 = 200\ 000\ 000$). Including electron correlation adds significantly to the computational cost; for example, MP2 calculations scale as the fifth power of the number of basis functions. Electron correlation methods may also require significantly more memory and disk than the comparable SCF calculation.

In practice, ab initio calculations often scale as a significantly smaller power than four. It is found that in favourable cases the computational cast of a direct SCF calculation on a large molecule scales as approximately the square of the number of basis functions used. This significant reduction (from four to two) is due to several factors. We have already noted some of the ways in which a carefully chosen basis set can reduce the computational effort, for example by making many of the integrals (particularly the two-electron integrals) identical by using the same Gaussian exponents for s and p orbitals in the same shell. Symmetry in the molecule may also be exploited, sometimes to great effect. The most effective way to reduce the computational effort is to identify integrals which are so small that ignoring them (i.e. setting them to zero) will not affect the results. The number of "important" integrals is believed to scale as K^2 ln K. The negligible integrals are determined by calculating an upper limit for each integral. This can be done rapidly and so those integrals that are guaranteed to be negligible can be identified and so ignored. The cutoff value which determines whether an integral is explicitly calculated or is set to zero can vary from one program to another, so it is always useful to check its value if different programs give different results for a given calculation.

2.5.12 Setting up the calculation and the choice of coordinates

The traditional way to provide the nuclear coordinates to a quantum mechanical program is via a Z-matrix, in which the positions of the nuclei are defined in terms of a set of internal. Some programs also accept coordinates in Cartesian format, which can be more convenient for large systems. It can sometimes be important to choose an appropriate set of internal coordinates, especially when locating minima or transition points or when following reaction pathways.

2.5.13 Calculating derivatives of the energy

Considerable effort has been spent devising efficient ways of calculating the first and second derivatives of the energy with respect to the nuclear coordinates. Derivatives are primarily used during minimisation procedures for finding equilibrium structures and are also used by methods which locate transition structures and determine reaction pathways. To calculate derivatives of the energy it is necessary to calculate the derivatives of the various electron integrals. For Gaussian basis sets the derivatives can be obtained analytically, and it is relatively straightforward to obtain first derivatives for many levels of theory. The time taken to calculate the derivatives is comparable to that required for the calculation of the total energy. Second derivatives are more difficult and expensive to calculate, even at the lower levels of theory.

2.5.14 Basis set superposition error

Suppose we wish to calculate the energy of formation of a bimolecular complex, such as the energy of formation of a hydrogen-bonded water dimer. Such complexes are sometimes referred to as "supermolecules". One might expect that this energy value could be obtained by first calculating the energy of a single water molecule, then calculating the energy of the dimer, and finally subtracting the energy of the two isolated water molecules (the "reactants") from that of the dimer (the "product"). However, the energy difference obtained by such an approach will invariably be an overestimate of the true value. The discrepancy arises from a phenomenon known as basis set superposition error (BSSE). As the two water molecules approach, the energy

of the system falls not only because of the favourable intermolecular interactions but also because the basis functions on each molecule provide a better description of the electronic structure around the other molecule. It is clear that the BSSE would be expected to be particularly significant when small, inadequate basis sets are used (e.g. the minimal basis STO-nG basis sets) which do not provide for an adequate representation of the electron distribution far from the nuclei, particularly in the region where non-covalent interactions are strongest. One way to estimate the basis set superposition error is via the counterpoise correction method of Boys and Bernardi [43] in which the entire basis set is included in all calculations [1970]. Thus, in the general case:

$$A + B \equiv AB$$

$$\Delta E = E(AB) - [E(A) + E(B)]$$

The calculation of the energy of the individual species A is performed in the presence of "ghost" orbitals of B; that is, without the nuclei or electrons of B. A similar calculation is performed for B using ghost orbitals on A. An alternative approach is to use a basis set in which the orbital exponents and contraction coefficients have been optimised for molecular calculations rather than for atoms. The relevance of the basis set superposition error and its dependence upon the basis set and the level of theory employed.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Equipment

3.1.1 Chemicals

▪ Tetrabutylammonium trifluoromethanesulfonate	Electrochemical grade, Fluka, Switzerland
▪ Tetrabutylammonium hydroxide 1.0 M	Analar grade, Fluka, Switzerland
▪ Zinc(II) trifluoromethanesulfonate	Analar grade, Aldrich, U.S.A.
▪ Perchloric acid 70-72 %	Analar grade, Merck, Germany
▪ Potassium hydrogen phthalate	Analar grade, Carlo Erba, Italy
▪ Methanol	Gradient grade, Merck, Germany
▪ 25,26,27,28-*tetra*(2-ethoxyaniline)calix [4]arene, cone conformation (**cL**)	Synthetic ligand
▪ 25,26,27,28-*tetra*(2-ethoxyaniline)calix [4]arene, partial cone conformation (**pcL**)	Synthetic ligand
▪ Argon gas	Ultra high purity grade, TGI, Thailand

3.1.2 Equipment

- Automatic titrator, Mettler, Model DL 25, Switzerland
- Thermostat bath, Model DT-2, Denmark
- Combined pH electrode, Mettler, Model DG 113-SC, Switzerland
- Personal Computer IBM 300GL, PII/350, RAM 128 MB

3.2 Potentiometry

3.2.1 Preparation of solution

Inert background electrolyte, used in the research, was 0.01 M $Bu_4NCF_3SO_3$ in methanol which obtained by dissolution of a weighed quantity of dried $Bu_4NCF_3SO_3$, Electrochemical grade, Fluka, in Methanol. Methanol with very low water content was used without further purification. Stock solutions of the ligands of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, cone (**cL**) and partial cone (**pcL**) conformations used in the titrations were 0.001 M in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$. Tetrabutylammonium hydroxide (Bu_4NOH) of which concentration about 1.0×10^{-3} M made by dilution of the commercial solution of 1.0 M $Bu_4NCF_3SO_3$ in methanol which ionic strength of 0.01 M $Bu_4NCF_3SO_3$ was used as the titrant base. The primary standard solution of potassium hydrogen phthalate (KHP) was prepared by dilution of a weighed quantity of dried KHP in water. The stock solution of perchloric acid ($HClO_4$) was made by dilution of the commercial concentrated solution (70-72 %) in methanol. The pH standard solutions of pH = 2.0 and pH = 3.0 in the methanolic solution of constant ionic strength of 0.01 M $CF_3SO_3^-$ were prepared by dilution of the stock solution of perchloric acid. The stock solution of perchloric acid was used for preparation of standard solution of 0.05 M $HClO_4$ in the methanolic solution of 0.01 M $Bu_4NCF_3SO_3$, standardized using Bu_4NOH titrant.

The methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ of the 0.05 M $Zn(CF_3SO_3)_2$ was used in the titration for the complex formation study of the ligands of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene cone and partial cone conformations.

3.2.2 The Calibration of Electrode

An automatic titrator, Mettler DL25 including combined pH electrode of Mettler DG113-SC was used in the titration. The pH electrode was calibrated by standard pH solutions of pH 2.00 and 3.00 as mentioned in the preparation of solution, at 25 ± 0.1 °C. The standard pH 2.00 and 3.00 were prepared in methanol and in 0.009 M $Bu_4NCF_3SO_3$ /MeOH, respectively. Accuracy of the pH measurement was indicated by parameters a and b of the pH correction equation as follows :

$$pH_{corrected} = pH_{measured} + a + b\,[H^+] \qquad (3.1)$$

Parameters a and b obtianed by solving two different pH-values' set (pH 2.00 and 3.00) of equation (3.1). The measured pH according to the standard pH 2.00 was kept as 2.00 to form the first equation by adjusted its Nernstian slope, defined as the ratio of pH to potential in millivolt based on the isopotential point of pH 8.30 = 0.0 millivolt. The measured pH value obtained from the measurement of standard pH 3.00 formed the second equation. The a and b were solved from those two different equations.

The titration were performed under ultrapure argon gas satulated by 0.01 M $Bu_4NCF_3SO_3$ vapour, through the titration beaker. The titration beaker was kept constantly at 25 °C with deviation of ± 0.1 °C by the external circulation control of thermostat bath. Each titration, at least 50 titrating data were recorded and at least 3 titrations were performed.

3.2.3 Potentiometric Titration

Each titrations, 0.001 M of the ligands of 25,26,27,28-*tetra*(2-ethoxyaniline) calix[4]arene in methanol of 10 cm^3 was used. The titrant base, 0.05 M Bu_4NOH in 0.01 M $Bu_4NCF_3SO_3$ was standardized against the primary standard solution of potassium hydrogen phthalate For standard solution of 0.05 M $HClO_4$ in the methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ was standardized against the titrant base. The standard solution of $HClO_4$ was used to adjust the pH of the working solution.

The titrations were performed under ultrapure argon gas, saturated by 0.1 M potassium nitrate vapour, through the titration beaker. The titration beaker was kept constantly at 25 °C with deviation of ± 0.1 °C by the external circulation control of thermostat bath. Each titration, at least 50 titrating data were recorded and at least 3 titrations were performed for each ligand .

3.2.4 Experimental Data

The titrating data for determination of basicity constants of 25,26,27,28-*tetra* (2-ethoxyaniline)calix[4]arene, partial cone was evaluated by the computer refinement program. The calculations were performed on the Personal computer IBM 300GL PII/350. The titrating data obtained from the measurements were used in the evaluation and the optimization process by the SUPERQUAD program [44]. The range of titrating data for the titration of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, partial cone is shown in Table 3.1..

Table 3.1 Titration data range of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene (**L**), partial cone conformation in 0.01 M $Bu_4NCF_3SO_3$ in methanol at 25 °C.

Titration	Initial Concentration (mM)		pH range	Data point
	L	$HClO_4$		
1	0.907	7.745	2.35 – 12.16	53
2	0. 872	7.745	2.84 - 11.27	52
3	0.109	4.900	2.27 – 12.66	64
4	0.105	1.278	4.27 - 11.49	50

3.3 Quantum Chemical Calculations

3.3.1 Structure Optimization

The optimized structure of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] were determined by semiempirical PM3 method. The structure of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene ligand obtained from MM method using standard geometrical parameters, were employed in above process of structure optimization. The structures of protonated species of cone (**cL**) and partial cone (**pcL**) configurations of the ligands, modified from the neutral structures, were optimized using PM3 method.

3.3.2 Ab initio Calculations

The SCF energies of the optimized structures were obtained by the ab initio calculations with STO-3G and 6-32G basis set. The possible protonated speices of **cL** and **pcL** were optimized and computed of theire energies at the STO-3G and 6-31G levels.

All calculations were performed on the Pentium II/350 IBM-PC300Gl of RAM 128 MB. The program Gaussian 94W [45] were used for all quantum-chemical computations. Countetpoise correction method was not included in all calculations.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Basicity Constant of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene

The chemical equilibria of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] (symbolized as L) in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ are written as following equations

$$K_1 : L + H^+ \rightleftharpoons LH^+ \quad (4.1)$$

$$K_2 : LH^+ + H^+ \rightleftharpoons LH_2^{2+} \quad (4.2)$$

$$K_3 : LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+} \quad (4.3)$$

$$K_4 : LH_3^{3+} + H^+ \rightleftharpoons LH_4^{4+} \quad (4.4)$$

K_1, K_2, K_3, and K_4 are first, second, third and fourth protonation constants , so called basicity constants. The basicity constants of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4], partial cone conformation, expressed in terms of logarithm are shown in Table 4.1.

Table 4.1 Logarithm of the basicity constant of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C.

Protonation						log K
K_1	: L	+	H^+	$\rightleftharpoons$	LH^+	11.87 ± 0.06
K_2	: LH^+	+	H^+	$\rightleftharpoons$	LH_2^{2+}	5.59 ± 0.12
K_3	: LH_2^{2+}	+	H^+	$\rightleftharpoons$	LH_3^{3+}	4.62 ± 0.13
$K4$	: LH_3^{3+}	+	H^+	$\rightleftharpoons$	LH_4^{4+}	4.62 ± 0.13

The titration curves of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] (**L**) partial cone conformation in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C are shown in Figure 4.1.

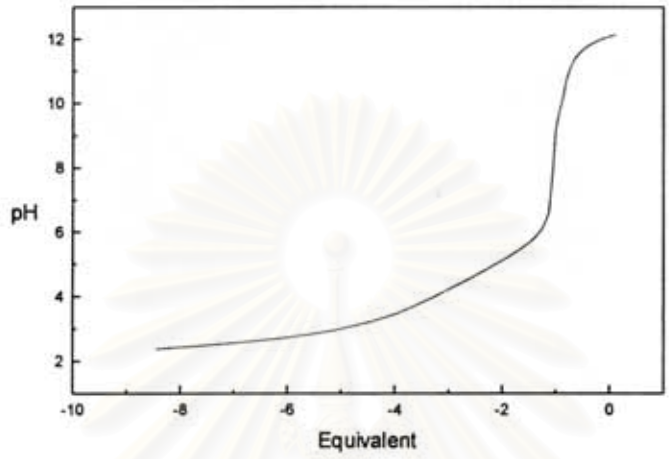


Figure 4.1 Potentiometric titration curves of 25,26,27,28-*tetra*(2-ethoxyaniline) calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C, based on the initial concentration ratio of the ligand to proton of 1.92 mM : 7.62 mM; equivalent is defined as the ratio of $(n_{OH^-} - n_{acid})$ to n_{ligand}.

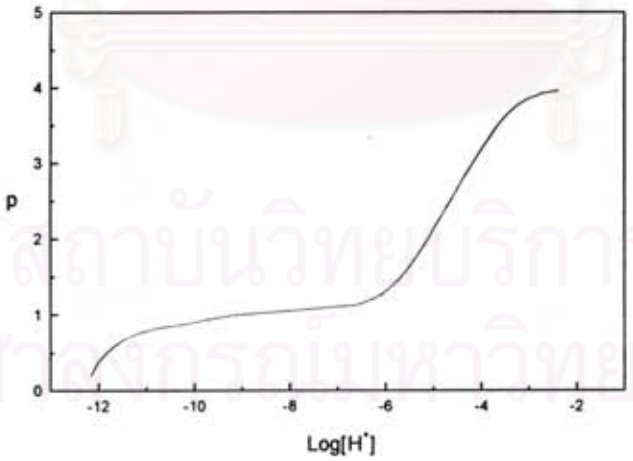


Figure 4.2 Plot between p and log[H^+] for 25,26,27,28-*tetra*(2-ethoxyaniline) calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C, based on the initial concentration ratio of the ligand to proton of 1.92 mM : 7.62 mM.

The plot between p and log[H^+] for 25,26,27,28-*tetra*(2-ethoxyaniline) calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C, based on the initial concentration ratio of the ligand to proton of 1.92 mM : 7.62 mM, is shown inFigure 4.2. The species distribution curves of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C are shown in Figure 4.3.

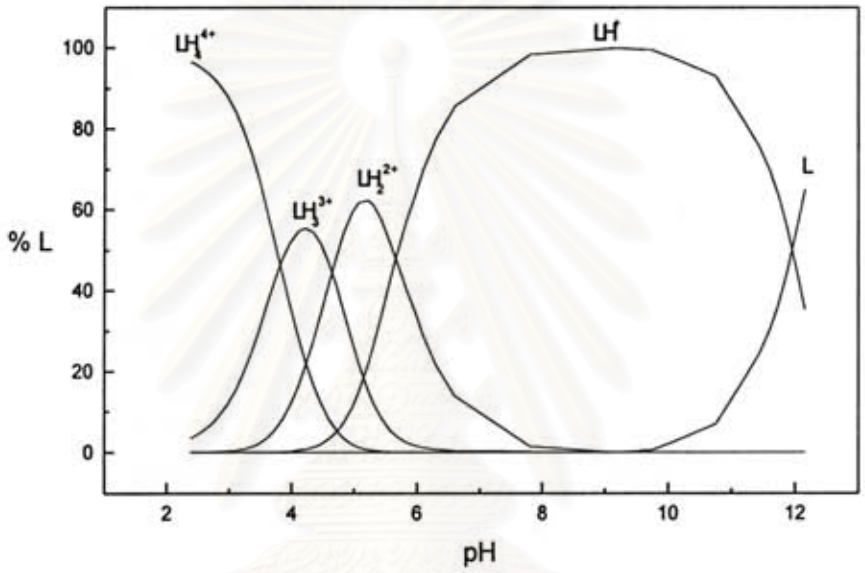


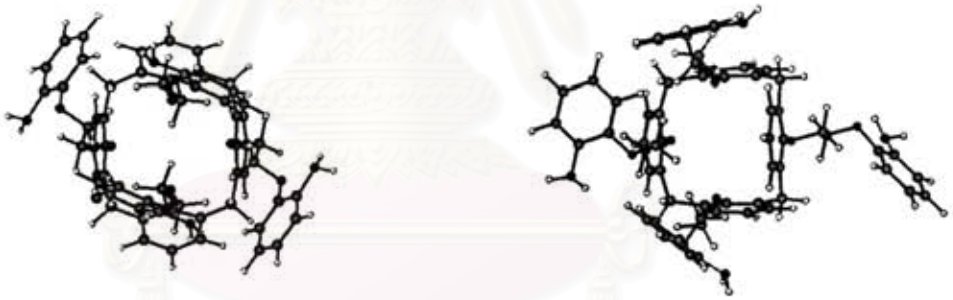
Figure 4.3 Species distribution curves of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4] (**L**), partial cone conformation, in methanolic solution of 0.01 M $Bu_4NCF_3SO_3$ at 25 °C, with initial concentration of 9.07×10^{-4} M.

All protonated species of partial cone (**pcL**) present in the pH below 9.0, except LH^+ exists in the pH range of 4.5 to 12.0. Higher than 50 % of the complete-protonated species , LH_4^{4+} is located at pH below 4.0. Over 50 % of LH_3^{3+} and LH_2^{2+} exist in the narrow range of pH 3.5 to 5.0. All protonated species coexist in the pH range of 4.2 to 5.2 At basic pH range (pH < 8.3), almost 100% of LH^+ exists in methanolic solution. Free ligand, L species, is liberated at pH above 10.0 and becomes dominant species at pH above 12. At pH 12, populations of LH^+ and L species are almost the same number (50%).

4.2 Quantum chemical calculations of the 25,26,27,28-*tetra*(2-ethoxyaniline)calix [4]arene

4.2.1 Structure optimization of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene

The optimized structures of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, are cone and partial cone conformations. The optimization method for determination of the structural conformations of the 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene has been employed using the PM3 method of quantum chemical calculations. Cone and partial cone conformations obtained from the structure optimization are shown in Figure 4.4.



cL **pcL**

Figure 4.4 Cone, **cL** and partial cone, **pcL** conformations obtained from the structure optimization by PM3 method of quantum-chemical calculations

4.2.2 Structure optimization of protonated species of cone and partial cone conformations of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene

The protonated species of the cone and partial cone conformations of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, were optimized using PM3 method. The structure of cone and partial cone conformations obtained from the structure optimization are shown in Figure 4.5 and 4.6, respectively. The SCF energies of the optimized structures of all possible protonated speices of **cL** and **pcL** were obtained by *ab initio* calculations with STO-3G and 6-31G basis set as shown in Table 4.2 and 4.3, respectively.

4.2.3 The stabilization energies of protonations and protonation pathways of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene

The protonation process of 7 pathways of the **cL** and 24 pathways of the **pcL** are shown in Table 4.4 and 4.5, respectively. The stabilization energies of protonations of cone and partial cone conformations of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, computed by *ab initio* method with STO-3G and 6-31G basis set are tabulated in Table 4.6 and 4.7, respectively.

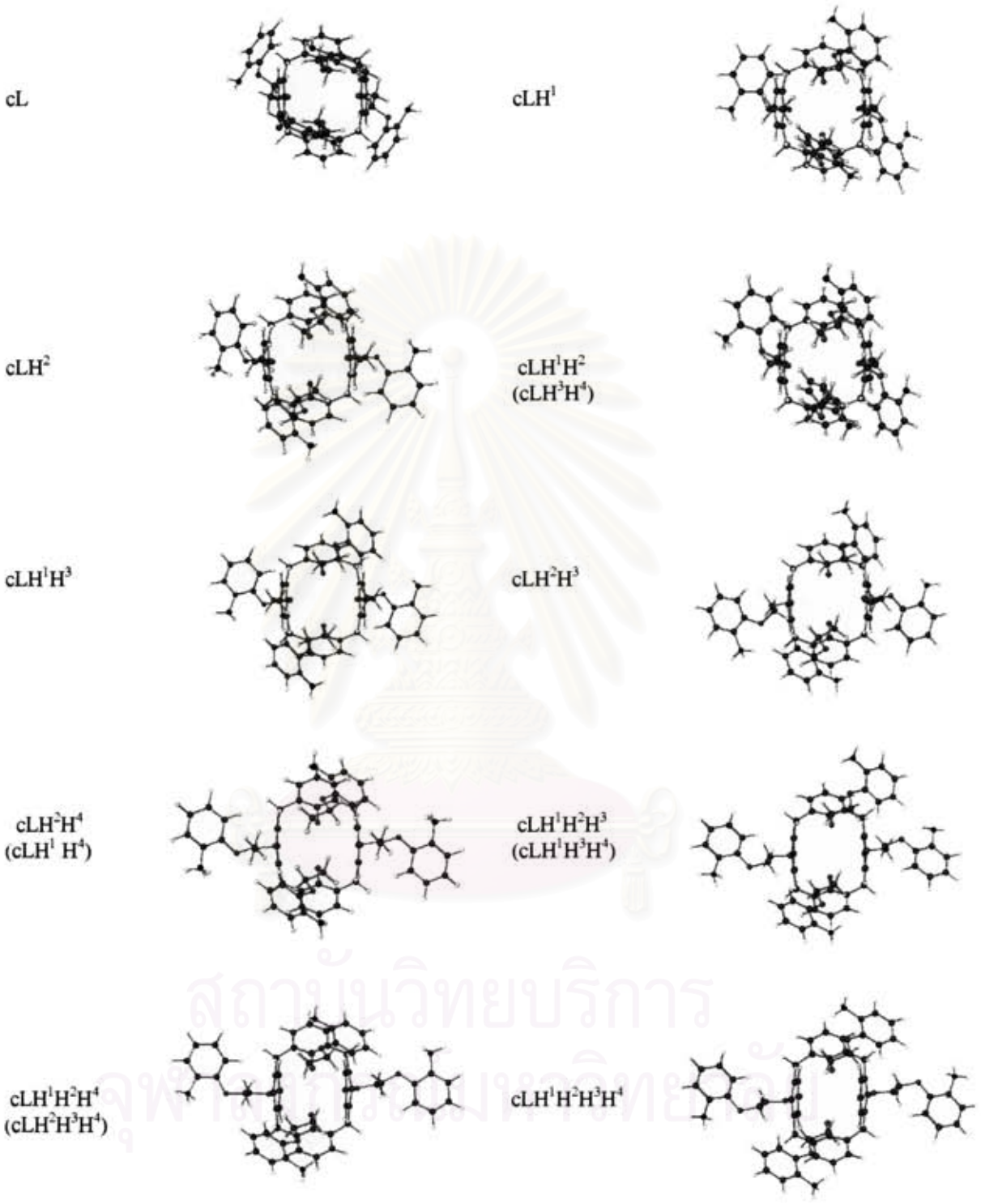


Figure 4.5 The 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene cone conformation, **cL** obtained from the structure optimization by PM3 method of quantum-chemical calculations (see Appendix A).

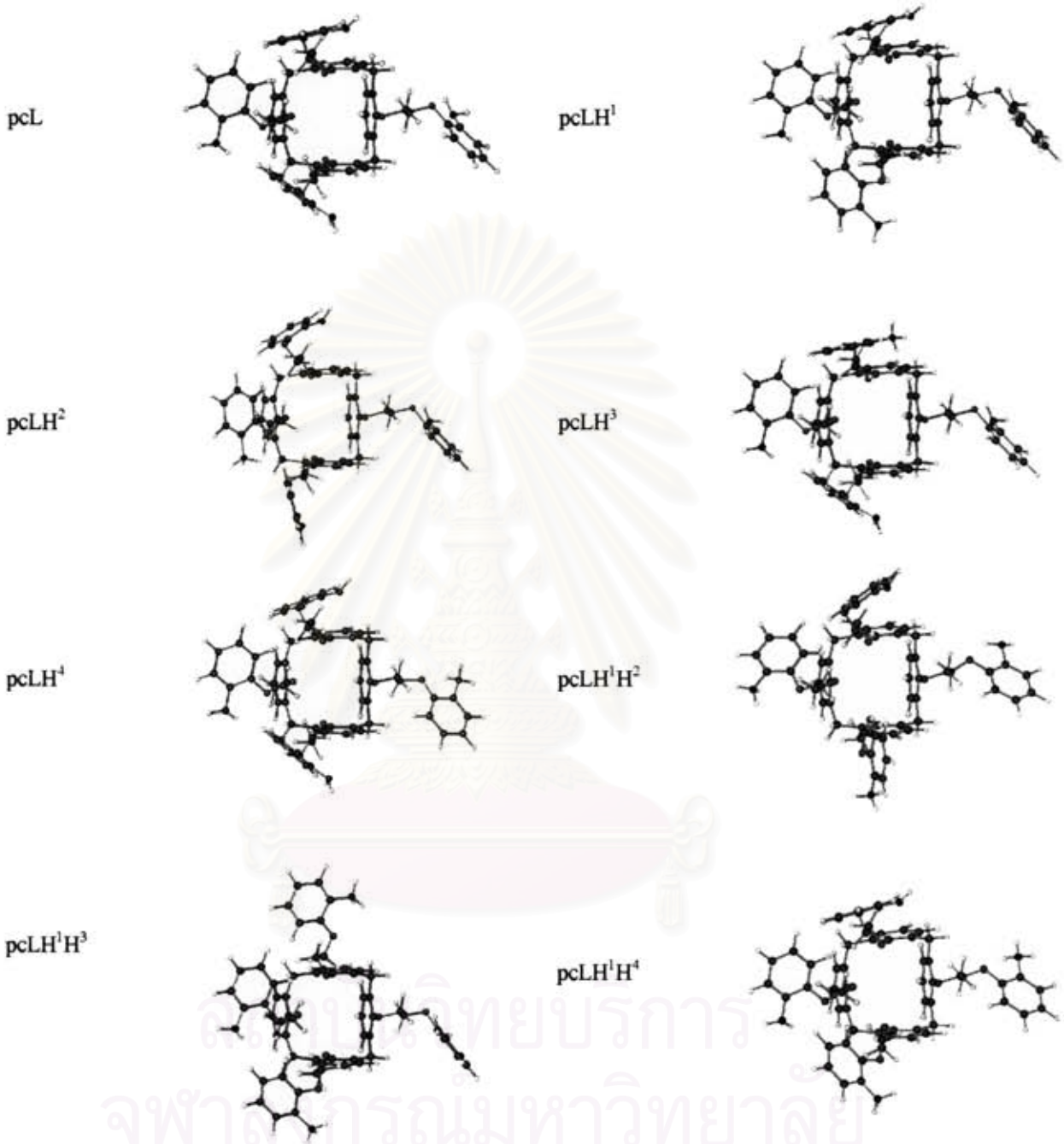


Figure 4.6 The 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene partial cone conformation, **pcL** obtained from the structure optimization by PM3 method of quantum-chemical calculations (see Appendix B).

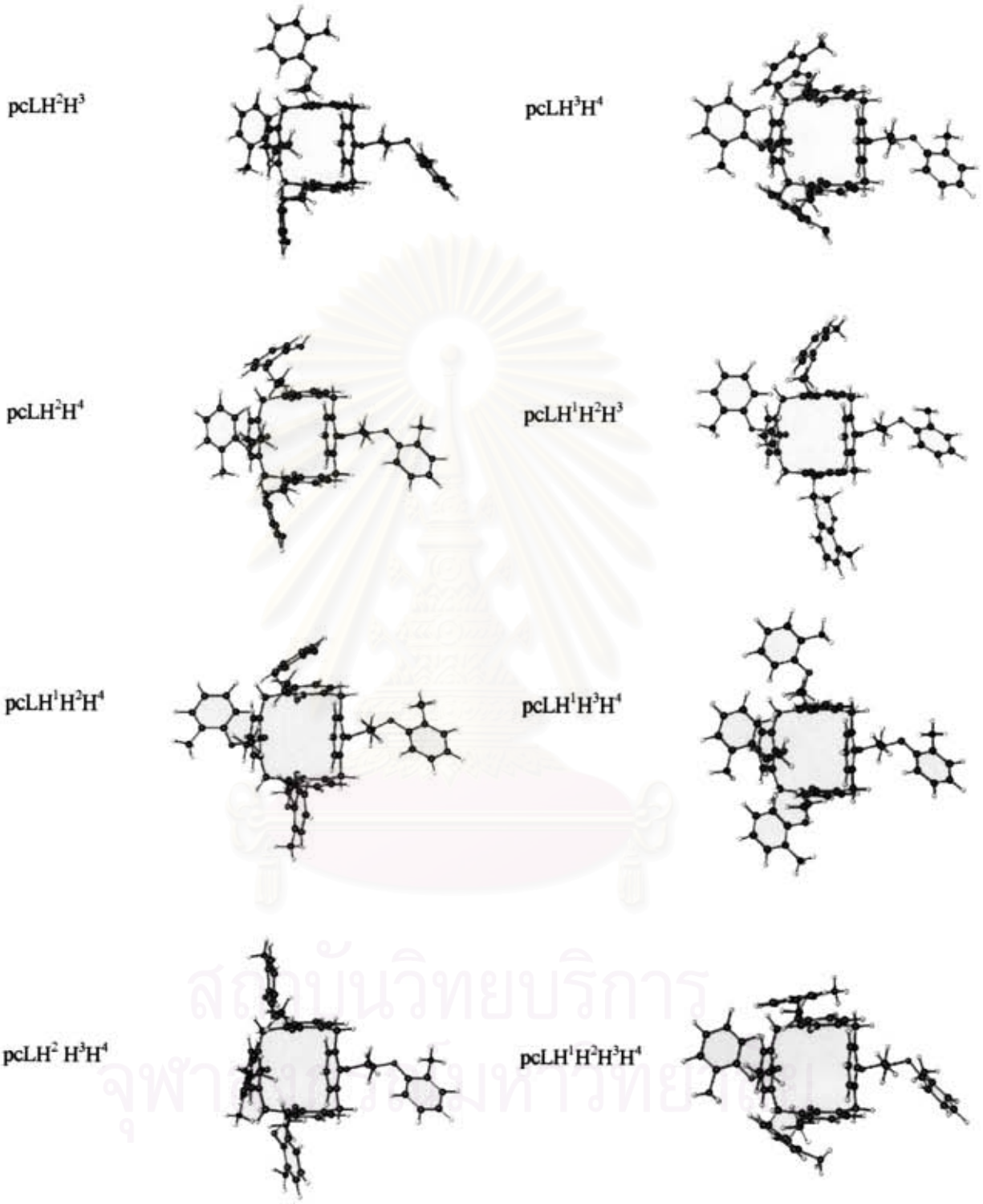


Figure 4.6 (continued)

Table 4.2 The SCF energies of protonated species of cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene computed by LCAO-MO-SCF with STO-3G and 6-31G basis set.

Species	SCF energy (hartree)	
	STO-3G	6-31 G
cL	-3084.835132	-3122.301177
cLH^1	-3085.266633	-3122.684859
cLH^2	-3085.264951	-3122.681046
cLH^1H^2 (cLH^3H^4)	-3085.644124	-3122.999970
cLH^1H^3	-3085.662431	-3123.021298
cLH^2H^3 (cLH^1H^4)	-3085.671069	-3123.009764
cLH^2H^4	-3085.656638	-3123.027889
$cLH^1H^2H^3$ ($cLH^1H^3H^4$)	-3086.006783	-3123.287449
$cLH^1H^2H^4$ ($cLH^2H^3H^4$)	-3085.994525	-3123.301316
$cLH^1H^2H^3H^4$	-3086.288631	-3123.521363

cLH^n is the protonated species of the protonation at the n^{th} nitrogen atom on the ligand cL.

Table 4.3 The SCF energies of protonated species of partial cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene computed by LCAO-MO-SCF with STO-3G and 6-31G basis set.

Species	SCF energy (hartree)	
	STO-3G	6-31 G
pcL	-3084.840315	-3122.312896
$pcLH^1$	-3085.265539	-3122.681978
$pcLH^2$	-3085.279438	-3122.700790
$pcLH^3$	-3085.264924	-3122.677342
$pcLH^4$	-3085.274135	-3122.688569
$pcLH^1H^2$	-3085.634498	-3122.988723
$pcLH^1H^3$	-3085.648468	-3123.001338
$pcLH^1H^4$	-3085.666590	-3123.022247
$pcLH^2H^3$	-3085.644583	-3123.001806
$pcLH^3H^4$	-3085.661025	-3123.014023
$pcLH^2H^4$	-3085.674449	-3123.033716
$pcLH^1H^2H^3$	-3085.674449	-3123.272873
$pcLH^1H^2H^4$	-3085.993382	-3123.286796
$pcLH^1H^3H^4$	-3086.007795	-3123.299952
$pcLH^2H^3H^4$	-3086.026914	-3123.317325
$pcLH^1H^2H^3H^4$	-3086.302327	-3123.532681

cLH^n is the protonated species of the protonation at the n^{th} nitrogen atom on the ligand cL.

Table 4.4 The protonation process of possible pathways of the cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, **cL**.

1st pathway :	cL	$\xrightarrow{\Delta E_1^{(1)}}$	cLH^1	$\xrightarrow{\Delta E_2^{(1)}}$	cLH^1H^2	$\xrightarrow{\Delta E_3^{(1)}}$	$cLH^1H^2H^3$	$\xrightarrow{\Delta E_4^{(1)}}$	$cLH^1H^2H^3H^4$
2nd pathway :	cL	$\xrightarrow{\Delta E_1^{(2)}=\Delta E_1^{(1)}}$	cLH^1	$\xrightarrow{\Delta E_2^{(2)}=\Delta E_2^{(1)}}$	cLH^1H^2	$\xrightarrow{\Delta E_3^{(2)}}$	$cLH^1H^2H^4$	$\xrightarrow{\Delta E_4^{(2)}}$	$cLH^1H^2H^3H^4$
3rd pathway :	cL	$\xrightarrow{\Delta E_1^{(3)}=\Delta E_1^{(1)}}$	cLH^1	$\xrightarrow{\Delta E_2^{(3)}}$	cLH^1H^3	$\xrightarrow{\Delta E_3^{(3)}}$	$cLH^1H^2H^3$	$\xrightarrow{\Delta E_4^{(3)}=\Delta E_4^{(1)}}$	$cLH^1H^2H^3H^4$
4th pathway :	cL	$\xrightarrow{\Delta E_1^{(4)}}$	cLH^2	$\xrightarrow{\Delta E_2^{(4)}}$	cLH^1H^2	$\xrightarrow{\Delta E_3^{(4)}=\Delta E_3^{(1)}}$	$cLH^1H^2H^3$	$\xrightarrow{\Delta E_4^{(3)}=\Delta E_4^{(1)}}$	$cLH^1H^2H^3H^4$
5th pathway :	cL	$\xrightarrow{\Delta E_1^{(5)}=\Delta E_1^{(4)}}$	cLH^2	$\xrightarrow{\Delta E_2^{(5)}=\Delta E_2^{(4)}}$	cLH^1H^2	$\xrightarrow{\Delta E_3^{(5)}=\Delta E_3^{(2)}}$	$cLH^1H^2H^4$	$\xrightarrow{\Delta E_4^{(5)}=\Delta E_4^{(2)}}$	$cLH^1H^2H^3H^4$
6th pathway :	cL	$\xrightarrow{\Delta E_1^{(6)}=\Delta E_1^{(4)}}$	cLH^2	$\xrightarrow{\Delta E_2^{(6)}}$	cLH^2H^3	$\xrightarrow{\Delta E_3^{(6)}}$	$cLH^1H^2H^3$	$\xrightarrow{\Delta E_4^{(6)}=\Delta E_4^{(1)}}$	$cLH^1H^2H^3H^4$
7th pathway :	cL	$\xrightarrow{\Delta E_1^{(7)}=\Delta E_1^{(4)}}$	cLH^2	$\xrightarrow{\Delta E_2^{(7)}}$	cLH^2H^4	$\xrightarrow{\Delta E_3^{(7)}}$	$cLH^1H^2H^4$	$\xrightarrow{\Delta E_4^{(7)}=\Delta E_4^{(2)}}$	$cLH^1H^2H^3H^4$

Table 4.5 The protonation process of possible pathways of the partial cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, **pcL**.

1st pathway :	pcL $\xrightarrow{\Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(1)}}$	$pcLH^1H^2$ $\xrightarrow{\Delta E_3^{(1)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
2nd pathway :	pcL $\xrightarrow{\Delta E_1^{(2)} = \Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(2)} = \Delta E_2^{(1)}}$	$pcLH^1H^2$ $\xrightarrow{\Delta E_3^{(2)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
3rd pathway :	pcL $\xrightarrow{\Delta E_1^{(3)} = \Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(3)}}$	$pcLH^1H^3$ $\xrightarrow{\Delta E_3^{(3)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(3)} = \Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
4th pathway :	pcL $\xrightarrow{\Delta E_1^{(4)} = \Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(4)} = \Delta E_2^{(3)}}$	$pcLH^1H^3$ $\xrightarrow{\Delta E_3^{(4)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
5th pathway :	pcL $\xrightarrow{\Delta E_1^{(5)} = \Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(5)}}$	$pcLH^1H^4$ $\xrightarrow{\Delta E_3^{(5)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(5)} = \Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
6th pathway :	pcL $\xrightarrow{\Delta E_1^{(6)} = \Delta E_1^{(1)}}$	$pcLH^1$ $\xrightarrow{\Delta E_2^{(6)} = \Delta E_2^{(5)}}$	$pcLH^1H^4$ $\xrightarrow{\Delta E_3^{(6)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(6)} = \Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
7th pathway :	pcL $\xrightarrow{\Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(7)}}$	$pcLH^1H^2$ $\xrightarrow{\Delta E_3^{(7)} = \Delta E_3^{(1)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(7)} = \Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
8th pathway :	pcL $\xrightarrow{\Delta E_1^{(8)} = \Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(8)} = \Delta E_2^{(7)}}$	$pcLH^1H^2$ $\xrightarrow{\Delta E_3^{(8)} = \Delta E_3^{(2)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(8)} = \Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
9th pathway :	pcL $\xrightarrow{\Delta E_1^{(9)} = \Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(9)}}$	$pcLH^2H^3$ $\xrightarrow{\Delta E_3^{(9)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(9)} = \Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
10th pathway :	pcL $\xrightarrow{\Delta E_1^{(10)} = \Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(10)} = \Delta E_2^{(9)}}$	$pcLH^2H^3$ $\xrightarrow{\Delta E_3^{(10)}}$	$PcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$
11st pathway :	pcL $\xrightarrow{\Delta E_1^{(11)} = \Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(11)}}$	$pcLH^2H^4$ $\xrightarrow{\Delta E_3^{(11)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(11)} = \Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
12nd pathway :	pcL $\xrightarrow{\Delta E_1^{(12)} = \Delta E_1^{(7)}}$	$pcLH^2$ $\xrightarrow{\Delta E_2^{(12)} = \Delta E_2^{(11)}}$	$pcLH^2H^4$ $\xrightarrow{\Delta E_3^{(12)}}$	$pcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(12)} = \Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$
13rd pathway :	pcL $\xrightarrow{\Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(13)}}$	$pcLH^1H^3$ $\xrightarrow{\Delta E_3^{(13)} = \Delta E_3^{(3)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(13)} = \Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
14th pathway :	pcL $\xrightarrow{\Delta E_1^{(14)} = \Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(14)} = \Delta E_2^{(13)}}$	$pcLH^1H^3$ $\xrightarrow{\Delta E_3^{(14)} = \Delta E_3^{(4)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(14)} = \Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
15th pathway :	pcL $\xrightarrow{\Delta E_1^{(15)} = \Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(15)}}$	$pcLH^2H^3$ $\xrightarrow{\Delta E_3^{(15)} = \Delta E_3^{(9)}}$	$pcLH^1H^2H^3$ $\xrightarrow{\Delta E_4^{(15)} = \Delta E_4^{(1)}}$ $pcLH^1H^2H^3H^4$
16th pathway :	pcL $\xrightarrow{\Delta E_1^{(16)} = \Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(16)} = \Delta E_2^{(15)}}$	$pcLH^2H^3$ $\xrightarrow{\Delta E_3^{(16)} = \Delta E_3^{(10)}}$	$pcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(16)} = \Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$
17th pathway :	pcL $\xrightarrow{\Delta E_1^{(17)} = \Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(17)}}$	$pcLH^3H^4$ $\xrightarrow{\Delta E_3^{(17)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(17)} = \Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
18 th pathway :	pcL $\xrightarrow{\Delta E_1^{(18)} = \Delta E_1^{(13)}}$	$pcLH^3$ $\xrightarrow{\Delta E_2^{(18)} = \Delta E_2^{(17)}}$	$pcLH^3H^4$ $\xrightarrow{\Delta E_3^{(18)}}$	$pcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(18)} = \Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$
19 th pathway :	pcL $\xrightarrow{\Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(19)}}$	$pcLH^1H^4$ $\xrightarrow{\Delta E_3^{(19)} = \Delta E_3^{(5)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(19)} = \Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
20th pathway :	pcL $\xrightarrow{\Delta E_1^{(20)} = \Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(20)} = \Delta E_2^{(19)}}$	$pcLH^1H^4$ $\xrightarrow{\Delta E_3^{(20)} = \Delta E_3^{(6)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(20)} = \Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
21st pathway :	pcL $\xrightarrow{\Delta E_1^{(21)} = \Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(21)}}$	$PcLH^2H^4$ $\xrightarrow{\Delta E_3^{(21)} = \Delta E_3^{(11)}}$	$pcLH^1H^2H^4$ $\xrightarrow{\Delta E_4^{(21)} = \Delta E_4^{(2)}}$ $pcLH^1H^2H^3H^4$
22nd pathway :	pcL $\xrightarrow{\Delta E_1^{(22)} = \Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(22)} = \Delta E_2^{(21)}}$	$pcLH^2H^4$ $\xrightarrow{\Delta E_3^{(22)} = \Delta E_3^{(12)}}$	$pcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(22)} = \Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$
23rd pathway :	pcL $\xrightarrow{\Delta E_1^{(23)} = \Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(23)}}$	$pcLH^3H^4$ $\xrightarrow{\Delta E_3^{(23)} = \Delta E_3^{(17)}}$	$pcLH^1H^3H^4$ $\xrightarrow{\Delta E_4^{(23)} = \Delta E_4^{(4)}}$ $pcLH^1H^2H^3H^4$
24th pathway :	pcL $\xrightarrow{\Delta E_1^{(24)} = \Delta E_1^{(19)}}$	$pcLH^4$ $\xrightarrow{\Delta E_2^{(24)} = \Delta E_2^{(23)}}$	$pcLH^3H^4$ $\xrightarrow{\Delta E_3^{(24)} = \Delta E_3^{(18)}}$	$pcLH^2H^3H^4$ $\xrightarrow{\Delta E_4^{(24)} = \Delta E_4^{(10)}}$ $pcLH^1H^2H^3H^4$

Table 4.6 The stabilization energies of protonation of the cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, **cL,** calculated by *ab initio* method with STO-3G and 6-31G basis set.

Protonation					ΔE (Kcal/mole)	
					STO-3G	6-31G
$\Delta E_1^{(1)} = \Delta E_1^{(2)} = \Delta E_1^{(3)}$	:	cL	⟶	cLH^1	-270.8	-240.8
$\Delta E_2^{(1)} = \Delta E_2^{(2)}$	:	cLH^1	⟶	cLH^1H^2	-236.9	-197.7
$\Delta E_3^{(1)} = \Delta E_3^{(4)}$	:	cLH^1H^2	⟶	$cLH^1H^2H^3$	-227.6	-180.4
$\Delta E_4^{(1)} = \Delta E_4^{(3)} = \Delta E_4^{(6)}$	:	$cLH^1H^2H^3$	⟶	$cLH^1H^2H^3H^4$	-176.9	-146.8
$\Delta E_3^{(2)} = \Delta E_3^{(5)}$	:	cLH^1H^2	⟶	$cLH^1H^2H^4$	-219.9	-189.1
$\Delta E_4^{(2)} = \Delta E_4^{(5)} = \Delta E_4^{(7)}$	:	$cLH^1H^2H^4$	⟶	$cLH^1H^2H^3H^4$	-184.6	-138.1
$\Delta E_2^{(3)}$	:	cLH^1	⟶	cLH^1H^3	-248.4	-211.1
$\Delta E_3^{(3)}$	:	cLH^1H^3	⟶	$cLH^1H^2H^3$	-216.1	-168.0
$\Delta E_1^{(4)} = \Delta E_1^{(5)} = \Delta E_1^{(6)} = \Delta E_1^{(7)}$	:	cL	⟶	cLH^2	-269.7	-238.4
$\Delta E_2^{(4)} = \Delta E_2^{(5)}$	:	cLH^2	⟶	cLH^1H^2	-237.9	-200.1
$\Delta E_2^{(6)}$	:	cLH^2	⟶	cLH^2H^3	-254.8	-206.3
$\Delta E_3^{(6)}$	:	cLH^2H^3	⟶	$cLH^1H^2H^3$	-210.7	-174.3
$\Delta E_2^{(7)}$	:	cLH^2	⟶	cLH^2H^4	-245.8	-217.7
$\Delta E_3^{(7)}$	:	cLH^2H^4	⟶	$cLH^1H^2H^4$	-212.0	-171.6

$\Delta E_n^{(p)}$ is the stabilization energy of the n^{th} protonation of pathway p^{th} protonation.

Table 4.7 The stabilization energies of protonation of the partial cone conformation of 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene, **pcL**, calculated by *ab initio* method with STO-3G and 6-31G basis set.

Protonation				ΔE (Kcal/mole)	
				STO-3G	6-31G
$\Delta E_1^{(1)}=\Delta E_1^{(2)}=\Delta E_1^{(3)}=\Delta E_1^{(4)}=\Delta E_1^{(5)}=\Delta E_1^{(6)}$	:	pcL	$\longrightarrow$ $pcLH^1$	-266.8	-231.6
$\Delta E_2^{(1)}=\Delta E_2^{(2)}$	:	$pcLH^1$	$\longrightarrow$ $pcLH^1H^2$	-231.5	-192.5
$\Delta E_3^{(1)}=\Delta E_3^{(7)}$	:	$pcLH^1H^2$	$\longrightarrow$ $pcLH^1H^2H^3$	-218.1	-178.3
$\Delta E_4^{(1)}=\Delta E_4^{(3)}=\Delta E_4^{(7)}=\Delta E_4^{(9)}=\Delta E_4^{(13)}=\Delta E_4^{(15)}$	:	$pcLH^1H^2H^3$	$\longrightarrow$ $pcLH^1H^2H^3H^4$	-201.0	-163.0
$\Delta E_3^{(2)}=\Delta E_3^{(8)}$	:	$pcLH^1H^2$	$\longrightarrow$ $pcLH^1H^2H^4$	-225.2	-187.0
$\Delta E_4^{(2)}=\Delta E_4^{(5)}=\Delta E_4^{(8)}=\Delta E_4^{(11)}=\Delta E_4^{(19)}=\Delta E_4^{(21)}$	:	$pcLH^1H^2H^4$	$\longrightarrow$ $pcLH^1H^2H^3H^4$	-193.9	-154.3
$\Delta E_2^{(3)}=\Delta E_2^{(4)}$	:	$pcLH^1$	$\longrightarrow$ $pcLH^1H^3$	-240.3	-200.4
$\Delta E_3^{(3)}=\Delta E_3^{(13)}$	:	$pcLH^1H^3$	$\longrightarrow$ $pcLH^1H^2H^3$	-209.3	-170.4
$\Delta E_3^{(4)}=\Delta E_3^{(14)}$	:	$pcLH^1H^3$	$\longrightarrow$ $pcLH^1H^3H^4$	-225.5	-187.4
$\Delta E_4^{(4)}=\Delta E_4^{(6)}=\Delta E_4^{(14)}=\Delta E_4^{(17)}=\Delta E_4^{(20)}=\Delta E_4^{(23)}$	:	$pcLH^1H^3H^4$	$\longrightarrow$ $pcLH^1H^2H^3H^4$	-184.8	-146.0
$\Delta E_2^{(5)}=\Delta E_2^{(6)}$	:	$pcLH^1$	$\longrightarrow$ $pcLH^1H^4$	-251.7	-213.5
$\Delta E_3^{(5)}=\Delta E_3^{(19)}$	:	$pcLH^1H^4$	$\longrightarrow$ $pcLH^1H^2H^4$	-205.1	-166.0
$\Delta E_3^{(6)}=\Delta E_3^{(20)}$	:	$pcLH^1H^4$	$\longrightarrow$ $pcLH^1H^3H^4$	-214.1	-174.3
$\Delta E_1^{(7)}=\Delta E_1^{(8)}=\Delta E_1^{(9)}=\Delta E_1^{(10)}=\Delta E_1^{(11)}=\Delta E_1^{(12)}$	:	pcL	$\longrightarrow$ $pcLH^2$	-275.6	-243.4
$\Delta E_2^{(7)}=\Delta E_2^{(8)}$	:	$pcLH^2$	$\longrightarrow$ $pcLH^1H^2$	-222.8	-180.7
$\Delta E_2^{(9)}=\Delta E_2^{(10)}$	:	$pcLH^2$	$\longrightarrow$ $pcLH^2H^3$	-229.1	-188.9
$\Delta E_3^{(9)}=\Delta E_3^{(15)}$	:	$pcLH^2H^3$	$\longrightarrow$ $pcLH^1H^2H^3$	-211.8	-170.1
$\Delta E_3^{(10)}=\Delta E_3^{(16)}$	:	$pcLH^2H^3$	$\longrightarrow$ $pcLH^2H^3H^4$	-239.9	-198.0
$\Delta E_4^{(10)}=\Delta E_4^{(12)}=\Delta E_4^{(16)}=\Delta E_4^{(18)}=\Delta E_4^{(22)}=\Delta E_4^{(24)}$	:	$pcLH^2H^3H^4$	$\longrightarrow$ $pcLH^1H^2H^3H^4$	-172.8	-135.1
$\Delta E_2^{(11)}=\Delta E_4^{(12)}$	:	$pcLH^2$	$\longrightarrow$ $pcLH^2H^4$	-247.9	-208.9
$\Delta E_3^{(11)}=\Delta E_3^{(21)}$	:	$pcLH^2H^4$	$\longrightarrow$ $pcLH^1H^2H^4$	-200.1	-158.8
$\Delta E_3^{(12)}=\Delta E_3^{(22)}$	:	$pcLH^2H^4$	$\longrightarrow$ $pcLH^2H^3H^4$	-221.2	-178.0
$\Delta E_1^{(13)}=\Delta E_1^{(14)}=\Delta E_1^{(15)}=\Delta E_1^{(16)}=\Delta E_1^{(17)}=\Delta E_1^{(18)}$	:	pcL	$\longrightarrow$ $pcLH^3$	-266.4	-228.7
$\Delta E_2^{(13)}=\Delta E_2^{(14)}$	:	$pcLH^3$	$\longrightarrow$ $pcLH^1H^3$	-240.7	-203.3
$\Delta E_2^{(15)}=\Delta E_2^{(16)}$	:	$pcLH^3$	$\longrightarrow$ $pcLH^2H^3$	-238.2	-203.6
$\Delta E_2^{(17)}=\Delta E_2^{(18)}$	:	$pcLH^3$	$\longrightarrow$ $pcLH^3H^4$	-248.6	-211.3
$\Delta E_3^{(17)}=\Delta E_3^{(23)}$	:	$pcLH^3H^4$	$\longrightarrow$ $pcLH^1H^3H^4$	-217.6	-179.4
$\Delta E_3^{(18)}=\Delta E_3^{(24)}$	:	$pcLH^3H^4$	$\longrightarrow$ $pcLH^2H^3H^4$	-229.6	-190.3
$\Delta E_1^{(19)}=\Delta E_1^{(20)}=\Delta E_1^{(21)}=\Delta E_1^{(22)}=\Delta E_1^{(23)}=\Delta E_1^{(24)}$	:	pcL	$\longrightarrow$ $pcLH^4$	-272.2	-235.7
$\Delta E_2^{(19)}=\Delta E_2^{(20)}$	:	$pcLH^4$	$\longrightarrow$ $pcLH^1H^4$	-246.3	-209.4
$\Delta E_2^{(21)}=\Delta E_2^{(22)}$	:	$pcLH^4$	$\longrightarrow$ $pcLH^2H^4$	-251.2	-216.6
$\Delta E_2^{(23)}=\Delta E_2^{(24)}$	:	$pcLH^4$	$\longrightarrow$ $pcLH^3H^4$	-242.8	-204.2

$\Delta E_n^{(p)}$ is the stabilization energy of the n^{th} protonation of pathway p^{th} protonation.

CHAPTER V

CONCLUSION

This research work can be concluded as listed below :

- 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene exists at least two conformations, namely cone and partial cone.
- The partial cone is more stable than cone conformation.
- The partial cone conformation can be protonated at four aniline-nitrogen atoms of the ligand, and their protonation constants correspond to their stabilization energies of protonation.
- protonation constant of cone conformation has been not obtained but their protonations can be confirmed by the optimization and calculation model.
- The most possible protonation pathways of cone (**cL**) and partial cone (**pcL**) conformations, indicated by their stabilization energies of STO-3G and 6-31G levels, are the 3 rd and 12 nd pathways, respectively.

$$3^{rd}\text{ pathway : } cL \xrightarrow{\Delta E_1^{(3)}} cLH^1 \xrightarrow{\Delta E_2^{(3)}} cLH^1H^3 \xrightarrow{\Delta E_3^{(3)}} cLH^1H^2H^3 \xrightarrow{\Delta E_4^{(3)}} cLH^1H^2H^3H^4$$

$$12^{nd}\text{ pathway : } pcL \xrightarrow{\Delta E_1^{(12)}} pcLH^2 \xrightarrow{\Delta E_2^{(12)}} pcLH^2H^4 \xrightarrow{\Delta E_3^{(12)}} pcLH^2H^3H^4 \xrightarrow{\Delta E_4^{(12)}} pcLH^1H^2H^3H^4$$

- The stabilization energy of protonations of cone conformation is in the sequence of $\Delta E_1^{(3)} < \Delta E_2^{(3)} < \Delta E_3^{(3)} < \Delta E_4^{(3)}$ as -240.8 *(-270.8)* < -211.1(*-248.4*) < -168.0 *(-216.1)* < -146.8^a(*-176.9*)^b, in Kcal/mole (where ^{a} and ^{b} indicate the 6-31G and STO-3G energy levels, respectively).
- The stabilization energy of protonations of partial cone conformation is in the sequence of $\Delta E_1^{(12)} < \Delta E_2^{(12)} < \Delta E_3^{(12)} < \Delta E_4^{(12)}$ as -243.4 (*-275.6*) < -208.9 (*-247.9*) < -178.0.0 (*-221.2*) < -135.1^a (*-172.8*)^b, in Kcal/mole. The sequence of these stabilization energies corresponds to their protonation constants $\log K_1 > \log K_2 > \log K_3 > \log K_4$ as $11.87 > 5.59 > 4.62 > 4.62$.

Suggestion For the Future Work

The calculations of the stabilization energies of higher energy level than 6-31G and including the polarization functions such as 6-31G(p), 6-31G(p,d) should be continued for correcting the interaction of nitrogen donating group. The experiment for determination of protonation constants of cone conformation of the 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene may be repeated by different techniques. Stability constants of their complexes with heavy metal ions in different solution, should be examed by uv spectroscopic method.

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Appendix A

Figure A.1 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene cone conformation, **cL** obtained from the structure optimization by PM3 method of quantum-chemical calculations.

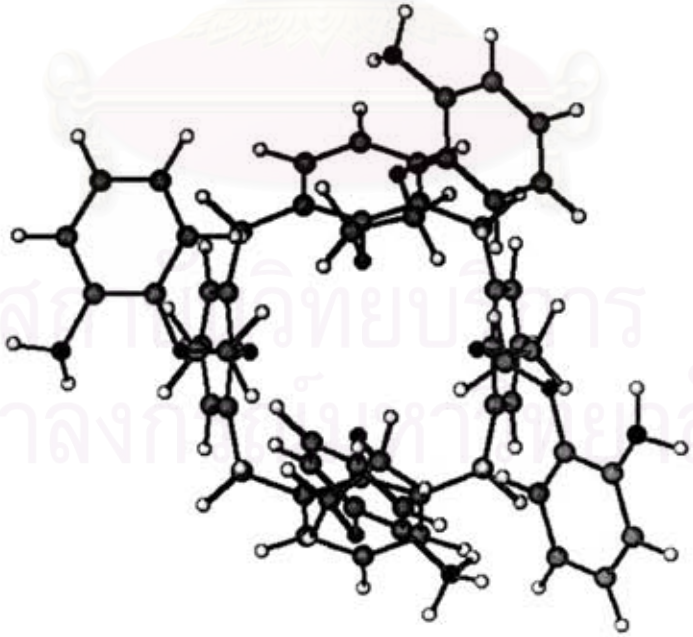

Figure A.2 **cLH**^{1} configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

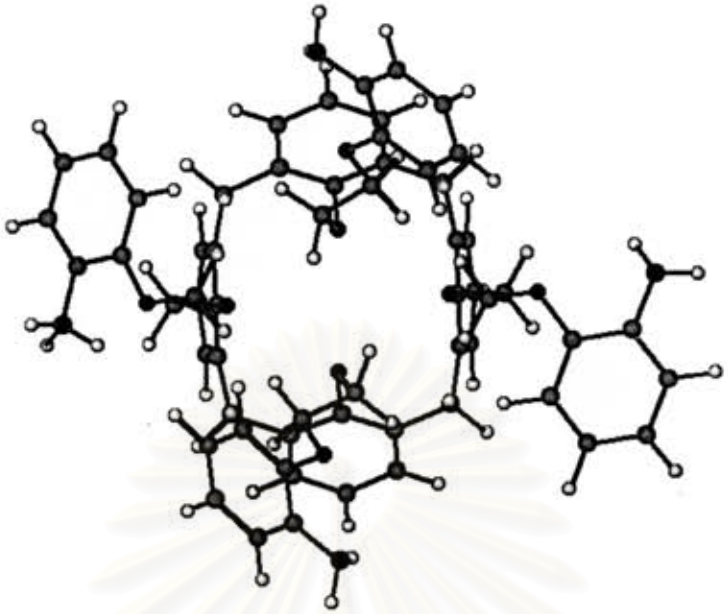

Figure A.3 cLH^2 configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

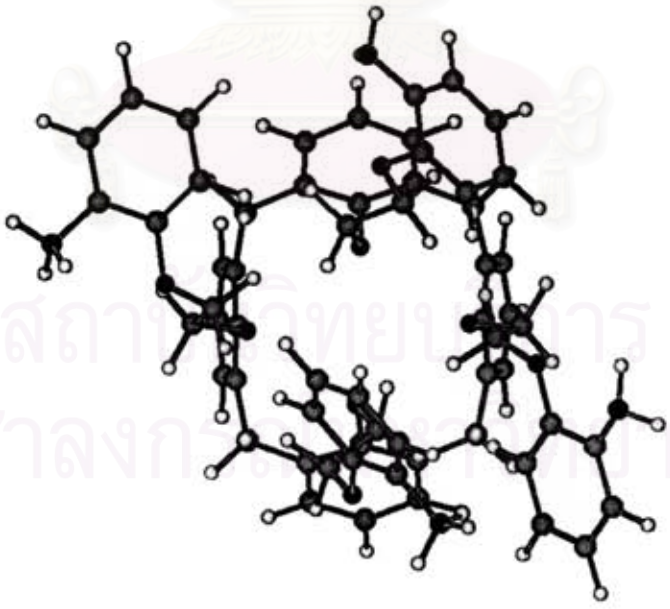

Figure A.4 cLH^1H^2 configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

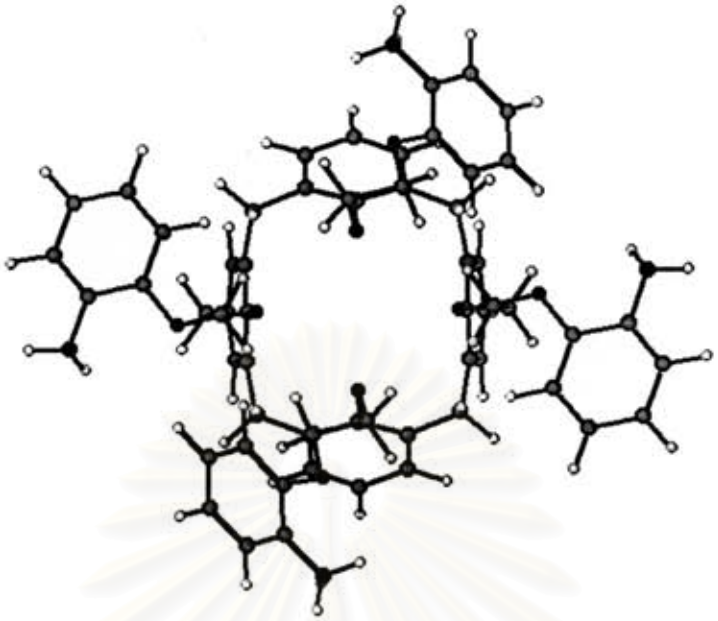

Figure A.5 cLH^1H^3 configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

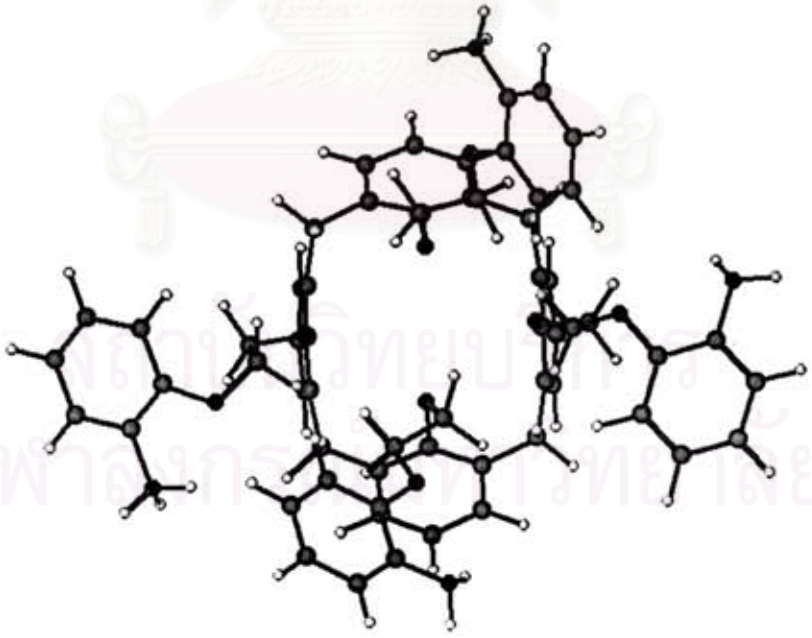

Figure A.6 cLH^2H^3 configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

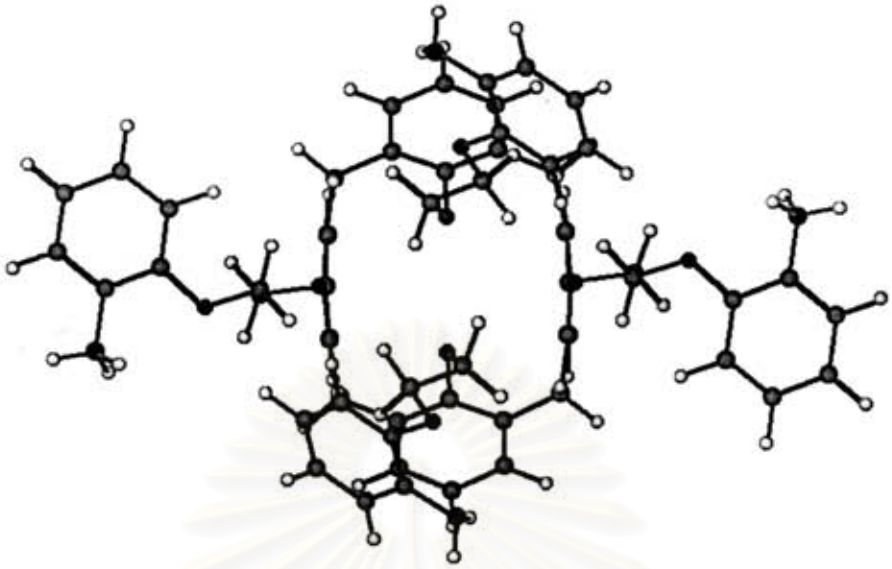

Figure A.7 cLH^2H^4 configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

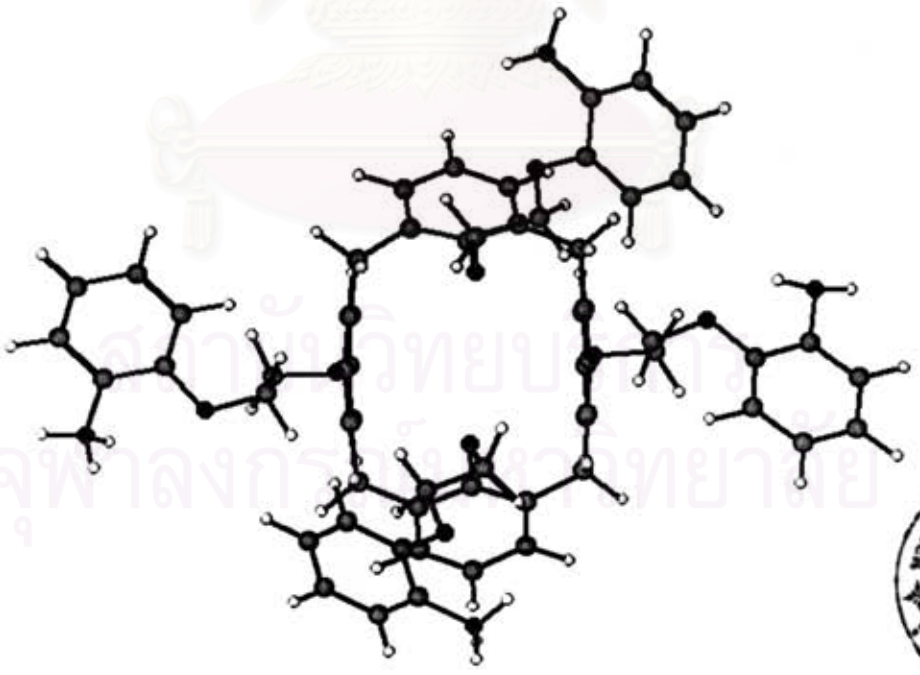

Figure A.8 $cLH^1H^2H^3$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

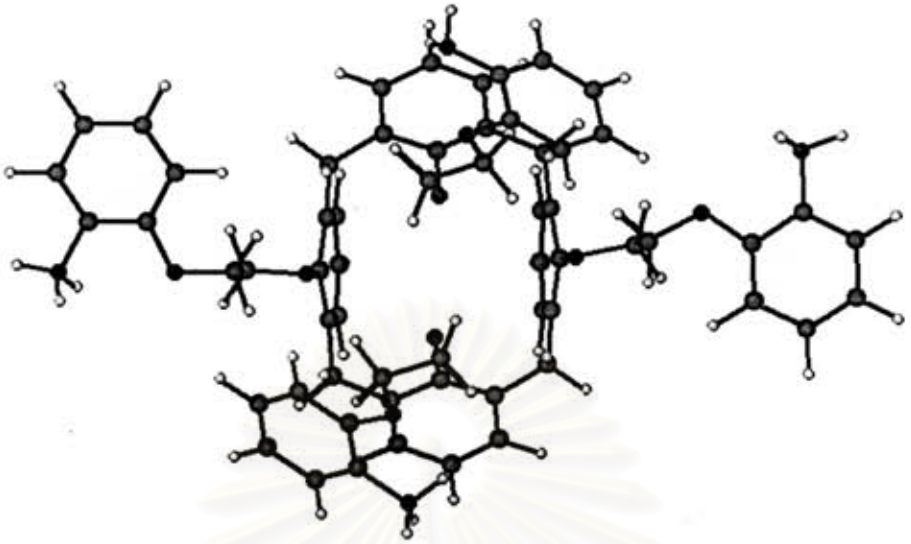

Figure A.9 $cLH^1H^2H^4$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

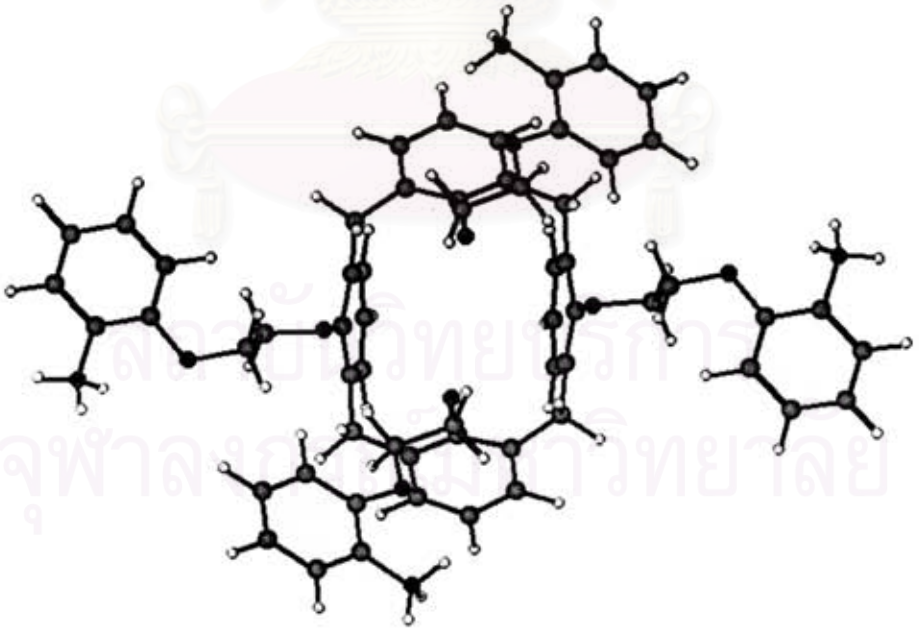

Figure A.10 $cL\ H^1H^2H^3H^4$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

Appendix B

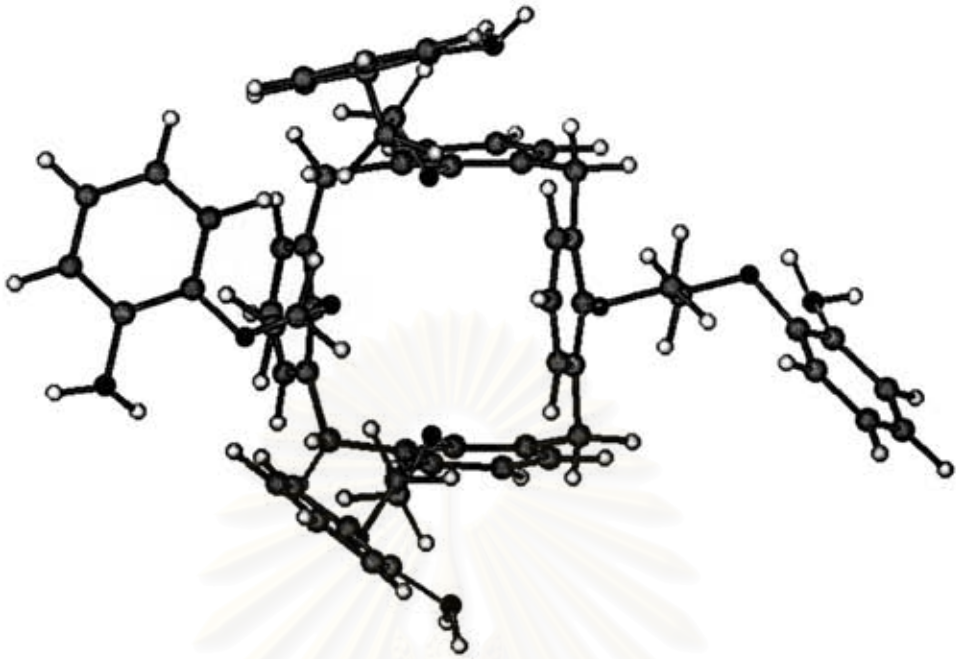

Figure B.1 25,26,27,28-*tetra*(2-ethoxyaniline)calix[4]arene partial cone conformation, **pcL** obtained from the structure optimization by PM3 method of quantum-chemical calculations.

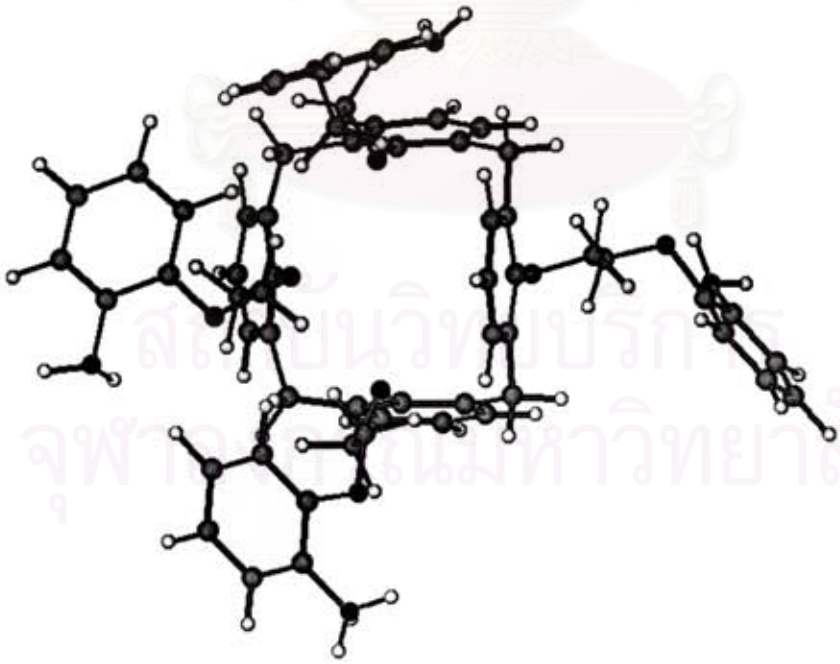

Figure B.2 **pcLH**^{1} configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

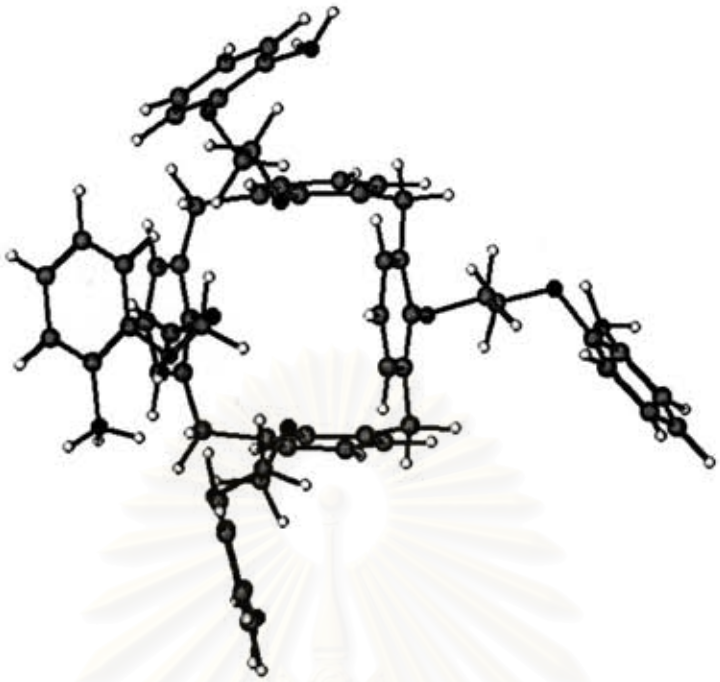

Figure B.3 **pcLH^2** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

Figure B.4 **pcLH^3** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

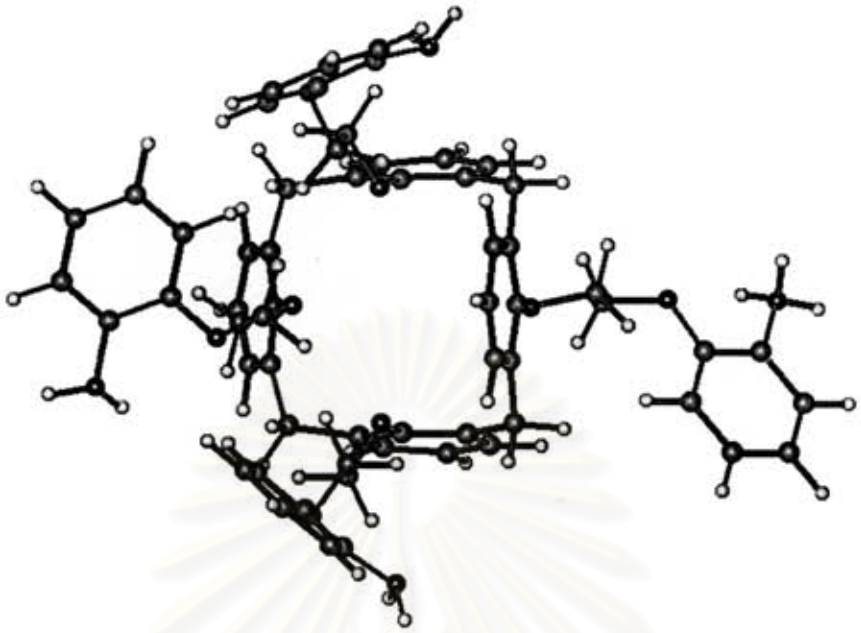

Figure B.5 **pcLH^4** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

Figure B.6 **pcLH^{1}H^2** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

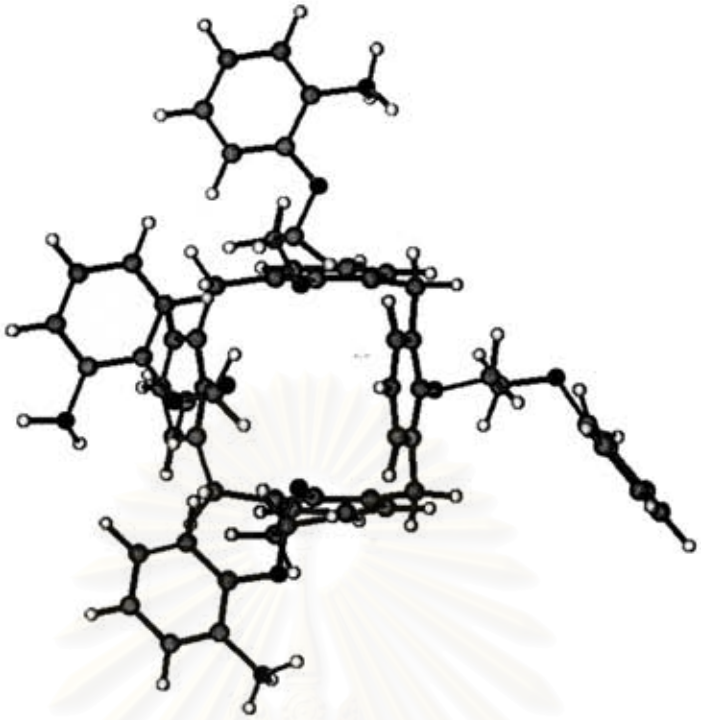

Figure B.7 **pcLH^{1}H^3** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

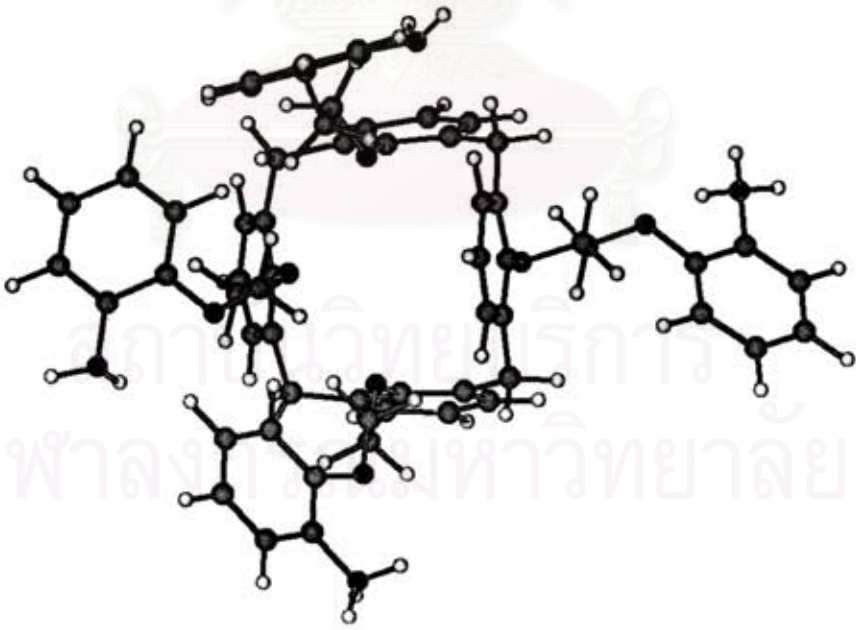

Figure B.8 **pcLH^{1}H^4** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

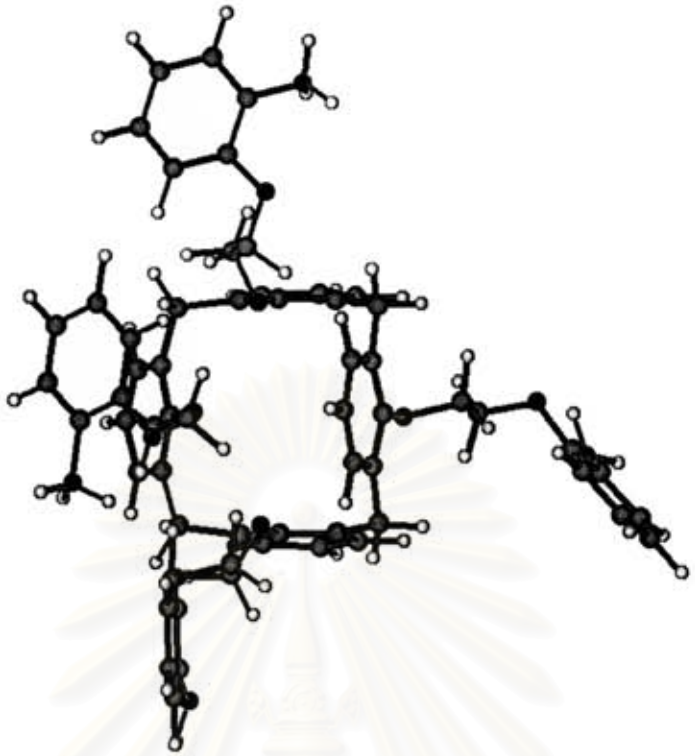

Figure B.9 $pcLH^2H^3$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

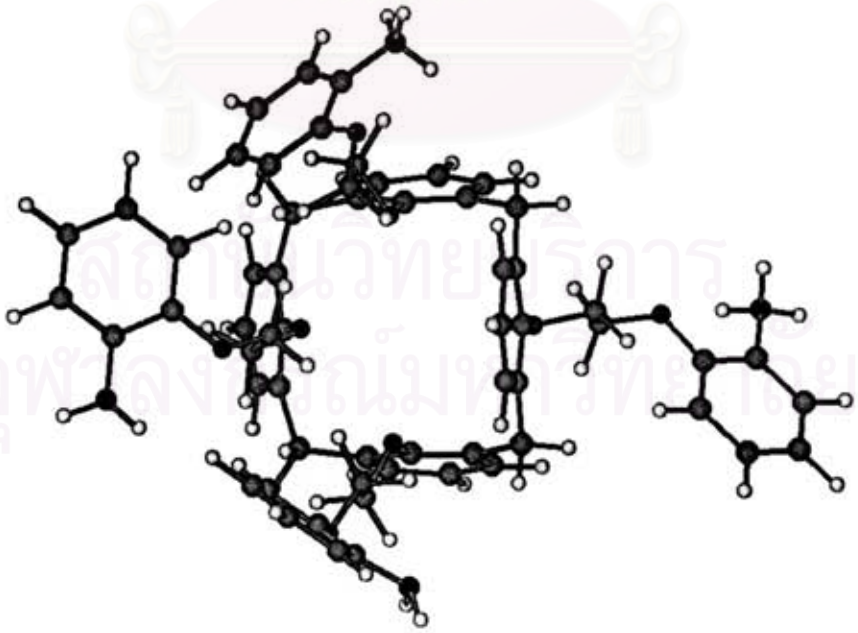

Figure B.10 $pcLH^3H^4$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

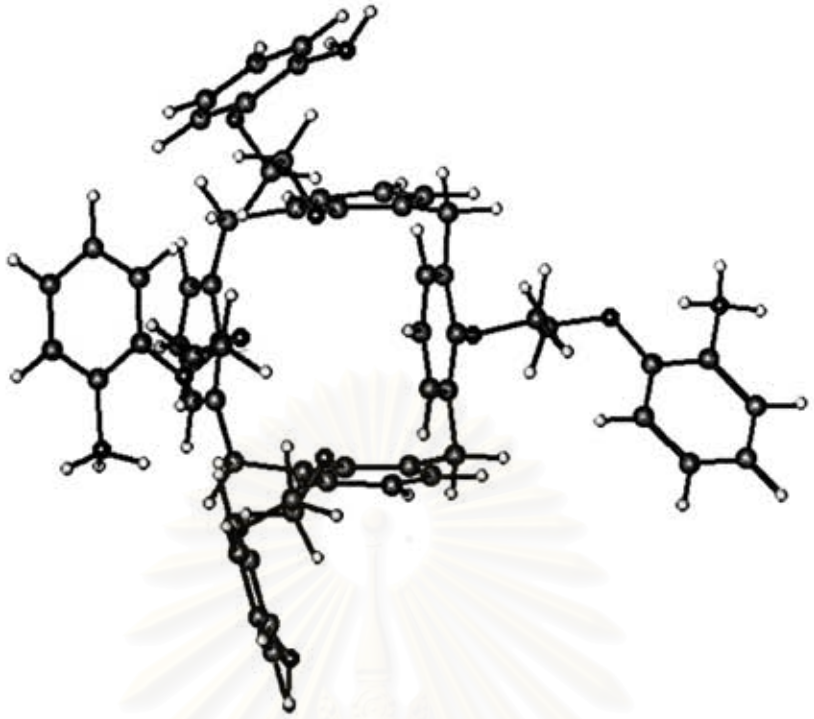

Figure B.11 **pcLH^{2}H^4** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

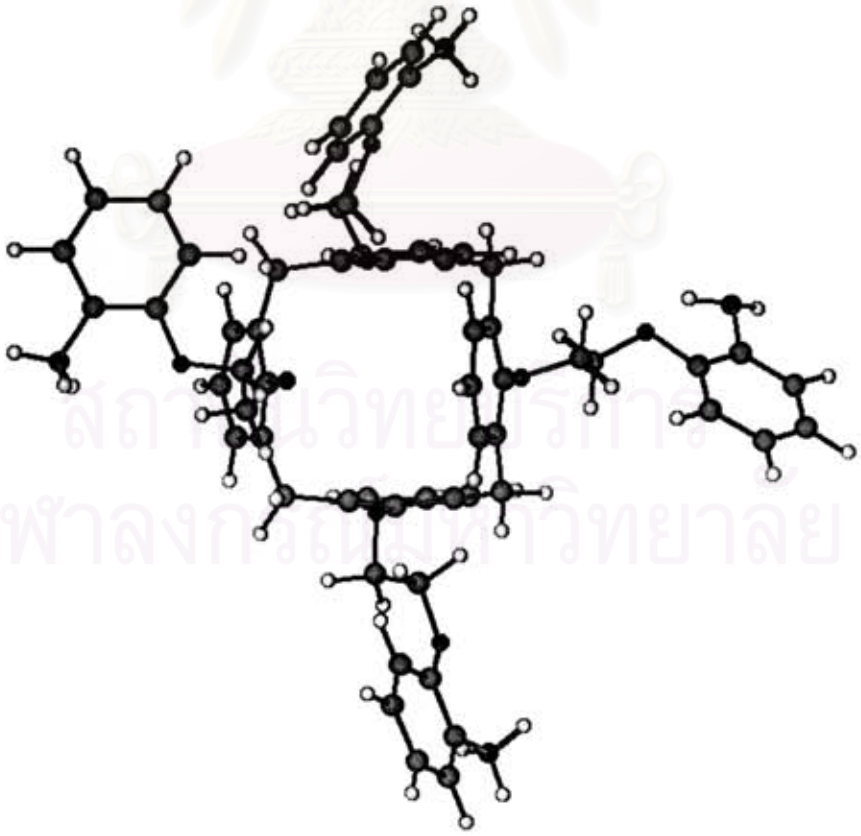

Figure B.12 **pcLH^{1}H^{2}H^3** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

Figure B.13 **pcLH^{1}H^{2}H^4** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

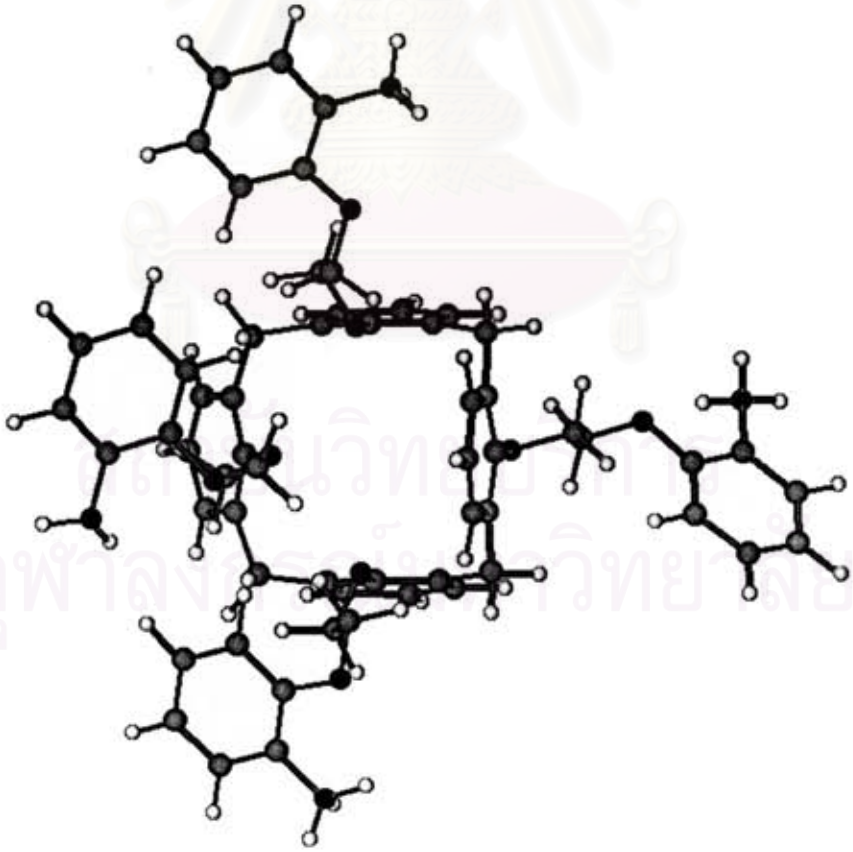

Figure B.14 **pcLH^{1}H^{3}H^4** configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

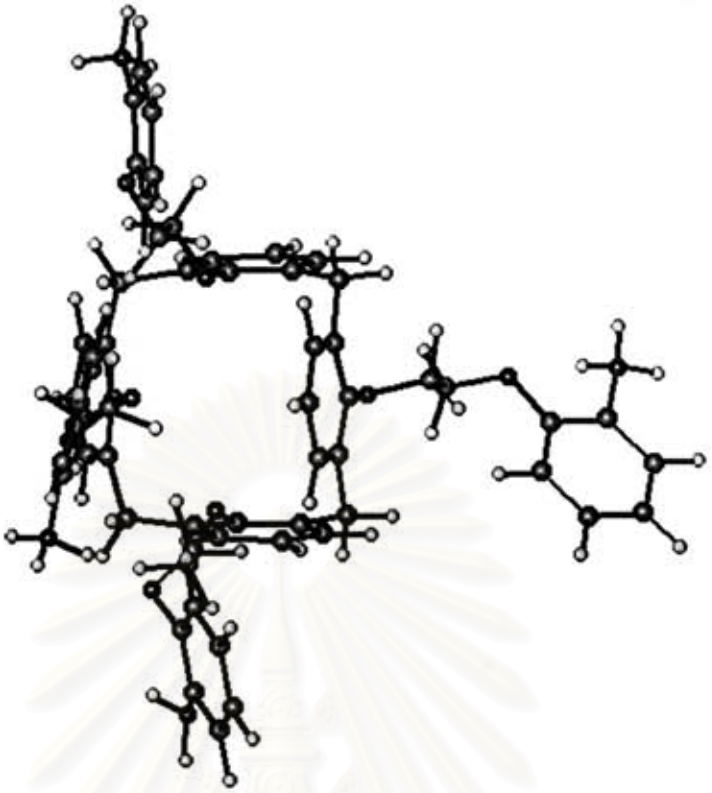

Figure B.15 $pcLH^2H^3H^4$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.

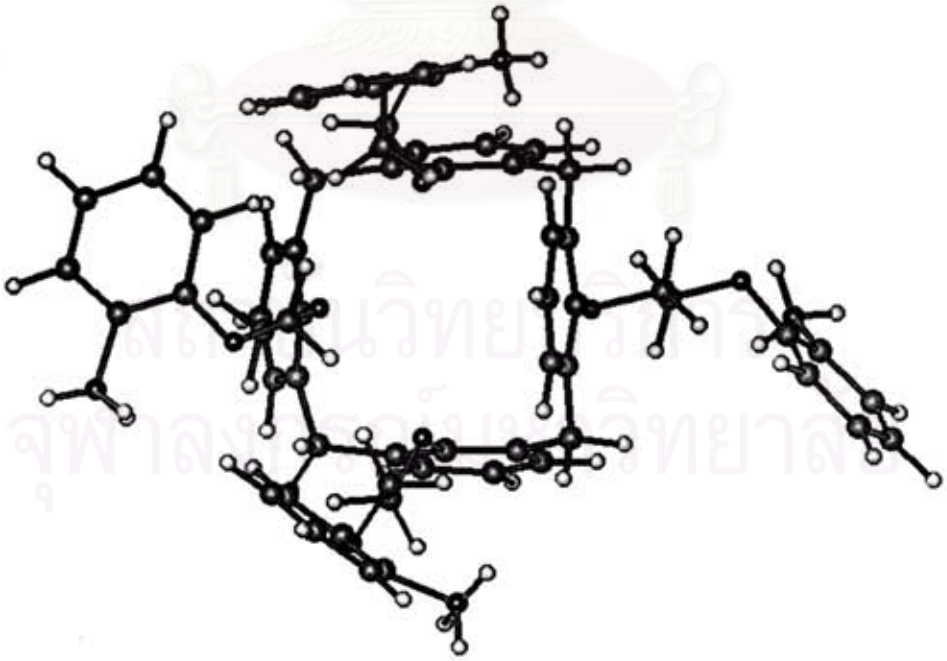

Figure B.16 $pcLH^1H^2H^3H^4$ configuration obtained from the structure optimization by PM3 method of quantum-chemical calculations.