



จุฬาลงกรณ์มหาวิทยาลัย
ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานวิจัย

การศึกษาสมดุลงรูปและโปรตอนแอฟฟิซิตีของ
สารประกอบไฮอากาลิกซ์[4]เอรีน และการเกิด
สารประกอบเชิงซ้อนกับแคตไอออน

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Chulalongkorn University

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Research Report

**Investigation of Conformational Equilibrium and Proton Affinity of
Thiacalix[4]arenes and Their Complexes with Cations**

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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การการศึกษาสมดุลงรูปและโปรตอนแอฟฟิเนติของสารประกอบไฮอากาลิกซ์[4]เอรีน และ การ
เกิดสารประกอบเชิงซ้อนกับแคตไอออน

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บทคัดย่อ

การหาโครงสร้างและโครงรูปของพาราเทอร์เซียร์บิวทิลซัลโฟนิลคาลิก[4]เอรีน, ซัลโฟนิลคาลิก[4]เอรีน และ สารประกอบเชิงซ้อนที่เกิดกับสังกะสีโดยวิธี AM1 โครงสร้างได้รับการเปรียบเทียบกับคาลิก[4]เอรีน และ ไพธาลิกซ์[4]เอรีน พลังงานของโครงสร้างต่าง ๆ คำนวณโดยวิธี HF/6-31G* และ B3LYP/6-31G* พลังงาน ที่เสถียรที่สุดของ ซัลโฟนิลคาลิก[4]เอรีน และ พาราเทอร์เซียร์บิวทิลซัลโฟนิลคาลิก[4]เอรีน คือ โครงรูป 1,2-อัลเทอเนต และ 0011-AAAA 1,2-อัลเทอเนต ตามลำดับ พบว่าเกิดพันธะไฮโดรเจนสองชนิดบน โครงชนิดโคน และ พาร์เซียร์โคน ของ ซัลโฟนิลคาลิก[4]เอรีน และ พาราเทอร์เซียร์บิวทิลซัลโฟนิลคาลิก[4]เอรีนชนิดโคน พบ โครงสร้างของสารประกอบเชิงซ้อนระหว่างสังกะสีกับพาราเทอร์เซียร์บิวทิลซัลโฟนิลคาลิก [4]เอรีนมีผลลัพธ์ตรงกับ โครงสร้างที่ได้จากเอกซ์เรย์

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Project Title Investigation of Conformational Equilibrium and Proton Affinity of Thiacalix[4]arenes and Their Complexes with Cations

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Abstract

The p-tert-butylsulfonylcalix[4]arene and sulfonylcalix[4]arene conformers have been obtained by AM1 geometry optimizations. The structural cavities of p-tert-butylsulfonylcalix[4]arene and sulfonylcalix[4]arene conformers of which phenol groups are bridged by sulfonyl sulfur have been compared to the calix[4]arene and thiacalix[4]arene. The conformational energies of p-tert-butylsulfonylcalix[4]arene have been compared with the energies of sulfonylcalix[4]arene, calix[4]arene and thiacalix[4]arene. The most stable conformer of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene are 1,2-alternate and 0011-AAAA 1,2-alternate conformers, respectively. Two different types of hydrogen bond presented in the sulfonyl calix[4]arene cone and partial cone conformers and p-tert-butylsulfonylcalix[4]arene cone conformer have been found. Ab initio energies of the AM1 optimized structures of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene conformers and their complexes with zinc(II) have been computed at HF/6-31G* and B3LYP/6-31G* theoretical levels. The optimized structure of complex species of p-tert-butylsulfonylcalix[4]arene with zinc(II) is in good agreement with recent x-ray geometry data.

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CHAPTER I

INTRODUCTION

1.1 Sulfonylcalix[4] arene, p-tert-butylsulfonylcalix[4]arene

Ability of recognition or selectivity of molecular systems with other molecules is very important roll in host-guest chemistry. The family of calix[n]arenes is one of model systems in supramolecular host-guest chemistry [1-3] . Calix[4]arene is one of the well known members of the calix[n]arene family. Calix[4]arenes have four characteristic conformations known as cone, partial cone, 1,2-alternate and 1,3-alternate conformers [1]. Many works of modeling calix[4]arene have been investigated by theoretical approaches as based on force field [4-9], semiempirical [4, 10, 11] and ab initio calculations [12]. Since heterocalix[4]arene as in which phenol units are bridged by sulfur atoms [13-20] have been synthesized, the conformational and structures of thiacalix[4]arene have been reported [21]. The calix[4]arene conformations have been known that their stabilities depend on the substituted R groups on the upper rim, R' groups on the lower rim and X groups as phenolic bridges as defined in Figure 1.1 [7].

As the calix[4]arene conformers are specified by substituted R/R'/X groups, it was found that the relative stabilities are in decreasing order : cone > partial cone > 1,2-alternate > 1,3-alternate for R/R'/X =H/OH/CH₂ and H/H/CH₂ [12], partial cone > 1,2-alternate > cone > 1,3-alternate for R/R'/X =t-Bu/OMe/CH₂ [7] and cone > partial cone > 1,3-alternate > 1,2-alternate for R/R'/X =H/OH/S [21]. The molecular properties of p-tert-butylcalix[4]arene were theoretically investigated by semi-empirical AM1 and ab initio methods [11]. Since the synthesis of p-tert-butylthiacalix[4]arene [13] was reported, the chemical reactions on alkylation [14, 18, 19, 22, 23, 24] and oxidations of the sulfur atoms to sulfoxides and sulfones [14, 15, 25, 26, 27] have been extensively researched. The structure and conformational

equilibrium of the thiacalix[4]arene has been studied by ab initio calculations and compared to the conformational equilibrium of calix[4]arene [21]. Due to a special ability of calix[4]arene structures to include transition metal cations [14-16] and neutral molecule [25] leading to useful applications, the sulfonylcalix[4]arene structures should have also special ability to form complexes with some cations. The solid structures of p-tert-butylsulfonylcalix[4]arene complexing with cobalt(II), nickel(II) and zinc(II) were recently synthesized and determined by x-ray crystallography [15, 28]. Nevertheless the structure details of their conformers and their complexes with metal cations have been not much revealed.

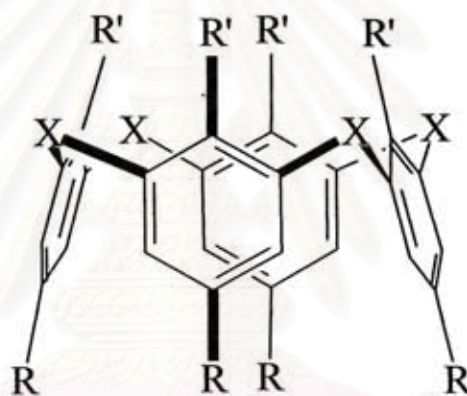


Figure 1.1 Calix[4]arenes specified by substituted R, R' and X groups

In the present work, we have determined the structures, conformations and energies of sulfonylcalix[4]arene, p-tert-butylsulfonylcalix[4]arene and their zinc complexes by theoretical approach. The sulfonylcalix[4]arene structures and energies have been investigated and compared to the calix[4]arene and thiacalix[4]arene molecules. The molecular cavities based on the sulfone bridges of p-tert-butylsulfonylcalix[4]arene and sulfonylcalix[4]arene, sulfur bridge of thiacalix[4]arene and methylene bridge of calix[4]arene, have been compared. The main purposes of this work are to determine the sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene conformers, their structural information, energies of their

interconversion and complexation with zinc(II) in comparison with the x-ray crystallographic structure.

1.2 Butylthiacalix[4]arene and p-tert-butylthiacalix[4]arene

Calix[4]arene and derivatives are well known supramolecular hosts [2, 3] that have ability to recognize or selectively interact with other molecules. The recognition of molecular systems strongly depend on the host-guest intermolecular interactions. Structures, conformational equilibrium and electronic properties of calix[4]arene have been investigated using density functional theory calculations in order to explain characteristic of calix[4]arene in host-guest chemistry [12]. Conformation optimizations and reaction paths of calix[4]arenes have been studied by theoretical calculations using force fields [4-9], semi-empirical [10, 11] and ab initio calculations [13]. Thiacalix[4]arene in which phenol units bridged by sulfur atoms and its derivatives have been synthesized and characterized by many researchers [13-20]. Structures and conformational energies of thiacalix[4]arene have been studied by quantum chemical calculations and found that the cone conformer is the most stable structure [21].

Since p-tert-butylcalix[4]arene was first synthesized by Sone et al. [29], its molecular properties theoretically investigated by semi-empirical AM1, Hartree-Fock (HF) and density functional theory (DFT) methods were reported [10]. The structure and conformational equilibrium of thiacalix[4]arene have been studied by DFT calculations and compared to calix[4]arene [21]. Conformational structures of sulfonylcalix[4]arene, p-tert-butylsulfonylcalix[4]arene and its zinc complex have been investigated by different theories of calculations [30]. Calix[4]arene can include transition metal cations [14-16] and neutral molecules [25] leading to useful applications. p-tert-butylthiacalix[4]arene should also have the ability to form complexes with some transition metal cations. Solid state structures of p-tert-butylthiacalix[4]arene complexing with zinc(II) were determined by X-ray

crystallography [31, 32]. Complexation abilities of p-tert-butylthiacalix[4]arene toward transition metal ions such as Co^{2+} , Cu^{2+} and Zn^{2+} were also reported [33]. Nevertheless, the structure details of their conformers and its complexes with metal cations have been rarely revealed.

In the present paper, the conformational structures, energies of p-tert-butylthiacalix[4]arene and its zinc complex are investigated by quantum chemical calculations. Thiacalix[4]arene and p-tert-butylthiacalix[4]arene conformational structures and energies are determined and compared to the sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene molecules [30]. The main purpose of this work is to determine p-tert-butylthiacalix[4]arene conformers, their structural information, energies of their interconversion, proton affinity and complex with zinc(II) cation. The optimized structures of the p-tert-butylthiacalix[4]arene cone conformer computed by various methods are compared to the X-ray crystallographic structure.



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CHAPTER II

THEORY

2.1 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. 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:

$$\int \Psi^* \Psi d\tau = 1 \quad (2.1)$$

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:

$$\int \Psi_m^* \Psi_n d\tau = 0 \quad (m \neq n) \quad (2.2)$$

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

$$\int \Psi_m^* \Psi_n d\tau = \delta_{mn} \quad (2.3)$$

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.

2.2 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:

$$\Psi_{\text{tot}}(\text{nuclei,electrons}) = \Psi(\text{electrons}) \Psi(\text{nuclei}) \quad (2.4)$$

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: $E_{\text{tot}} = E(\text{electrons}) + E(\text{nuclei})$.

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.

2.3 Ab Initio Hartree-Fock Methods

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:

$$\psi = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (2.5)$$

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 suggested a simpler analytical form for the radial functions:

$$R_{nl}(r) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} \quad (2.6)$$

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:

$$R_{1s}(r) = 2\zeta^{3/2} e^{-\zeta r} \quad (2.7)$$

$$R_{2s}(r) = R_{2p}(r) = \left(\frac{4\zeta^5}{3}\right)^{1/2} r e^{-\zeta r} \quad (2.8)$$

$$R_{3s}(r) = R_{3p}(r) = R_{3d}(r) = \left(\frac{8\zeta^7}{45}\right)^{1/2} r^2 e^{-\zeta r} \quad (2.9)$$

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 1s, 2s and 2p, orbitals :

$$\phi_{1s}(r) = \sqrt{(\zeta^3/\pi)} \exp(-\zeta r) \quad (2.10)$$

$$\phi_{2s}(r) = \sqrt{(\zeta^5/32\pi)} \exp(-\zeta r) \quad (2.11)$$

$$\phi_{2p_z}(r) = \sqrt{(\zeta^5/\pi)} \exp(-\zeta r) \cos\theta \quad (2.12)$$

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

$$\zeta = \frac{Z - \sigma}{n^*} \quad (2.13)$$

Z is the atomic number and σ 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, σ 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 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 3×0.35 under rule (b), 2.0 under rule (c), and 8×0.85 under rule (d), giving a total of 9.85. When subtracted from the atomic number (14) this gives 4.15 for the value of $Z - \sigma$.

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:

$$\psi_i = \sum_{\nu=1}^K c_{\nu i} \phi_{\nu} \quad (2.14)$$

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 (2.14) there are K basis functions and we should therefore expect to derive a total of K molecular orbitals (although not all of these will necessarily 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 $c_{\nu i}$ 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 $c_{\nu i}$. The objective is thus to determine the set of coefficients that gives the lowest energy for the system.

The Fock matrix is a $K \times K$ square matrix that is symmetric if real basis functions are used. The Roothaan-Hall equations can be conveniently written as a matrix equation:

$$\mathbf{FC} = \mathbf{SCE} \quad (2.15)$$

The elements of the $K \times K$ matrix C are the coefficients c_{vi} :

$$C = \begin{pmatrix} c_{1,1} & c_{1,2} & \cdots & c_{1,K} \\ c_{2,1} & c_{2,2} & \cdots & c_{2,K} \\ \vdots & \vdots & & \vdots \\ c_{K,1} & c_{K,2} & \cdots & c_{K,K} \end{pmatrix} \quad (2.16)$$

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

$$E = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix} \quad (2.17)$$

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 (2.15), 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 $H_{\mu\nu}^{\text{core}}$ 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 orthonormal set. A matrix X is determined by an equation, such that $X^T S X = I$. 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

$$U^T S U = D = \text{diag}(\lambda_1 \dots \lambda_K) \quad (2.18)$$

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 $U^{-1} S U = D$ since for real basis functions $U^{-1} = U^T$.) Then the matrix X is given by $X = U D^{-1/2} U^T$ 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: $S^{-1/2} S S^{-1/2} = I$.

The Roothaan-Hall equations can now be manipulated as follows. Both sides of equation (2.15) are pre-multiplied by the matrix $S^{-1/2}$:

$$S^{-1/2} F C = S^{-1/2} S C E = S^{1/2} C E \quad (2.19)$$

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

$$S^{-1/2} F (S^{-1/2} S^{1/2}) C = S^{1/2} C E \quad (2.20)$$

or

$$S^{-1/2} F S^{-1/2} (S^{1/2} C) = (S^{1/2} C) E \quad (2.21)$$

Equation (2.21) can be written $F' C' = C' E$, where $F' = S^{-1/2} F S^{-1/2}$ and $C' = S^{1/2} C$.

The matrix equation $F' C' = C' E$ can be solved using standard methods; a solution only exists if the determinant $|F' - E|$ 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. Form 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. Check 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, F_i . The energy of an electron in a spin orbital is calculated by adding the core interaction $H_{\mu\nu}^{\text{core}}$ to the Coulomb (J_{ij}) and exchange interactions (K_{ij}) with the other electrons in the system:

$$\varepsilon_i = H_{ii}^{\text{core}} + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \quad (2.22)$$

The total electronic energy of the ground state is given by equation (2.23):

$$E = 2 \sum_{i=1}^{N/2} H_{ii}^{\text{core}} + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \quad (2.23)$$

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

$$E = \sum_{i=1}^N \varepsilon_i - \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \quad (2.24)$$

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.

2.4 Basis Set

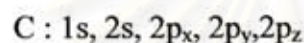
2.4.1 Basis Set Effects

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 quantum mechanical picture, electrons have a finite probability of existing anywhere in space; this limit corresponds to the infinite basis set. 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.

2.4.2 Minimal Basis Sets.

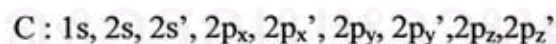
Minimal basis sets contain the minimum number of basis functions needed for each atom, as in these examples:



Minimal basis sets use fixed-size atomic-type orbitals. The STO-3G basis set¹⁴ 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.

2.4.3 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 and 6-31G, have two (or more) sizes of basis function for each valence orbital. For example, hydrogen and carbon are represented as:



Where the primed and unprimed orbitals differ in size. The double zeta basis sets, such as the Dunning-Huzinaga basis set (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, use three sizes of contracted functions for each orbital-type.

2.4.4 Polarized Basis Sets.

Split valence basis sets allow orbitals to change site, 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 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.

2.4.5 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.

2.4.6 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 Bernardi²⁸ in which the entire basis set is included in all calculations. 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.

2.4.7 Semi-empirical Methods

2.4.7.1 AM1 (Austin Model 1) Method

AM1 was modified from MNDO (Modified Neglect of Diatomic Overlap) method and became clear that there were certain systematic errors. For example the repulsion between two atoms which are 2-3 Å apart is too high. This has as a consequence that activation energies in general are too large. The source was traced

to too repulsive an interaction in the core-core potential. To remedy this, the core-core function was modified by adding Gaussian functions, and the whole model was reparameterized. The core-core repulsion of AM1 has the form

$$V_{nn}(A,B) = V_{nn}^{\text{MINDO}}(A,B) + \frac{Z'_A Z'_B}{R_{AB}} \times \left(\sum_k a_{kA} e^{-b_{kA}(R_{AB}-c_{kA})^2} + \sum_k a_{kB} e^{-b_{kB}(R_{AB}-c_{kB})^2} \right) \quad (2.25)$$

Where k is between 2 and 4 depending on the atom. It should be note that the Gaussian functions more or less were added as patches onto the underlying parameters, which explains why different number of Guassians are used for each atom. As with MINDO, the G_{ss} , G_{sp} , G_{pp} , G_{p2} , H_{sp} parameters are taken from atomic spectra, while the rest including the a_k , b_k and c_k constants, are fitted to molecular data.

2.4.7.2 PM3 Method

PM3 is a short name of MNDO-PM3 (Modified Neglect of Diatomic Overlap, Parametric Method Number 3). PM3 is a method of the optimization process automatic, by deriving and implementing formulas for the derivative of a suitable error function with respect to the parameters. All parameters could then be optimized simultaneously, including the two-electron terms, and a significantly larger trianing set with several hundred data could be employed. In this reparameterization, the AM1 expression for the core-core repulsion, equation (2.23), was kept, except that only 2 Gaussians were assigned to each atom. These Gaussian parameters were included as an integral part of the model, and allowed to vary freely.

CHAPTER III

EXPERIMENTAL

3.1 Potential energy surface scan for sulfonylcalix[4]arene

The conformers of sulfonylcalix[4]arene (LH₄) and p-tert-butylsulfonylcalix[4]arene (L'H₄) were searched using potential energy surface scan (PES) mode with AM1 method. The energies of the conformations were obtained with the rms value of energies gradient less than 0.001 kcal/mol Å. The structures of complex species of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene with Zn(II) and all related species were optimized by semi-empirical AM1 method. The energies of AM1-optimized structures were computed by single point ab initio and density functional calculations. From the AM1 geometries, the energies have been calculated using Hartree-Fock (HF) and density functional theory (DFT). Density functional calculations have been performed with the B3LYP method as a combination of the Beck exchange functional [34] and the Lee, Yang and Parr correlation functional [35] (LYP) with 6-31G* basis set.

3.2 Conformational definition for sulfonylcalix[4]arene

Four typical conformers of the sulfonylcalix[4]arene molecule as cone, partial cone, 1,2-alternate and 1,3-alternate are firstly generated using standard geometry parameters and optimized using semi-empirical AM1 method. Because of the tert-butyl groups of p-tert-butylsulfonylcalix[4]arene molecule affecting the conformational models, so that the possible number of these conformers must be increased. Due to the possibilities caused by a methyl group in tert-butyl group attached to each aromatic ring pointing along (A) aromatic hydroxyl group and another one pointing against (B) aromatic hydroxyl group, in combination with the four basic types of conformers which upward and downward aromatic hydroxyl groups are defined as the number 1 and 0, respectively (cone, partial cone, 1,2-

alternate and 1,3-alternate conformers (see figure 3.1) are, therefore, denoted as four digits : 0000, 0001, 0011 and 0101, respectively), the possible number of p-tert-butylsulfonylcalix[4]arene conformers must be six for cone (0000-AAAA, 0000-AAAB, 0000-AABB, 0000-ABAB, 0000-ABBB and 0000-BBBB), twelve for partial cone (0001-AAAA, 0001-AAAB, 0001-AABA, 0001-BAAA, 0001-AABB, 0001-BBAA, 0001-ABAB, 0001-BABA, 0001-ABBB, 0001-BBBA, 0001-BBAB and 0001-BBBB), seven for 1,2-alternate (0011-AAAA, 0011-AAAB, 0011-AABB, 0011-ABBA, 0011-ABAB, 0011-ABBB, 0011-BBBB) and six for 1,3-alternate (0101-AAAA, 0101-AAAB, 0101-AABB, 0101-ABAB, 0101-ABBB and 0101-BBBB) conformers. Finally, the existing p-tert-butylsulfonylcalix[4]arene conformers have been obtained by AM1 geometry optimizations. All calculations were performed with the GAUSSIAN 94 program [36] and graphically interfaced and facilitated by the MOLDEN 3.7 program [37].

3.3 Potential energy surface scan for thiacalix[4]arene

Conformers of thiacalix[4]arene and p-tert-butylthiacalix[4]arene were obtained by the potential energy surface scan (PES) using semi-empirical AM1 method. The single point energies of all AM1 optimized structures were obtained by ab initio Hartree-Fock (HF) and density functional theory (DFT) calculations. DFT calculations were carried out using the Becke three parameters hybrid [34] with the Lee, Yang and Parr (LYP) correlation functional [35] or B3LYP method. The most stable structures of p-tert-butylthiacalix[4]arene cone conformer, its deprotonated, protonated forms and zinc complex were fully reoptimized at B3LYP/6-31G* theoretical level. Energies of the AM1 optimized structures of all conformers were computed by single point calculations at HF/6-31G* and B3LYP/6-31G* levels.

Four typical conformations of thiacalix[4]arene : cone, partial cone, 1,2-alternate and 1,3-alternate were initially generated using standard geometry parameters with the HyperChem 7.0 program [38] and fully optimized using AM1 method with Gaussian 03 program [36]. The AM1 optimized geometries of thiacalix[4]arene conformers and their molecular arrangement are shown in Figure 3.2. The relative

energies of thiacalix[4]arene conformers were obtained using B3LYP/6-31G* calculations as reported in Table 4.1.

On the investigation of p-tert-butylthiacalix[4]arene conformers, their conformation names are defined as DDDD-LLLL notation. DDDD is a four-digit name of thiacalix[4]arene cone, partial cone, 1,2-alternate and 1,3-alternate conformers defined as 0000, 0001, 0011 and 0101, respectively as shown in Figure 3.2. LLLL is a four-letter name of which each letter indicates the geometrical arrangement according to the rotation of each tert-butyl group in p-tert-butylthiacalix[4]arene. Since two local minima of geometry according to the rotation of each tert-butyl group have been found, each letter in the four-letters name (LLLL) can be replaced with one of two geometrical types A and B (types A and B are described in Figure 3.3) and the position sequence of the letter L in LLLL name corresponds to each position sequence of four aromatic rings as defined in Figure 3.4.

3.4 Conformational definition thiacalix[4]arene

As a combination of two conformational types (A and B) and four aromatic rings, the geometrical possibility is, therefore, equivalent to sixteen conformations. Since the molecular symmetry of cone (C_4), partial cone (C_1), 1,2-alternate (C_{2v}) and 1,3-alternate (C_2) conformers of thiacalix[4]arene have been considered, the numbers of conformations of each typical conformers of p-tert-butylthiacalix[4]arene are equivalent to six, sixteen, seven and six conformations for cone, partial cone, 1,2-alternate and 1,3-alternate conformers, respectively. Due to the DDDD-LLLL nomenclature, names of the p-tert-butylthiacalix[4]arene conformers can be written as 0000-AAAA, 0000-AAAB, 0000-AABB, 0000-ABAB, 0000-ABBB and 0000-BBBB for cone, 0001-AAAA, 0001-AAAB, 0001-AABA, 0001-ABAA, 0001-BAAA, 0001-AABB, 0001-ABBA, 0001-BBAA, 0001-BAAB, 0001-ABAB, 0001-BABA, 0001-ABBB, 0001-BBBA, 0001-BBAB, 0001-BABB and 0001-BBBB for partial cone, 0011-AAAA, 0011-AAAB, 0011-AABB, 0011-ABBA, 0011-ABAB, 0011-ABBB and 0011-BBBB for 1,2-alternate and 0101-AAAA, 0101-AAAB, 0101-AABB, 0101-ABAB, 0101-ABBB and 0101-BBBB for 1,3-alternate. The expected

conformers of tert-butylthiacalix[4]arene obtained with the AM1 optimization method are equivalent to the possible number as named by DDDD-LLLL notation. All energy calculations were performed with the Gaussian 03 program package [36]. The Molden 3.7 program [37] was utilized to display the molecular geometries and observe the computational convergence via the Gaussian output files. The electrostatic potential surfaces have been generated with the Molekel 4.3 software [39] using the corresponding single point output file which contains Gaussian format data of full population analysis, current basis set and density fitting basis set.



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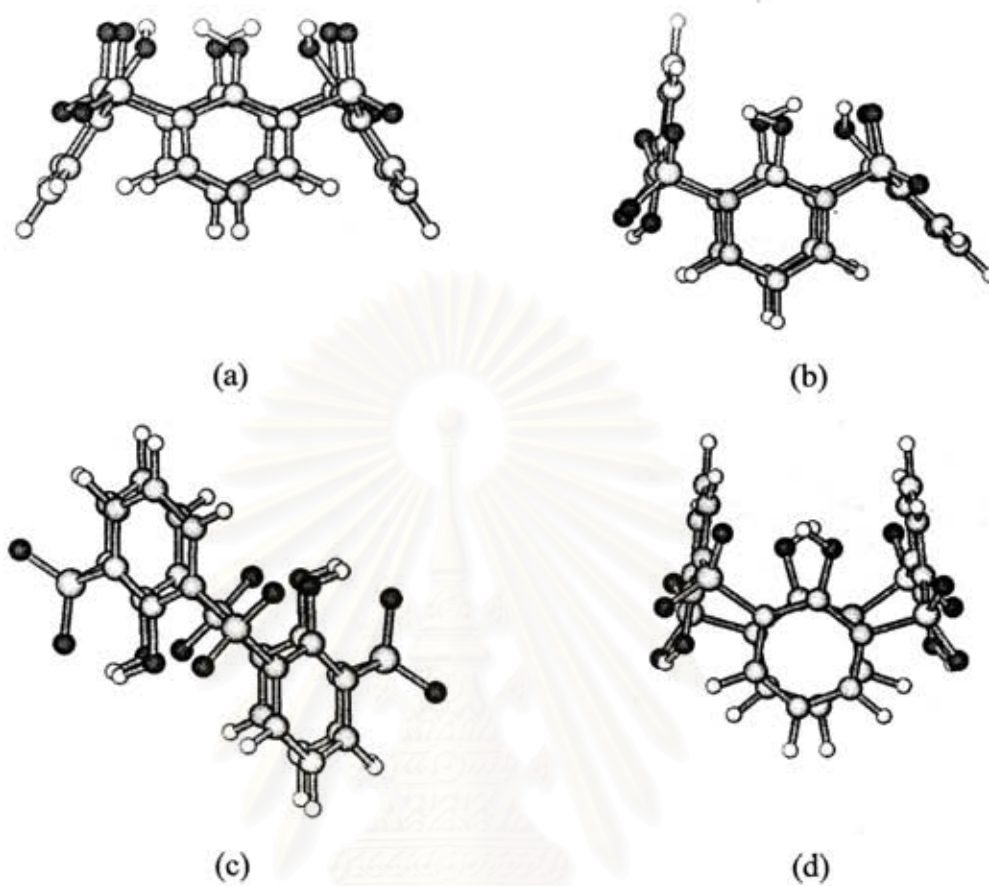


Figure 3.1 Four typical conformers of the sulfonycalix[4]arene : (a) cone, (b) partial cone, (c) 1,2-alternate and (d) 1,3-alternate.

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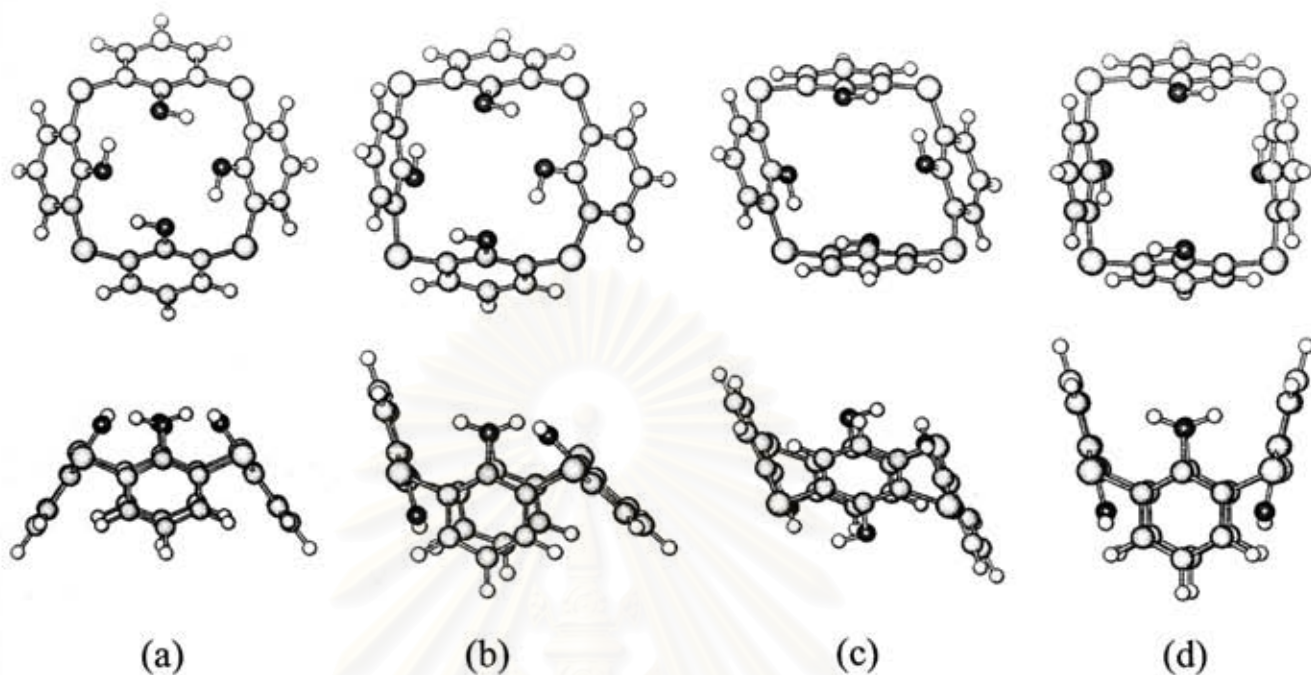


Figure 3.2 The AM1 optimized structures of thiacalix[4]arene (a) cone (0000), (b) partial cone (0001), (c) 1,2-alternate (0011) and (d) 1,3-alternate (0101). Structures above and below are top and side views.

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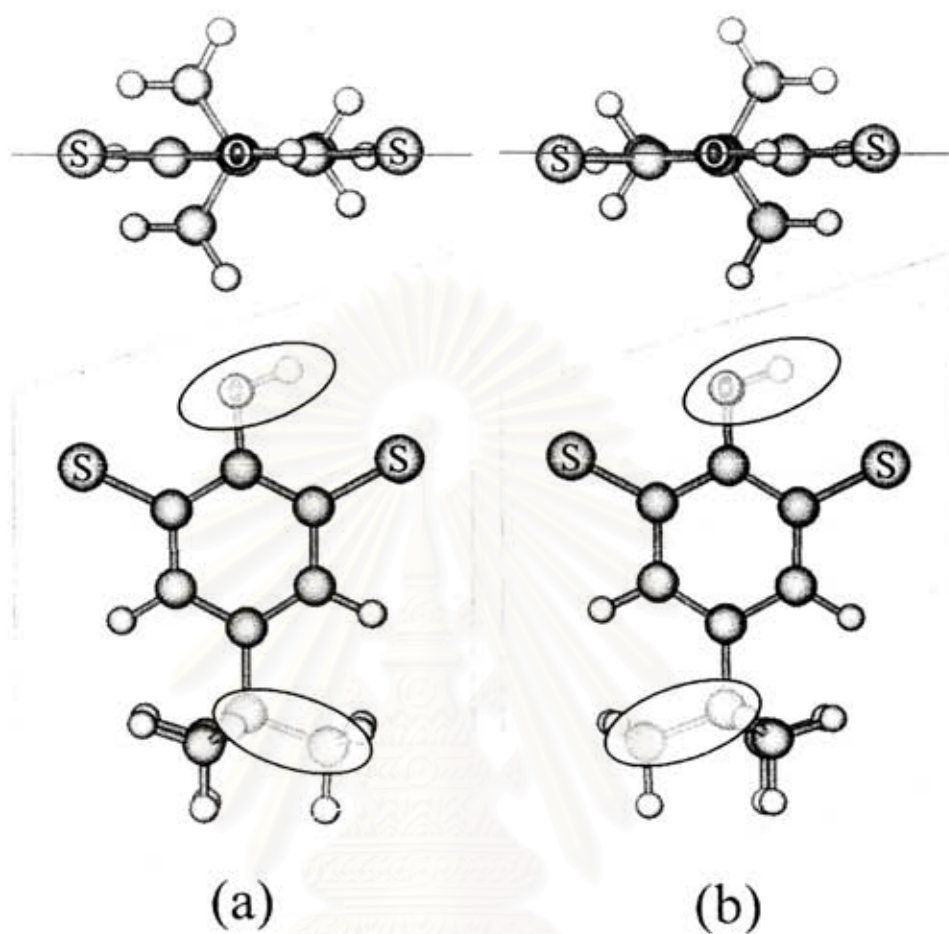


Figure 3.3 Two local minima of geometries defined as (a) type A and (b) type B. Partial structures above and below are top and side views.

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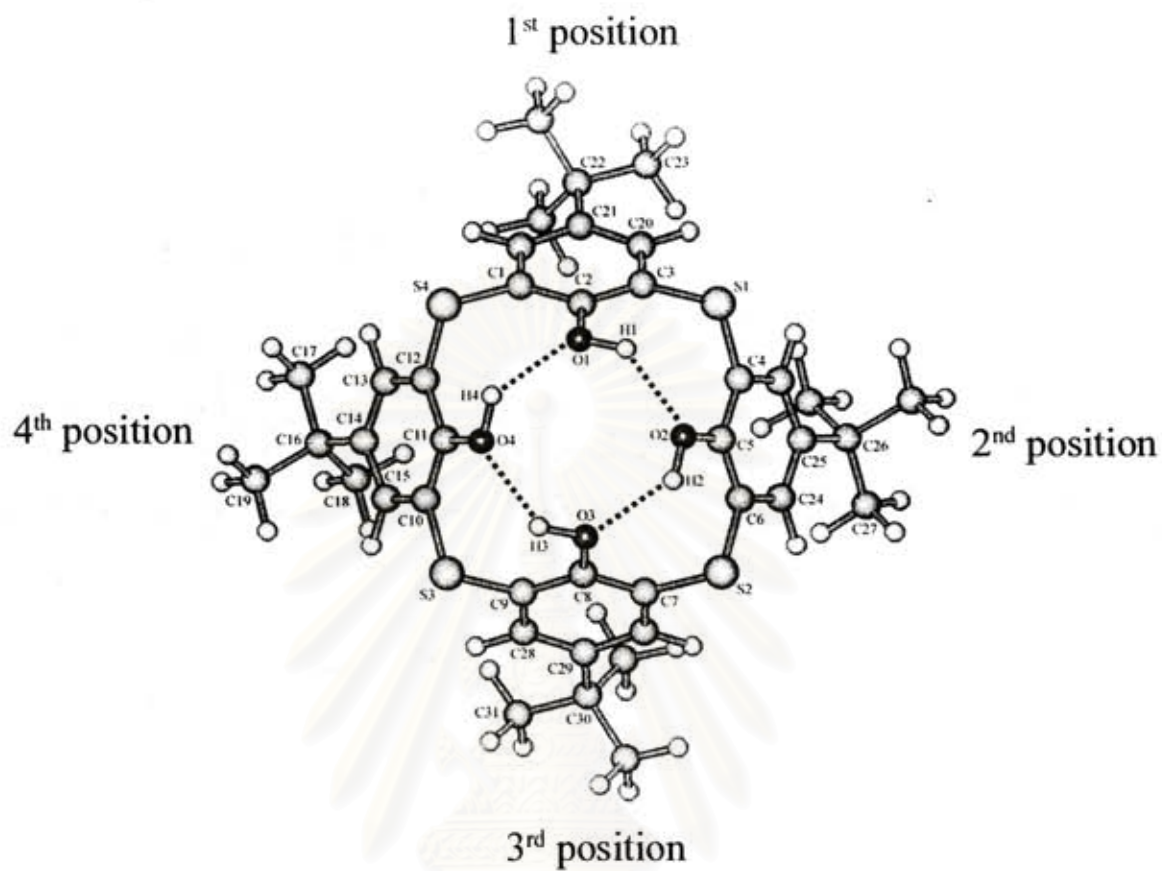


Figure 3.4 The AM1 optimized structure of p-tert-butylthiacalix[4]arene cone, 0000-AAAA conformer.

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CHAPTER IV

RESULTS AND DISCUSSION

4.1. Sulfonylcalix[4]arenes

Determination of the four sulfonylcalix[4]arene conformers, cone, partial cone, 1,2-alternate and 1,3-alternate have been carried out by the AM1 geometry optimizations (Figure 3.1). The total energies of AM1-optimized structures of sulfonylcalix[4]arene conformers and their relative energies, compared to the most stable conformer, 1,2-alternate, were obtained by single point ab initio calculations as reported in Table 4.1. The energy difference between the least and the most stable conformers of sulfonylcalix[4]arene (10.4 kcal/mole at B3LYP/6-31G*//AM1 level) is less than the energy difference of thiacalix[4]arene (16.5 kcal/mole at B3LYP/6-31G** level) [21] by 6 kcal/mole and calix[4]arene (18.6 kcal/mole at B3LYP/6-31G*) [12] by 8.6 kcal/mole. Stabilities of the sulfonylcalix[4]arene conformers are in the order : 1,2-alternate > 1,3-alternate > cone > partial cone (see Table 4.1) and the most stable conformer of sulfonylcalix[4]arene, 1,2-alternate, is different from the thiacalix[4]arene and calix[4]arene conformers of which cone conformers are the most stable species. From Table 4.2, it shows that the hydrogen bonds are present in every conformers of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene.

We found that all the sulfonylcalix[4]arene conformers are able to form stable complexes with zinc(II) ion, except the 1,3-alternate conformer. The zinc complex with deprotonated sulfonylcalix[4]arene cone conformer, $\text{LH}_2(\text{cone})\text{Zn}$, is the most stable complex. The energy differences between the sulfonylcalix[4]arene cone and 1,2-alternate conformers, $\Delta E_{\text{deform.}}(\text{LH}_4)$ and between the deprotonated and neutral forms of sulfonylcalix[4]arene cone conformers, $\Delta E_{\text{deprot.}}(\text{LH}_2)$ are 8.2 and 710.3 kcal/mole at B3LYP/6-31G* energy level, respectively. The energy of complexation between the deprotonated sulfonylcalix[4]arene 1,2-alternate conformer and Zn(II), $\Delta E_{\text{complex.}}(\text{LH}_2\text{-Zn})$, is -632.21 kcal/mole. Figure 4.6 shows hydrogen bonding presented in the sulfonylcalix[4]arene conformers. Since hydrogen bond types caused

by interaction between phenolic proton and adjacent phenolic oxygen (hydrogen bond type 1) and between phenolic proton and adjacent sulfonyl oxygen (type 2) are defined, both hydrogen bond types are presented in the cone and partial cone conformers but only hydrogen bond type 2 is presented in the 1,2-alternate and 1,3-alternate conformers. The cone conformer of sulfonylcalix[4]arene (see Figure 3.1) is a four-fold symmetric structure as same as of thiacalix[4]arene and calix[4]arene as reported in references [12, 21]. The circular hydrogen bonding in sulfonylcalix[4]arene cone conformer caused by the hydrogen bond type 1 is weaker than that in thiacalix[4]arene and calix[4]arene because each atomic charges of phenolic protons are shared by the sulfonyl oxygen to form hydrogen bond type 2. Nevertheless, the flip-flop hydrogen bonding [40] in sulfonylcalix[4]arene cone conformer should have occurred as same as in thiacalix[4]arene and calix[4]arene. Since an enlargement of the sulfonylcalix[4]arene cone cavity indicated by the C-S bond (1.79 Å) [28] in comparison with the C-C bond (1.53 Å) in calix[4]arene [41], the sulfonylcalix[4]arene cone complexes with the transition metal cations are therefore expected. The sulfonylcalix[4]arene cone conformer is a four-fold symmetric structure in which the O1-O7 and O4-O10 distances (see Figure 4.1a) are identical and equal to 3.91 Å. There are two types of hydrogen bond, type 1 and 2, presented in the sulfonylcalix[4]arene cone and partial cone conformers but only type 2 presented in 1,2-alternate and 1,3-alternate conformers are found as shown in Table 4.2.

Because of the tert-butyl groups in the p-tert-butylsulfonylcalix[4]arene molecule, the possible number of its conformers can be six for cone, twelve for partial cone, seven for 1,2-alternate and six 1,3-alternate conformers (see Table 4.3). Due to the structure optimizations using semi-empirical AM1 method, the existing number of cone, partial cone, 1,2-alternate and 1,3-alternate conformers are six, twelve, seven and three conformers, respectively. The total energies at B3LYP/6-31G* level of these conformers are shown in Table 4.3. The energy differences according to the rotation of tert-butyl groups for cone, partial cone, 1,2-alternate and 1,3-alternate conformers are less than 2.0, 4.5, 2.8 and 3.2 kcal/mol, respectively. The free rotation of tert-butyl groups in p-tert-butylsulfonylcalix[4]arene cone and 1,2-alternate conformers could be expected at room temperature.

The AM1-optimized structures of p-tert-butylsulfonylcalix[4]arene conformers and their total energies are reported in Table 4.3 and shown in Figure 4.2 to 4.5. As consideration of the most stable conformers of the four typical conformers, 0000-ABAB cone, 0001-BBBA partial cone, 0011-AAAA 1,2-alternate and 0101-AAAA 1,3-alternate are the most stable conformers as shown in Figure 4.6. The 0011-AAAA 1,2-alternate conformer is the most stable species and more stable than the 0000-ABAB cone, 0001-BBBA partial cone and 0101-AAAA 1,3-alternate conformers by approximately 0.6, 2.0 and 4.9 kcal/mol (see Table 4.1). Only the p-tert-butylsulfonylcalix[4]arene 0000-AAAA cone conformer is a four-fold symmetric structure in which the distances between opposite phenolic oxygen atoms are identical and equal to 3.92 Å. However, the distances between opposite phenolic oxygen atoms of other p-tert-butylsulfonylcalix[4]arene cone conformers are not identical and within approximately 3.91 to 3.93 Å. The reaction pathway of complexation between the deprotonated form of p-tert-butylsulfonylcalix[4]arene cone conformer, $L'H_2^{2-}$ (cone) and zinc(II) ion is proposed as shown in Scheme 1.1. The structures of p-tert-butylsulfonylcalix[4]arene as deprotonated form $L'H_2^{2-}$, $(L'H_2)Zn$ and $(L'H_2)Zn(tacn)$ complex species as shown in Figure 4.7 are the 0000-AABB cone conformers. According to the x-ray crystallographic structure of synthesized $(L'H_2)Zn(tacn)$ crystalline, the complex of p-tert-butylsulfonylcalix[4]arene cone conformer with zinc(II) included by the tetracyclononane (tacn) (Figure 4.8) is therefore proposed in the complexation process as shown in Scheme 1.

The total energies of p-tert-butylsulfonylcalix[4]arene conformers and their related species and the reaction energies of deformation, pre-organization and deprotonation of p-tert-butylsulfonylcalix[4]arene cone conformers and complexation of its zinc(II) complexes are reported in Table 4.4. The reaction energies of deformation ($\Delta E_{\text{deform.}} = 0.57$ kcal/mol) and pre-organization ($\Delta E_{\text{preorg.}} = 0.87$ kcal/mol) are very small in comparison with thermal energy at room temperature. The geometry data for $(L'H_2)Zn(tacn)$ complex obtained by AM1-geometry optimization are compared to the x-ray crystallographic data as shown in Table 4.5. The labeled atoms in p-tert-butylsulfonylcalix[4]arene complex species are referred by the geometry data in Table 4.5. As consideration of the hydrogen bonding presented in the

(L'H₂)Zn(tacn) complex, O3...H1 and O12...H2 distances, on the lower rim of p-tert-butylsulfonylcalix[4]arene molecule, two calculated hydrogen-bond distances are longer than the hydrogen-bond distances obtained from x-ray measurement by 0.39 and 0.40 Å (see Table 4.5).



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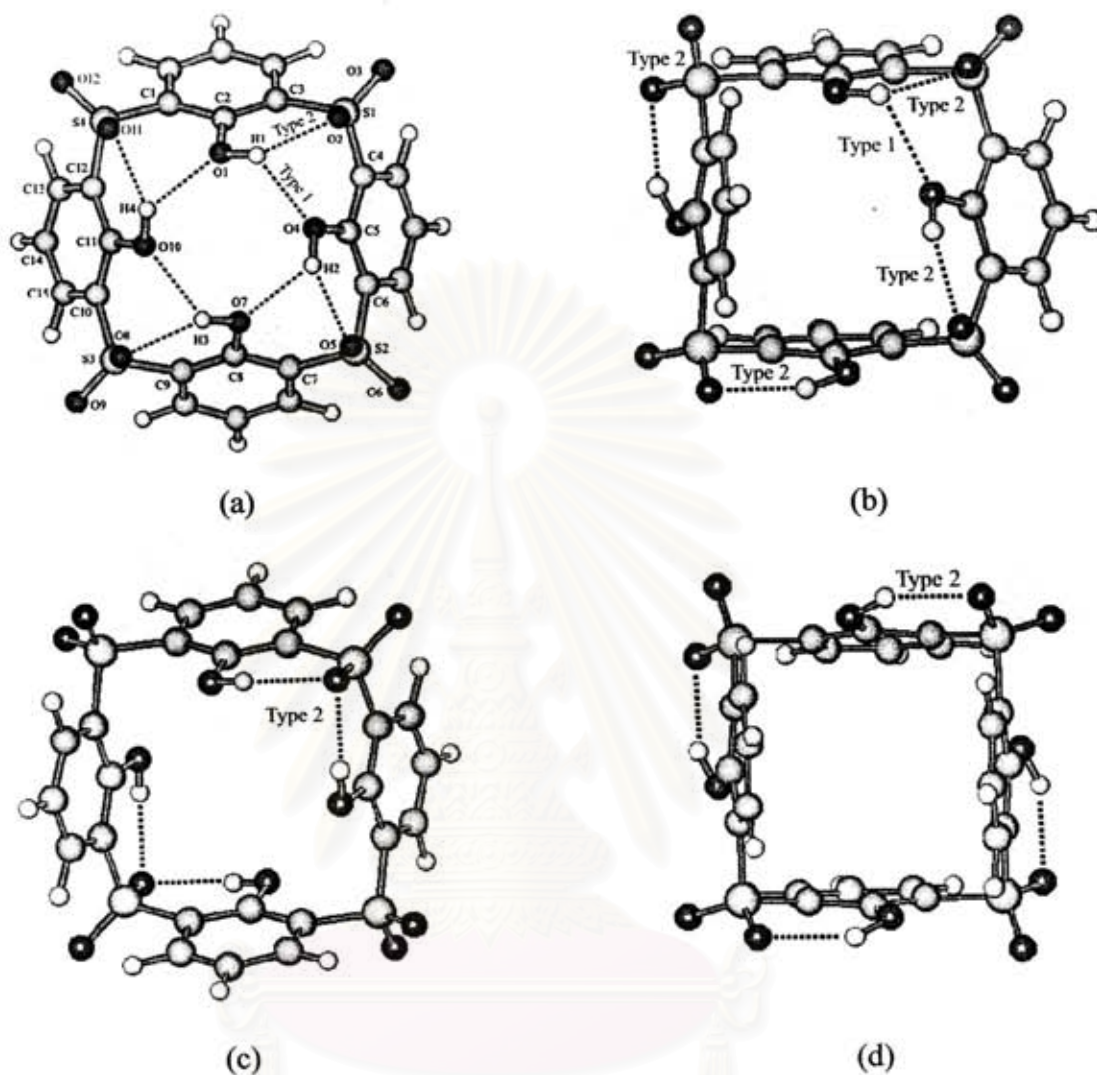


Figure 4.1 Hydrogen bonding presented in sulfonycalix[4]arene (a) cone, (b) partial cone, (c) 1,2-alternate and (d) 1,3-alternate conformers. Hydrogen bond type 1 and 2 are defined as an interaction between phenolic proton and adjacent phenolic oxygen and between phenolic proton and adjacent sulfonyl oxygen, respectively.

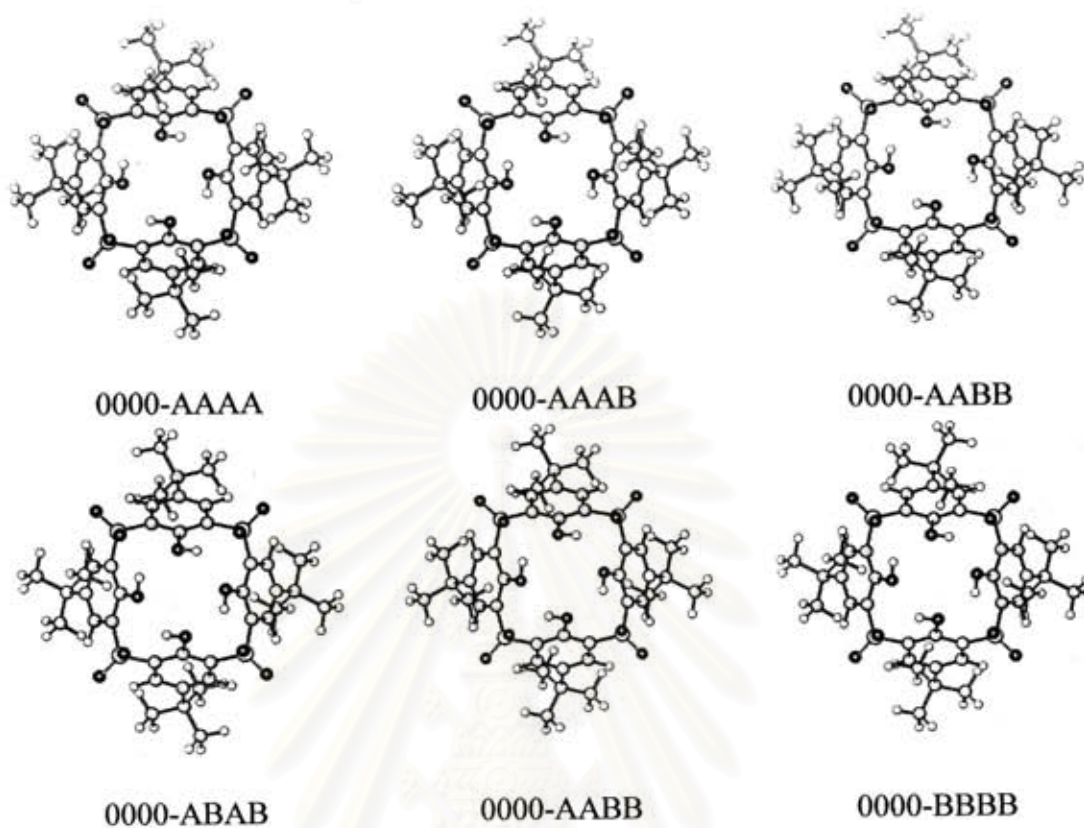


Figure 4.2 The AM1-optimized conformers of p-tert-butylsulfonylcalix[4]arene cone.

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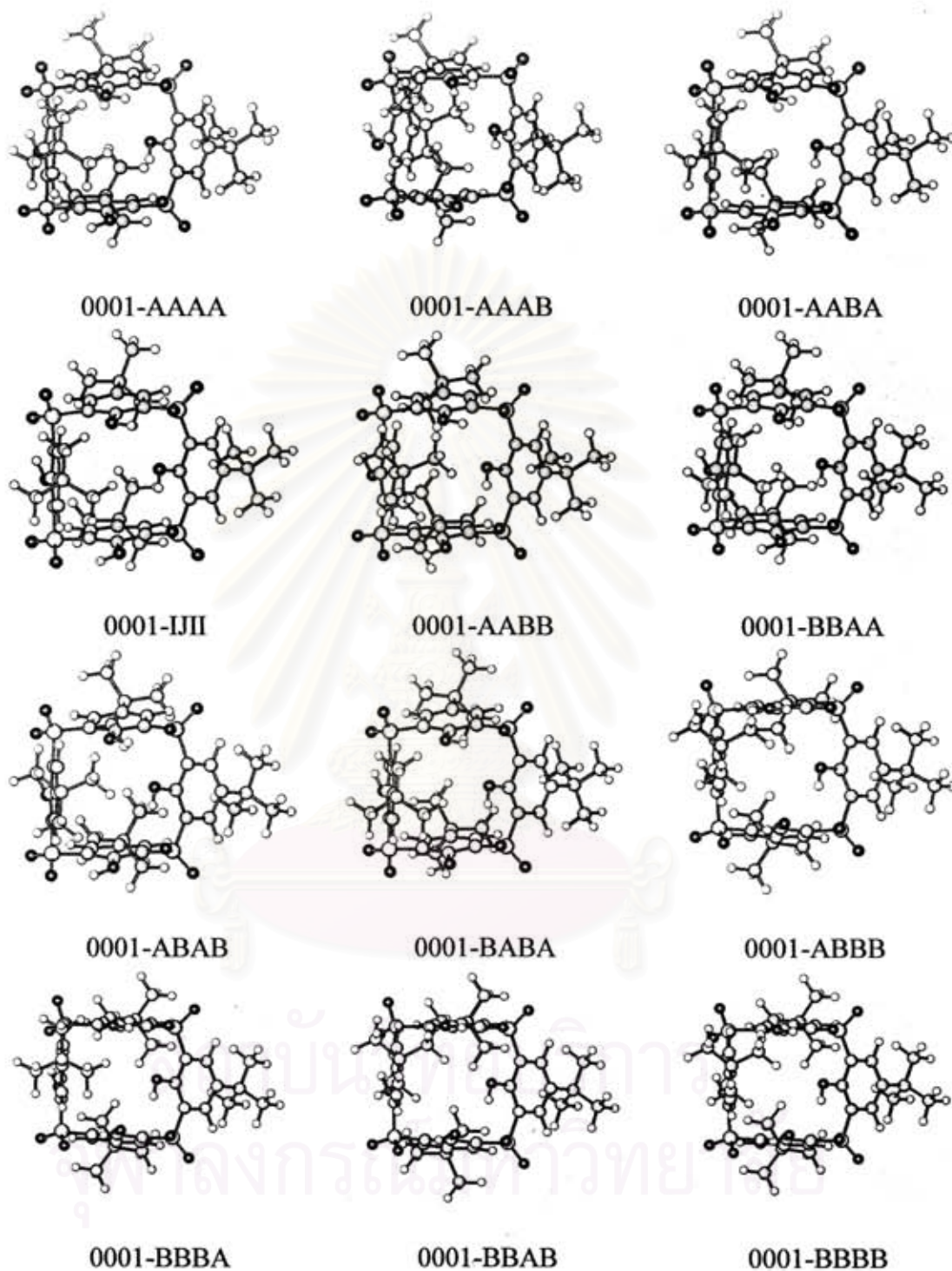


Figure 4.3 The AM1-optimized conformers of p-tert-butylsulfonylcalix[4]arene partial cone.

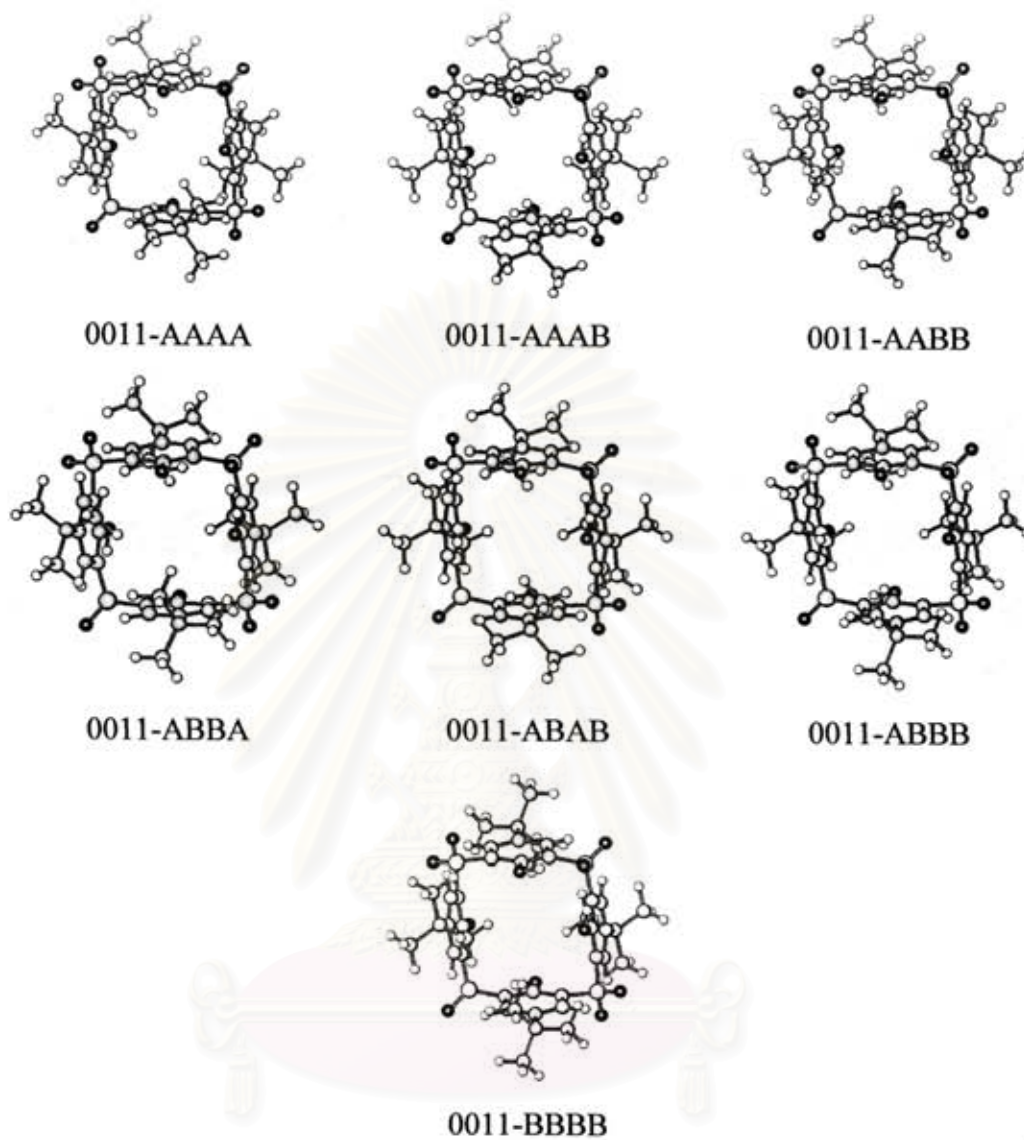


Figure 4.4 The AM1-optimized conformers of p-tert-butylsulfonylcalix[4]arene 1,2-alternate.

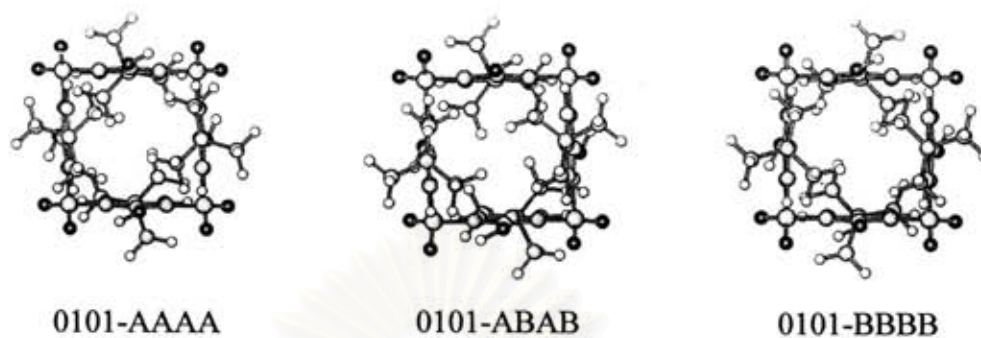


Figure 4.5 The AM1-optimized conformers of p-tert-butylsulfonylcalix[4]arene 1,3-alternate.

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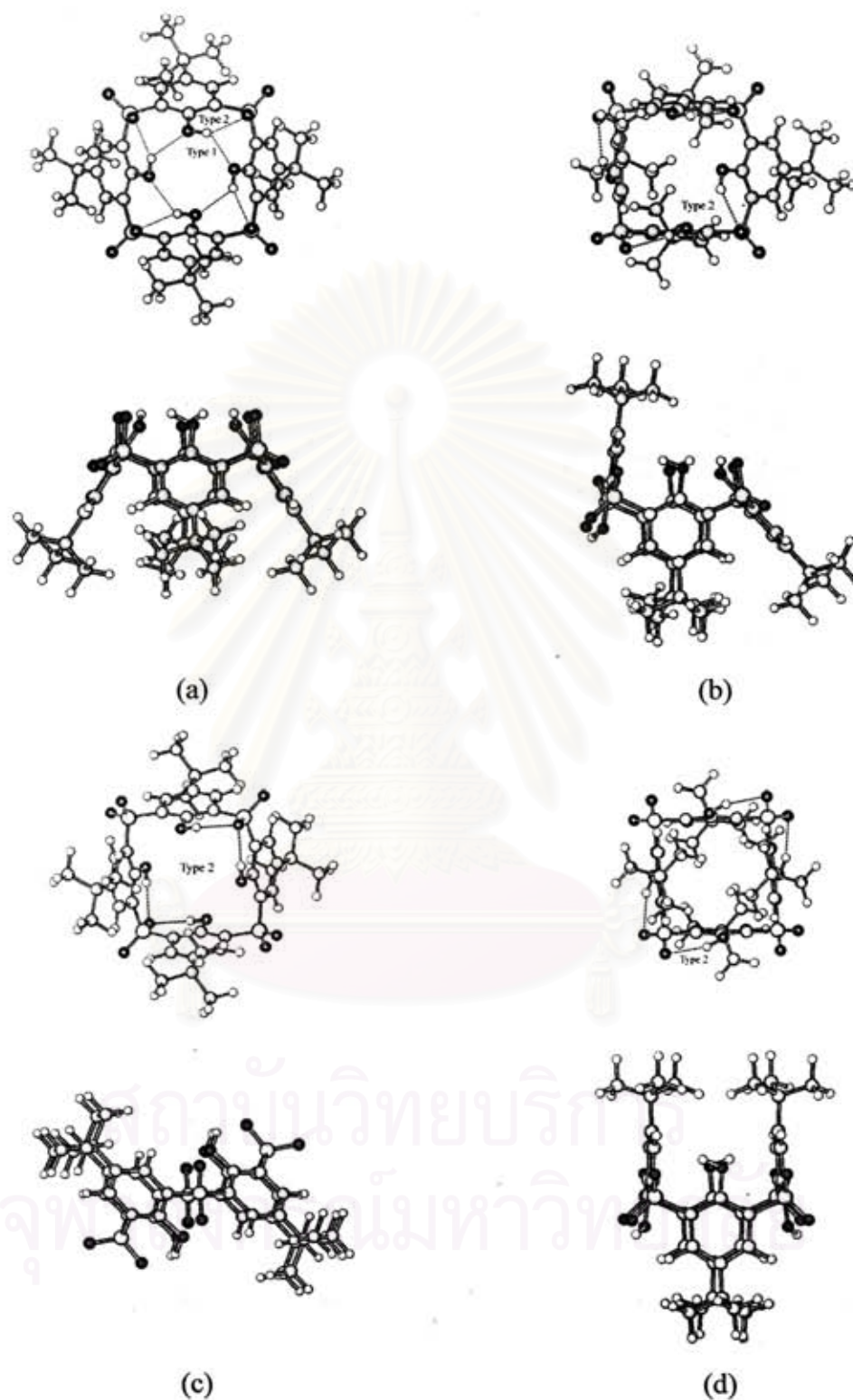


Figure 4.6 Conformers of p-tert-butylsulfonylcalix[4]arene (a) 0000-AAAA cone, (b) 0001-BBBA partial cone, (c) 0011-AAAA 1,2-alternate and (d) 0101-AAAA 1,3-alternate and their corresponding hydrogen bonding.

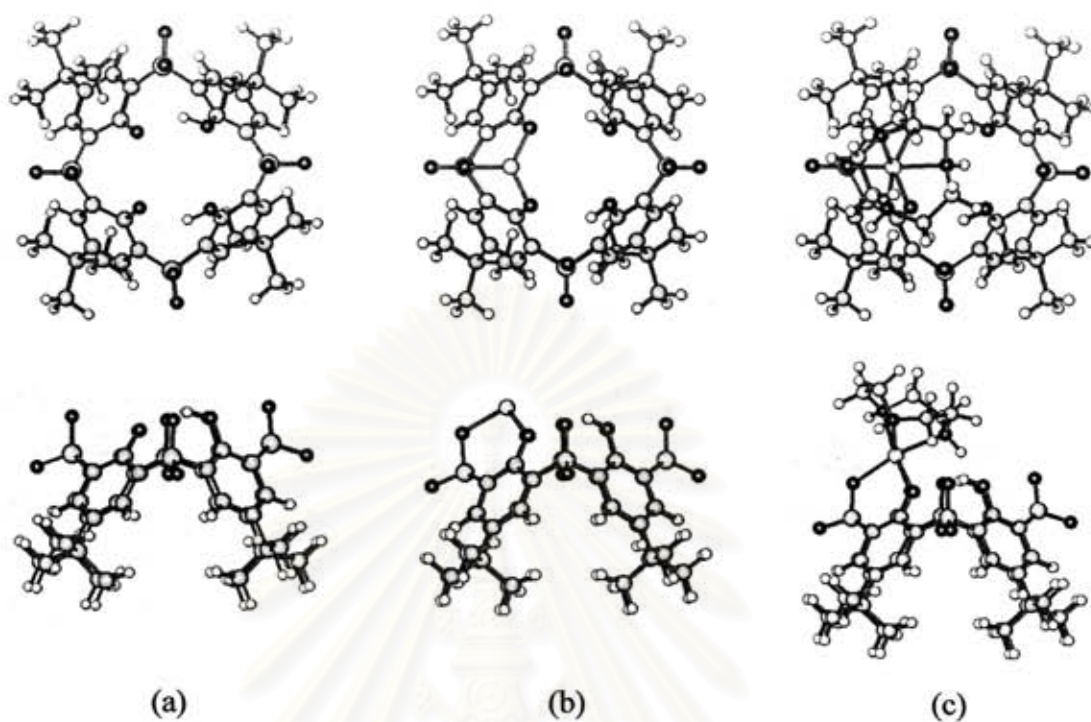


Figure 4.7 Structures of p-tert-butylsulfonylcalix[4]arene as (a) LH_2^{2-} , (b) $(LH_2)Zn$ and (c) $(LH_2)Zn(tacn)$ species. Structures above and below are the molecular top and side views.

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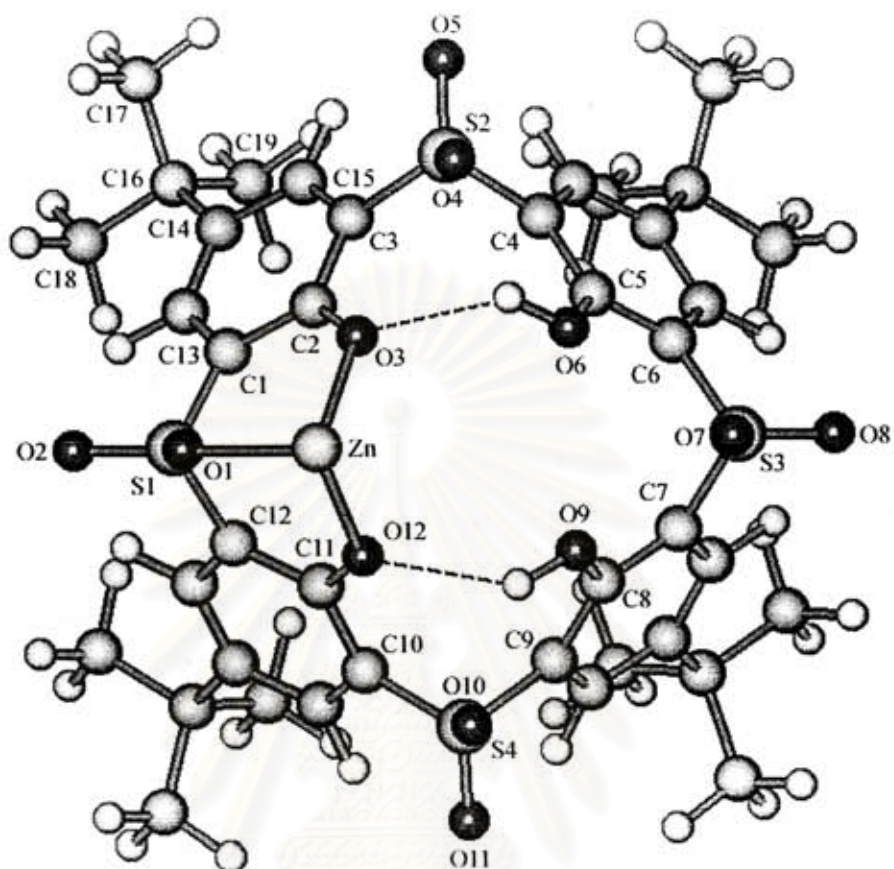
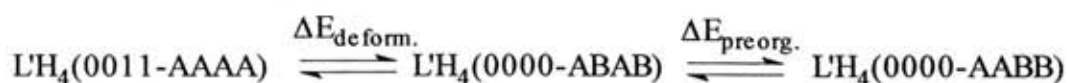


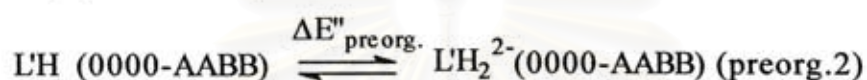
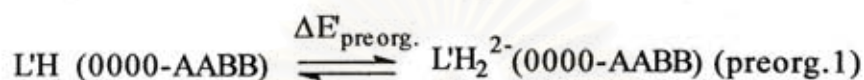
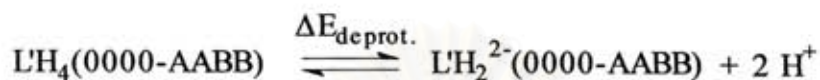
Figure 4.8 AM1-optimized structure of p-tert-butylsulfonylcalix[4]arene complex with zinc(II) included by tetracyclononane (tacn) molecule, (LH₂)Zn(tacn), displayed without tacn molecule. The labeled atoms in p-tert-butylsulfonylcalix[4]arene complex are correspond to atoms shown in Table 4.5.

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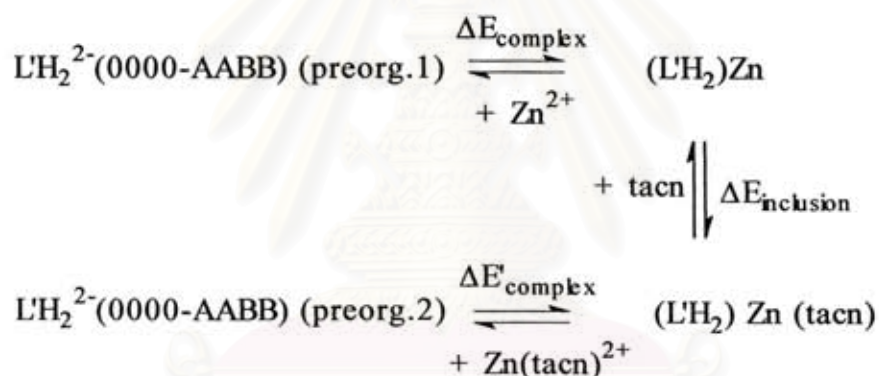
A. Conformational organization of neutral form :



B. Deprotonation and preorganization of deprotonated form :



C. Complexation :



Scheme 4.1 Proposed interaction pathways of interconversion of p-tert-butylsulfonylcalix[4]arene conformers and complexations of its deprotonated species zinc(II) included by a tetracyclononane (tacn) molecule

Table 4.1 Total energy and relative energy, ΔE_{rel} of the sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene conformers in comparison with thiacalix[4]arene and calix[4]arene conformers.

	$\Delta E_{\text{rel}}^{\text{a}}$			
	cone (0000)	partial cone (0001)	1,2-alternate (0011)	1,3-alternate (0101)
Sulfonylcalix[4]arene				
B3LYP/6-31G*	8.3 (-3419.223378) ^b	10.4 (-3419.219912) ^b	0.0 (-3419.236519) ^b	5.1 (-3419.228417) ^b
Thiacalix[4]arene				
B3LYP/6-31G** ^c	0.0	10.1	16.5	13.8
Calix[4]arene				
B3LYP/6-31G* ^d	0.0	10.7	18.6	18.1
p-tert-butylsulfonyl calix[4]arene				
B3LYP/6-31G*	0.57 ^e (-4048.230935) ^b	2.02 ^f (-4048.228627) ^b	0.0 ^g (-4048.231842) ^b	4.87 ^h (-4048.224084) ^b

^a Energies are relative to the most stable conformer, in kcal/mol. ^b Total energies, in hartree. ^c Taken from reference [21]. ^d Taken from reference [12]. ^e for 0000-ABAB conformer. ^f for 0001-BBBA conformer. ^g for 0011-AAAA conformer. ^h for 0101-AAAA conformer.

Table 4.2 Hydrogen bond distances and bond types for sulfonylcalix[4]arene and p-tert butylsulfonylcalix[4]arene in comparison with the thiacalix[4]arene and calix[4]arene.

	Bond type	Bond distance ^a			
		cone	partial cone	1,2-alternate	1,3-alternate
Sulfonylcalix[4]arene ^b	1 ^c	2.185 ^e	2.294 ^{f, g}	h	h
	2 ^d	2.059 ^e	2.002 ^g	1.983 ^e	2.003 ^e
p-tert butylsulfonylcalix[4]arene ^b	1	2.183 ^{e, i}	j	h	h
	2	2.061 ^{e, i}	1.969 ^k	1.918 ^l	2.129 ^m
Thiacalix[4]arene	1	1.82 ⁿ	h	h	h
Calix[4]arene	1	1.58 ^o	h	h	h

^a In Å. ^b AM1 geometry. ^c An interaction between phenolic proton and adjacent phenolic oxygen. ^d An interaction between phenolic proton and adjacent sulfonyl oxygen. ^e All are equivalent bond distances. ^f Defined as weak hydrogen bonding. ^g Shortest bond distance is reported. ^h Not exist. ⁱ Belongs to 0000-ABAB conformer, most stable cone conformer. ^j Very weak bond, interatomic distance is 2.463 Å. ^k Belongs to 0001-BBBA conformer, most stable partial cone conformer. ^l Belongs to 0011-AAAA conformer, most stable 1,2-alternate conformer. ^m Belongs to 0101-AAAA conformer, most stable 1,3-alternate conformer. ⁿ B3LYP/6-31G** geometry [21]. ^o B3LYP/6-31G* geometry [12].

Table 4.3 Total energy, E_{total} and relative energy, ΔE_{rel} at HF/6-31G* and BLYP/6-31G* levels of the AM1-optimized conformers of p-tert-butylsulfonylcalix[4]arene.

Conformer ^a	HF/6-31G*		B3LYP/6-31G*	
	E_{total} ^b	ΔE_{rel} ^c	E_{total} ^b	ΔE_{rel} ^c
Cone				
0000-AAAA	-4030.645775	2.93	-4048.229561	1.43
0000-AAAB	-4030.645602	3.04	-4048.230789	0.66
0000-AABB	-4030.645289	3.23	-4048.229697	1.35
0000-ABAB	-4030.645143	3.32	-4048.230935	0.57
0000-ABBB	-4030.645286	3.23	-4048.230525	0.83
0000-BBBB	-4030.644900	3.48	-4048.227830	2.52
Partial cone				
0001-AAAA	-4030.643549	4.32	-4048.226430	3.40
0001-AAAB	-4030.641282	5.75	-4048.222577	5.81
0001-AABA	-4030.644235	3.89	-4048.227595	2.67
0001-BAAA	-4030.642482	4.99	-4048.226408	3.41
0001-AABB	-4030.641653	5.51	-4048.226072	3.62
0001-BBAA	-4030.642433	5.02	-4048.225027	4.28
0001-ABAB	-4030.644015	4.03	-4048.221504	6.49
0001-BABA	-4030.640738	6.09	-4048.227798	2.54
0001-ABBB	-4030.643762	4.19	-4048.227191	2.92
0001-BBBA	-4030.645800	2.91	-4048.228627	2.02
0001-BBAB	-4030.642787	4.80	-4048.226403	3.41
0001-BBBB	-4030.643409	4.41	-4048.226928	3.08
1,2 Alternate				
0011-AAAA	-4030.650439	0.00	-4048.231842	0.00
0011-AAAB	-4030.647462	1.87	-4048.229606	1.40
0011-AABB	-4030.646944	2.19	-4048.229445	1.50
0011-ABBA	-4030.644673	3.62	-4048.227442	2.76
0011-ABAB	-4030.644358	3.82	-4048.227726	2.58
0011-ABBB	-4030.644165	3.94	-4048.227819	2.52
0011-BBBB	-4030.643777	4.18	-4048.227682	1.95
1,3 Alternate				
0101-AAAA	-4030.639433	6.91	-4048.224084	4.87
0101-AAAB	^d	-	^d	-
0101-AABB	^d	-	^d	-
0101-ABAB	-4030.637704	7.99	-4048.222226	6.03
0101-ABBB	^d	-	^d	-
0101-BBBB	-4030.636502	8.75	-4048.219137	7.97

^a the first four digits indicate the characteristic conformers and the letters indicate whether the methyl group in tert-butyl group attached to each aromatic ring points along (A) or against (B) aromatic hydroxyl groups.

^b in hartree.

^c energy are relative to the most stable conformer, in kcal/mol.

^d unstable species.

Table 4.4 Total energies, E_{total} and reaction energies B3LYP/6-31G* level of the AM1-optimized conformers of sulfonylcalix[4]arene, p-tert-butylsulfonylcalix[4]arene, their related species and Zn(II) complexes.

Species ^a	E_{total} ^b	Reaction energies ^c	
sulfonylcalix[4]arene			
LH ₄ (1,2-alternate)	-3419.236519	-	
LH ₄ (cone)	-3419.223378	ΔE_{deform}	= 8.25
LH ₂ ²⁻	-3418.091383	ΔE_{deprot}	= 710.34
LH ₂ ²⁻ (preorg.)	-3418.039473	ΔE_{preorg}	= 32.54
Zn ²⁺	-1778.107014	-	
(LH ₂)Zn	-5197.153976	$\Delta E_{\text{complex}}$	= -632.21
p-tert-butylsulfonylcalix[4]arene			
L'H ₄ (0011-AAAA) ^d	-4048.231842	-	
L'H ₄ (0000-ABAB) ^e	-4048.230935	ΔE_{deform}	= 0.57
L'H ₄ (0000-AABB) ^f	-4048.229697	ΔE_{preorg}	= 0.78
L'H ₂ ²⁻	-4047.094992	ΔE_{deprot}	= 712.04
L'H ₂ ²⁻ (preorg.1)	-4047.018237	$\Delta E'_{\text{preorg}}$	= 48.16
(L'H ₂)Zn	-5807.005983	$\Delta E_{\text{complex}}$	= -648.62
tacn ^g	-398.208416	-	
(L'H ₂)Zn(tacn) ^h	-6206.957330	$\Delta E_{\text{inclusion}}$	= -101.56
L'H ₂ ²⁻ (preorg.2)	-4047.072376	$\Delta E''_{\text{preorg}}$	= 14.19
Zn(tacn) ²⁺	-2176.255587	-	
(L'H ₂)Zn(tacn) ^h	-6206.957330	$\Delta E'_{\text{complex}}$	= -395.90

^a the AM1-optimized structures. ^b in hartree. ^c in kcal/mol. ^d the most stable conformer. ^e the lowest energy of cone conformer. ^f the same configuration of L'H₂²⁻ and complexed ligand. ^g stands for tetraazacyclononane. ^h the same structures.

Table 4.5 Data for the structure of p-tert-butylsulfonylcalix[4]arene presented in (LH₂)Zn(tacn) complex.

	AMI	Exp. ^a		AMI	Exp. ^a
Bond distances (Å)					
Zn-O12	2.24	2.07	O1-S1-C12	109.6	109.6
Zn-O3	2.25	2.12	C1-S1-C12	106.7	106.3
Zn-O1	2.11	2.16	O10-S4-O11	115.2	118.8
S1-O2	1.41	1.44	O10-S4C10	112.6	108.5
S1-O1	1.48	1.45	O11-S4C10	109.4	105.9
S1-C1	1.64	1.76	O10-S4C9	107.6	107.0
S1-C12	1.64	1.77	O11-S4C9	108.1	105.7
S4-O10	1.41	1.43	C10-S4C9	102.7	110.9
S4-O11	1.41	1.44	O7-S3-O8	115.6	118.4
S4-C10	1.65	1.78	O7-S3-C6	112.4	110.2
S4-C9	1.69	1.79	O8-S3-C6	107.3	105.9
S3-O7	1.40	1.43	O7-S3-C8	112.2	110.1
S3-O8	1.41	1.44	O8-S3-C8	107.4	105.3
S3-C6	1.69	1.78	C6-S3-C8	100.7	106.2
S3-C8	1.69	1.79	O5-S2-O4	115.6	118.4
S2-O5	1.41	1.43	O5-S2-C3	109.5	107.6
S2-O4	1.41	1.44	O4-S2-C3	112.7	109.2
S2-C3	1.65	1.77	O5-S2-C4	108.0	105.9
S2-C4	1.70	1.79	O4-S2-C4	107.6	108.7
O3-C2	1.21	1.30	C3-S2-C4	102.6	106.4
O3-H1 ^b	2.16	1.76	C2-O3-Zn	132.6	134.7
O12-C11	1.29	1.31	S1-O1-Zn	126.2	121.9
O12-H2 ^b	2.19	1.80	C11-O12-Zn	132.6	136.4
O9-C7	1.36	1.32	O3-C2-C1	123.3	124.6
O6-C5	1.36	1.33	O3-C2-C3	118.0	121.9
C2-C1	1.44	1.42	C1-C2-C3	118.7	113.5
C2-C3	1.45	1.43	C2-C1-S1	125.3	122.0
C1-C13	1.40	1.40	C2-C3-S2	123.8	120.5
C13-C14	1.39	1.38	O12-C11-C10	117.6	122.3
C14-C15	1.40	1.39	O12-C11-C12	123.5	123.1
C14-C16	1.50	1.54	C10-C11-C12	118.9	114.5
C15-C3	1.39	1.38	C11-C10-S4	123.1	121.3
C16-C19	1.53	1.50	C11-C12-S1	125.3	121.2
C16-C18	1.52	1.52	O9-C7-C8	122.8	118.5
C16-C17	1.53	1.53	O9-C7-C9	115.2	124.2
Bond angles (°)					
O12-Zn-O3	82.2	88.1	C8-C7-C9	122.0	117.2
O12-Zn-O1	84.9	85.8	C7-C8-S3	125.3	121.5
O3-Zn-O1	82.1	83.3	C7-C9-S4	126.2	121.9
O2-S1-O1	110.1	116.0	O6-C5-C6	115.2	120.5
O2-S1-C1	110.6	107.8	O6-C5-C4	122.4	122.8
O1-S1-C1	109.4	109.5	C6-C5-C4	122.4	116.7
O2-S1-C12	110.5	107.2	C5-C4-S2	125.4	121.6
			C5-C6-S3	124.6	123.0

^a taken from [28]. ^b hydrogen bond.

4.2. Thiacalix[4]arenes

The total energies of the most stable structure of p-tert-butylthiacalix[4]arene cone conformer and their relative energies, compared to the most stable cone conformer were obtained by single point B3LYP/6-31G* calculations as reported in Table 4.6. Stabilities of the p-tert-butylthiacalix[4]arene conformers are in the order : cone > partial cone > 1,3-alternate > 1,2-alternate (see Table 4.6). The stability order of p-tert-butylthiacalix[4]arene conformers, is in the same order of the calix[4]arene and thiacalix[4]arene conformers but different from the stability order of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene of which 1,2-alternate conformer are the most stable species. The most stable structure for p-tert-butylthiacalix[4]arene is a 0001-AAAA cone conformer as shown in Figure 3.2. Figure 3.2 also illustrates a cyclic hydrogen bonded array in the p-tert-butylthiacalix[4]arene 0001-AAAA cone conformer. The energy difference between cone (the most stable) and partial cone conformers of p-tert-butylthiacalix[4]arene is 9.05 kcal/mol using B3LYP/6-31G* level. Rotational energies according to the tert-butyl groups in the p-tert-butylthiacalix[4]arene cone, partial cone, 1,2-alternate and 1,3-alternate conformers are less than 1.0, 0.5, 1.0 and 2.0 kcal/mol, respectively. Free rotation of the tert-butyl groups in p-tert-butylthiacalix[4]arene conformers are therefore expected at room temperature.

The flip-flop hydrogen bonding in p-tert-butylthiacalix[4]arene cone conformer have also occurred as found in thiacalix[4]arene and calix[4]arene [40]. Since an enlargement of the p-tert-butylthiacalix[4]arene cone cavity indicated by the C-S bond of which identical bond length obtained from AM1 optimized and X-ray geometric

data are 1.789 and 1.709 Å, respectively [32], in comparison with the C-C bond (1.53 Å) in calix[4]arene [41], the p-tert-butylthiacalix[4]arene cone complexes with the transition metal cations are therefore expected. The p-tert-butylthiacalix[4]arene 0000-AAAA cone conformer is a four-fold symmetric structure in which the O1-O3 and O2-O4 distances (see Figure 3.2) are identical and equivalent to 4.048 Å. Hydrogen bond distances in p-tert-butylthiacalix[4]arene cone conformer are equivalent to 2.211 Å (1.822 Å for B3LYP/6-31G* optimized bond distance). Hydrogen bond distances in the cone conformer of sulfur bridged calix[4]arenes such as thiacalix[4]arene and sulfonylcalix[4]arene (1.82 to 2.18 Å) are much longer than those of the calix[4]arene cone conformer (1.58 Å), shown in Table 4.7. The cavity size expressed as distances between two diagonally opposite S atoms for 0000-AAAA, 0001-AAAA, 0011-AAAA and 0101-AAAA conformers of p-tert-butylthiacalix[4]arene are 7.749/7.759, 7.791/7.796, 7.228/8.317 and 7.890/7.910 Å, respectively.

The AM1 optimized geometries of p-tert-butylthiacalix[4]arene cone, partial cone, 1,2-alternate and 1,3-alternate conformers are shown in Figures 4.9, 4.10, 4.11 and 4.12, respectively. The total energies at HF/6-31G* and B3LYP/6-31G* theoretical levels of p-tert-butylthiacalix[4]arene conformers and their relative energies are shown in Table 4.8. The geometrical data for the p-tert-butylthiacalix[4]arene 0000-AAAA conformer obtained by AM1 and B3LYP/6-31G* methods are compared to the X-ray crystallographic data as shown in Table 4.9. It shows that the AM1 and B3LYP/6-31G* optimized structures of p-tert-butylthiacalix[4]arene cone 0000-AAAA conformer show good agreement with the X-ray structure. The geometries of

LH_2^{2-} , LH_3^- and LH_5^+ species of the p-tert-butylthiacalix[4]arene cone conformer (LH_4), obtained by the B3LYP/6-31G* calculations are shown in Figures. 4.11(a), 4.11(b) and 4.12, respectively. Data for these structures related to hydrogen bonding are compared to the neutral form (LH_4) of p-tert-butylthiacalix[4]arene as listed in Table 4.10. The proton affinities for the LH_2^{2-} , LH_3^- and LH_4 species derived from their total energies at B3LYP/6-31G* level of theory are listed in Table 4.11. The molecular geometries for LH_2^{2-} , LH_4 and LH_5^+ species are C_s , C_4 and C_1 symmetries, respectively. The hydrogen bonds in LH_2^{2-} , LH_3^- and LH_5^+ forms of p-tert-butylthiacalix[4]arene are shown in Figures. 4.13(a), 4.13(b) and 4.14, respectively. The proton affinity of LH_2^{2-} , LH_3^- and LH_4 species are $\text{PA}(1) = 411.12$, $\text{PA}(2) = 329.03$ and $\text{PA}(3) = 208.44$ kcal/mol, respectively (see Table 4.11). Binding energy ($\Delta E_{\text{binding}}$) between an isolated Zn^{2+} ion and the free form of deprotonated species (LH_2^{2-}) defined as a summation of preorganization energy (ΔE_{preorg}) of deprotonated species of p-tert-butylthiacalix[4]arene and complexation energy ($\Delta E_{\text{complex}}$) of $[\text{ZnLH}_2]$ is approximately -672.47 kcal/mole (listed in Table 4.11). The $[\text{ZnLH}_2]$ geometry optimized at the B3LYP/6-31G* level is shown in Figure 4.15.

The electrostatic potential of the LH_4 , LH_3^- and LH_2^{2-} species represented over an electronic isodensity surface of $\rho = 0.01 \text{ e } \text{\AA}^{-3}$, computed by the Molekel 4.3 software [39] are shown in Figure 4.16. The lower and upper limits (noted as $\phi_<$ and $\phi_>$, respectively) of the electrostatic potential have been constructed over isoelectronic density surfaces (in $\text{e } \text{\AA}^{-3}$) as shown in Figure 4.16(a) for LH_4 , Figure 4.16(b) for LH_3^- and Figure 4.16(c) for LH_2^{2-} structures. As consideration of

electrostatic potential of LH_2^{2-} and its negative value contributing over two phenolate oxygen ions and a neighboring sulfur atom between them, these two phenolate oxygen ions and one sulfur atom can coordinate to a Zn^{2+} ion (see Figure 4.16(c)). This suggests that complexation between p-tert-butylthiacalix[4]arene cone conformer and transition metal ions are likely formed. On the other hand, the positive charge of the phenolic protons of LH_4 species (Figure 4.16(a)) including its hydrogen-bonded array is a blockage of binding to large cationic species. Nevertheless, binding between the neutral form (LH_4) of p-tert-butylthiacalix[4]arene cone conformer and alkali metal cations such as Li^+ and Na^+ has been observed as reported in ref. [42]. Figure 4.16(b) shows electrostatic potential of LH_3^- species of which isoelectrostatic potential is a unsymmetrical contribution.



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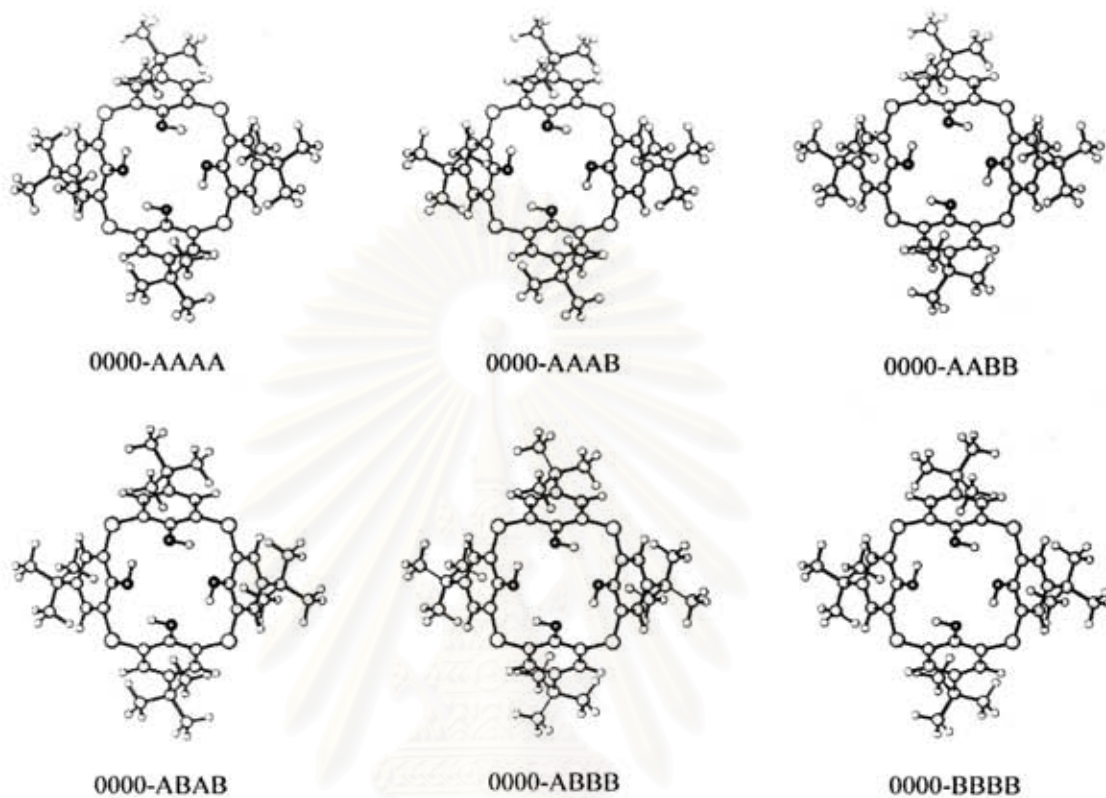


Figure 4.9 The AM1 optimized conformers of p-tert-butylthiacalix[4]arene cone.

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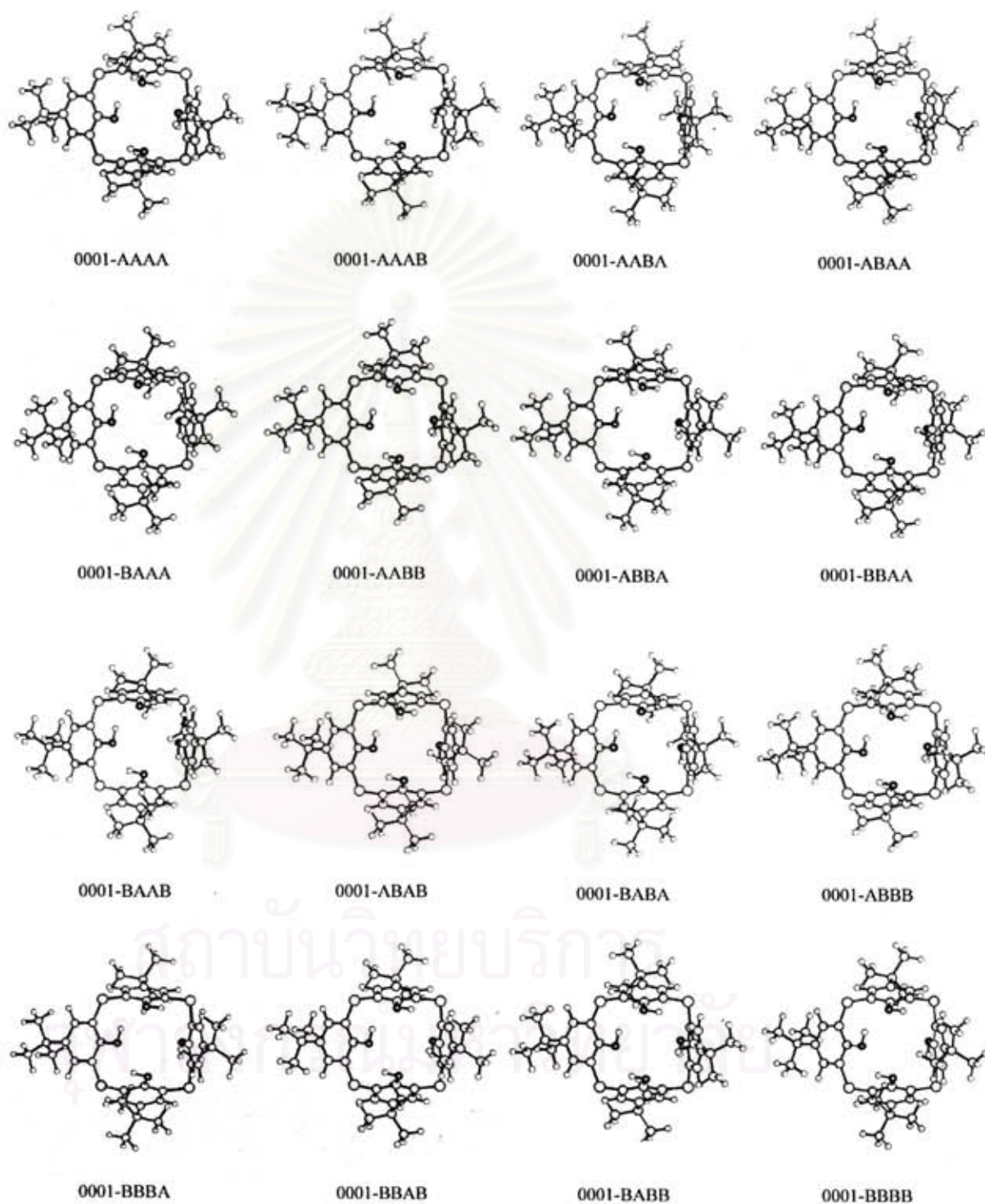


Figure 4.10 The AM1 optimized conformers of *p*-tert-butylthiacalix[4]arene partial cone.

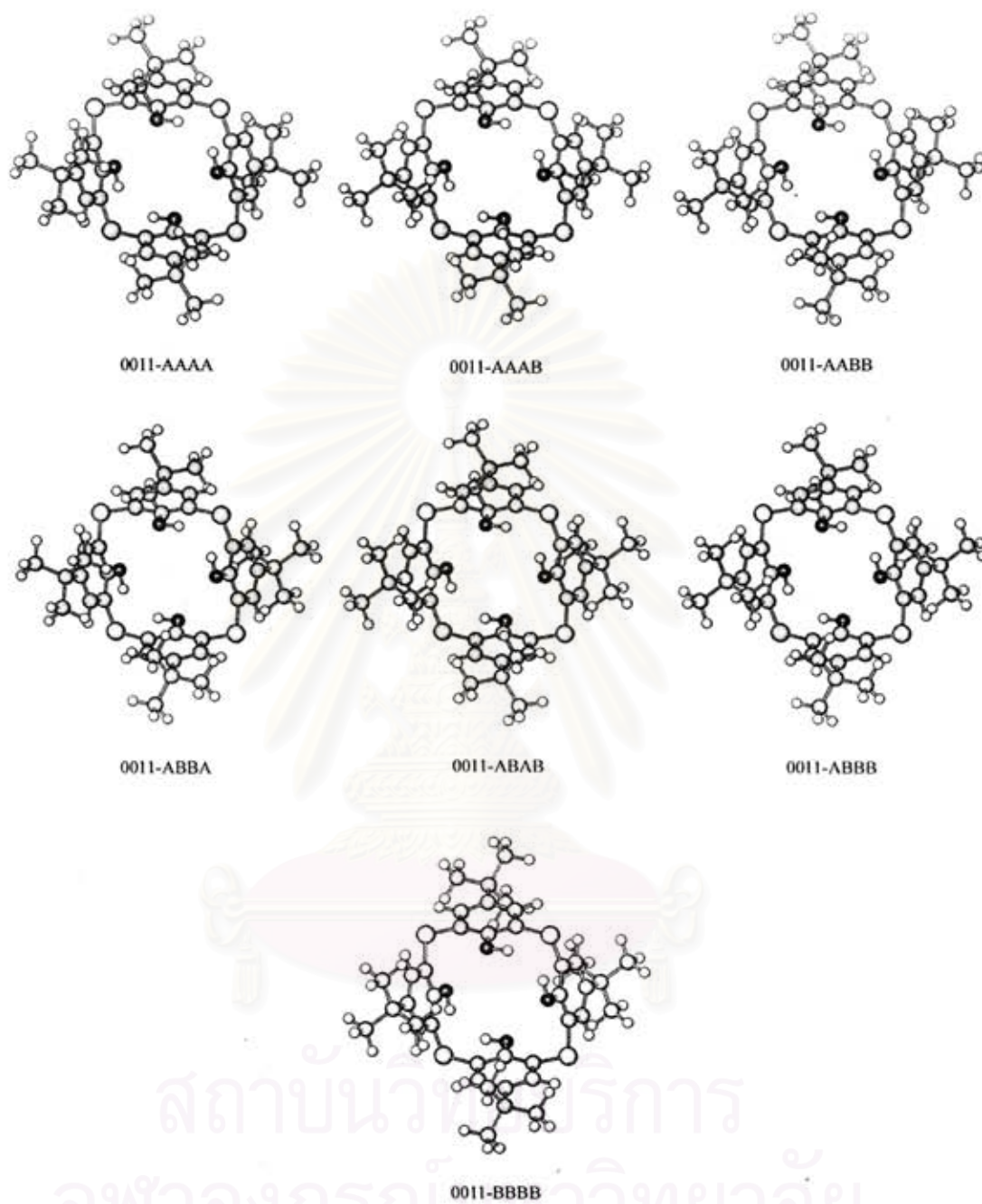


Figure 4.11 The AM1 optimized conformers of p-tert-butylthiacalix[4]arene 1,2-alternate.

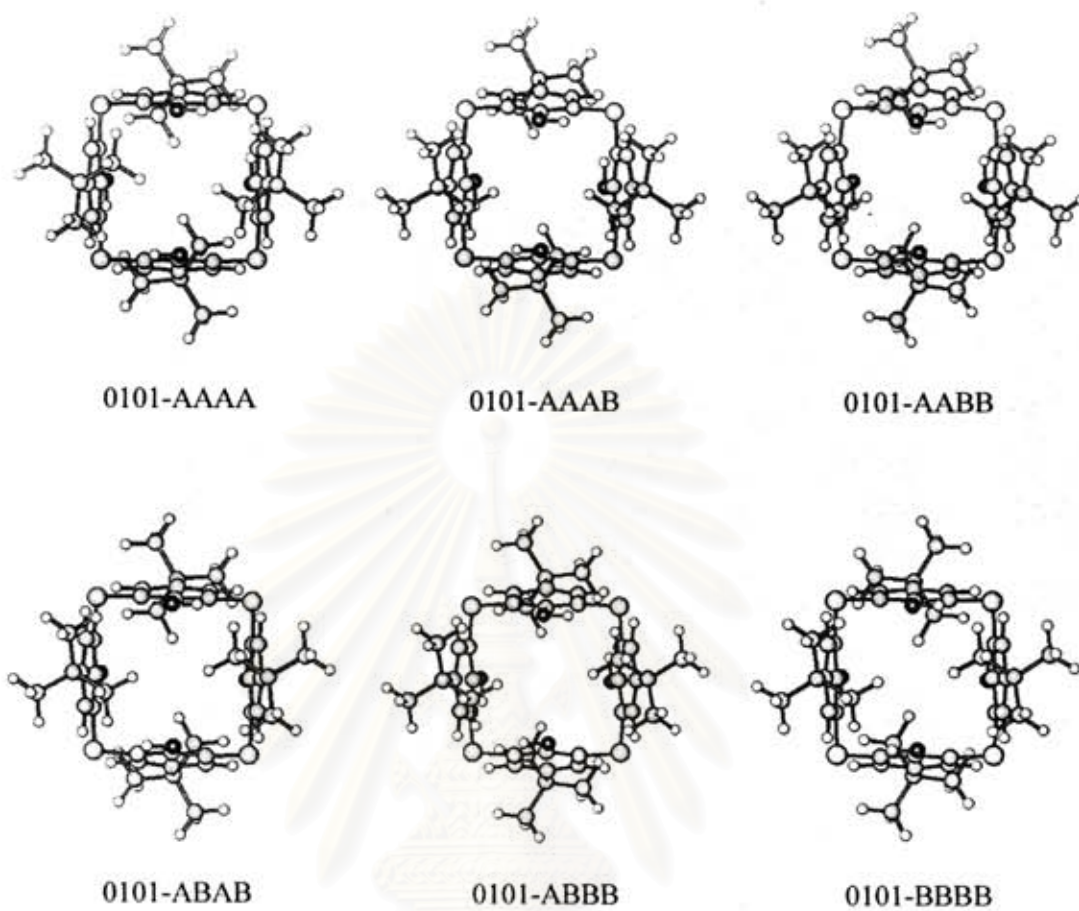


Figure 4.12 The AM1 optimized conformers of p-tert-butylthiacalix[4]arene 1,3-alternate.

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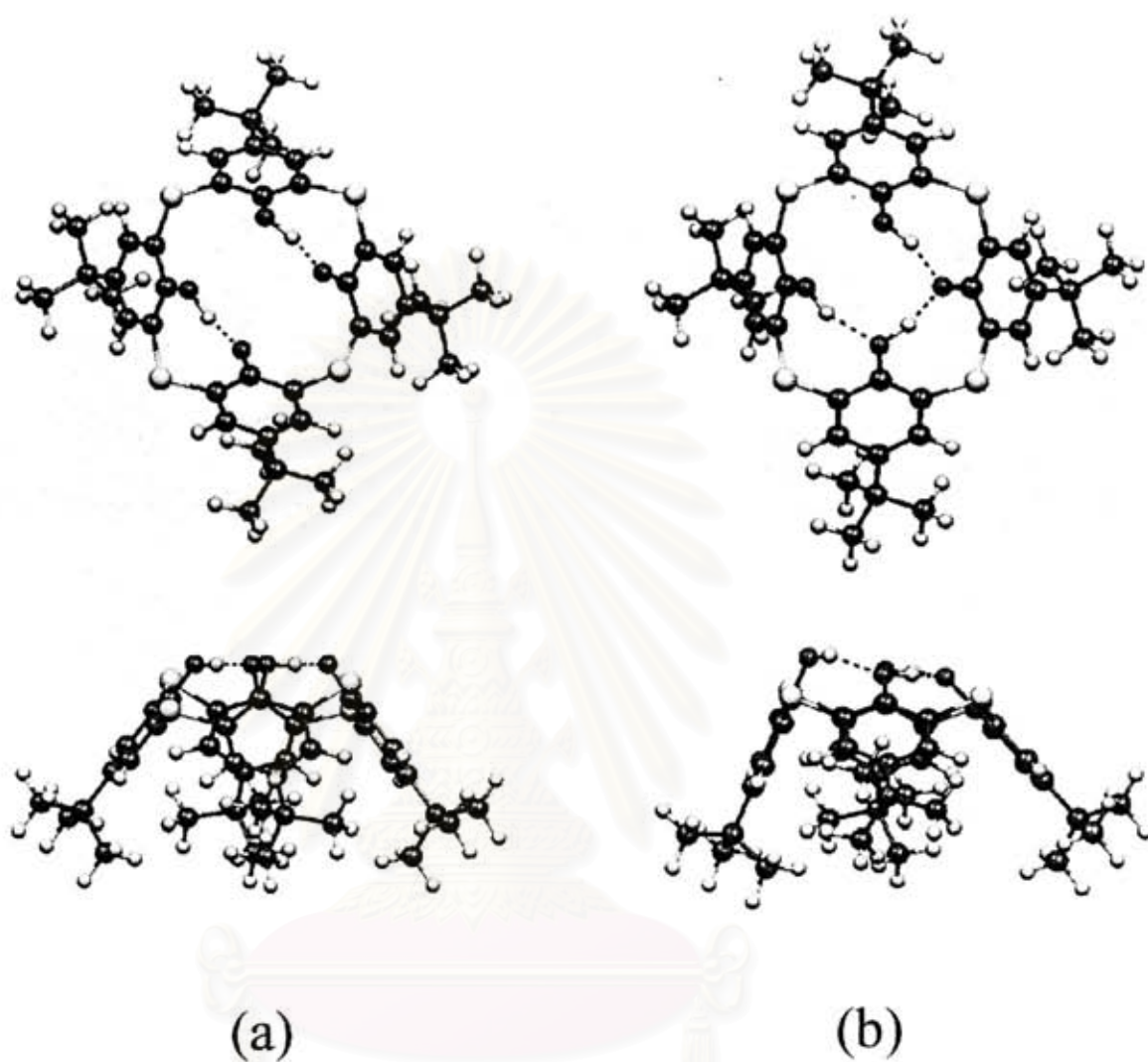


Figure 4.13 The B3LYP/6-31G* optimized structures of p-tert-butylthiacalix[4]arene cone conformer existing as deprotonated (a) LH_2^{2-} and (b) LH_3^- species. Structures above and below are top and side views of molecule.

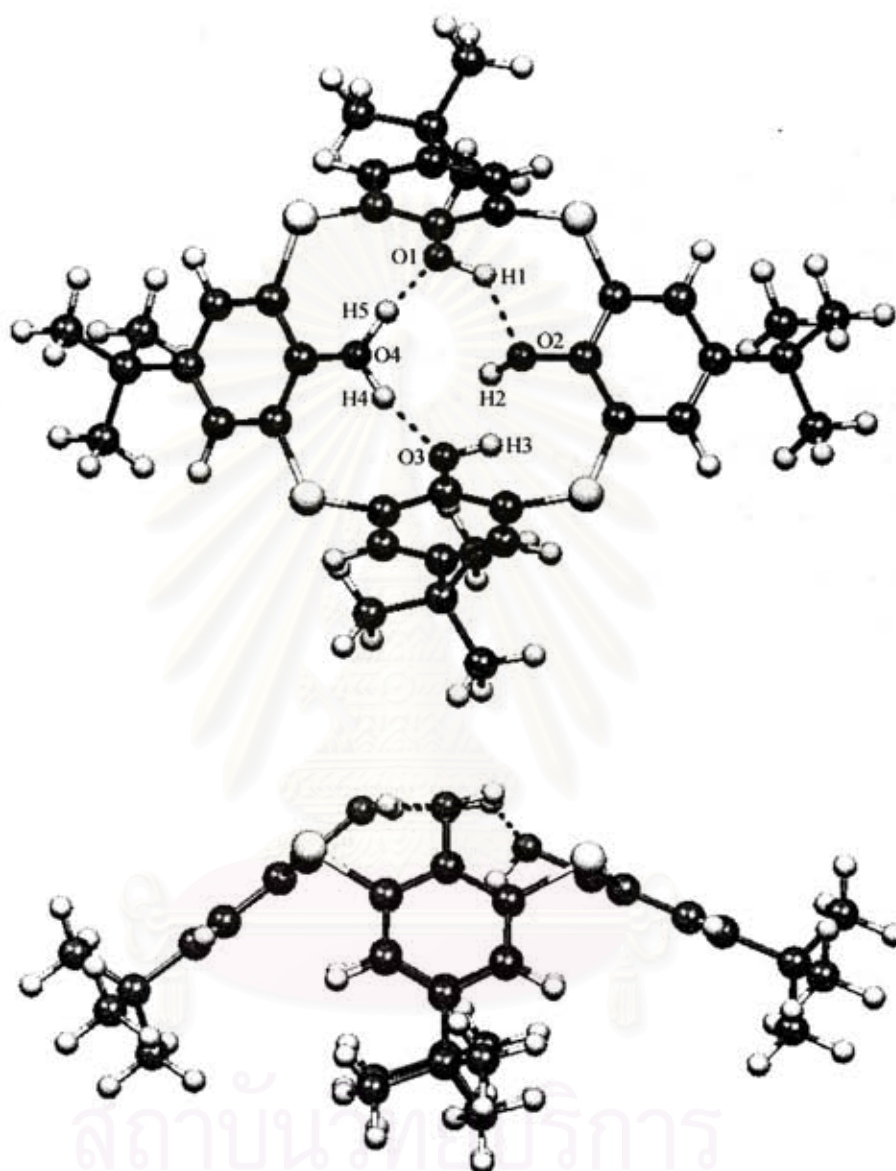


Figure 4.14 The B3LYP/6-31G* optimized structures of protonated LH_5^+ species of p-tert-butylthiacalix[4]arene cone conformer. Structures above and below are top and side views of molecule.

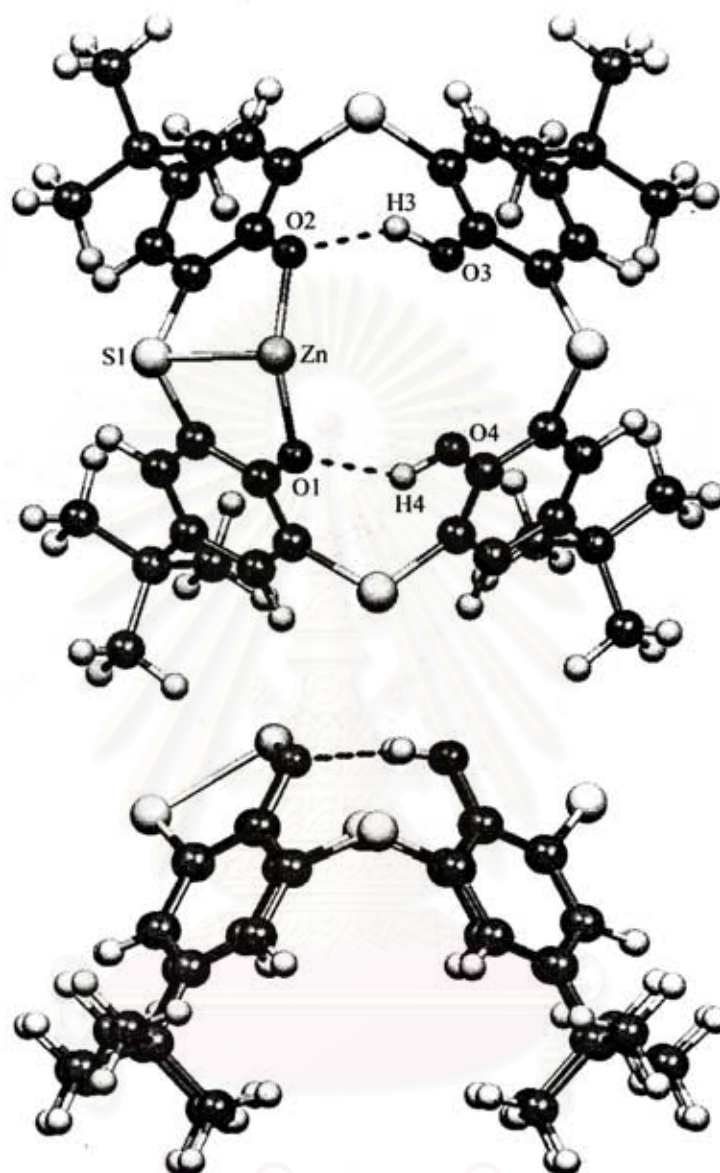


Figure 4.15 The B3LYP/6-31G* optimized structures of zinc complex of p-tert-butylthiacalix[4]arene cone species existing as $[Zn(LH_2)]$. Structures above and below are top and side views of molecule.

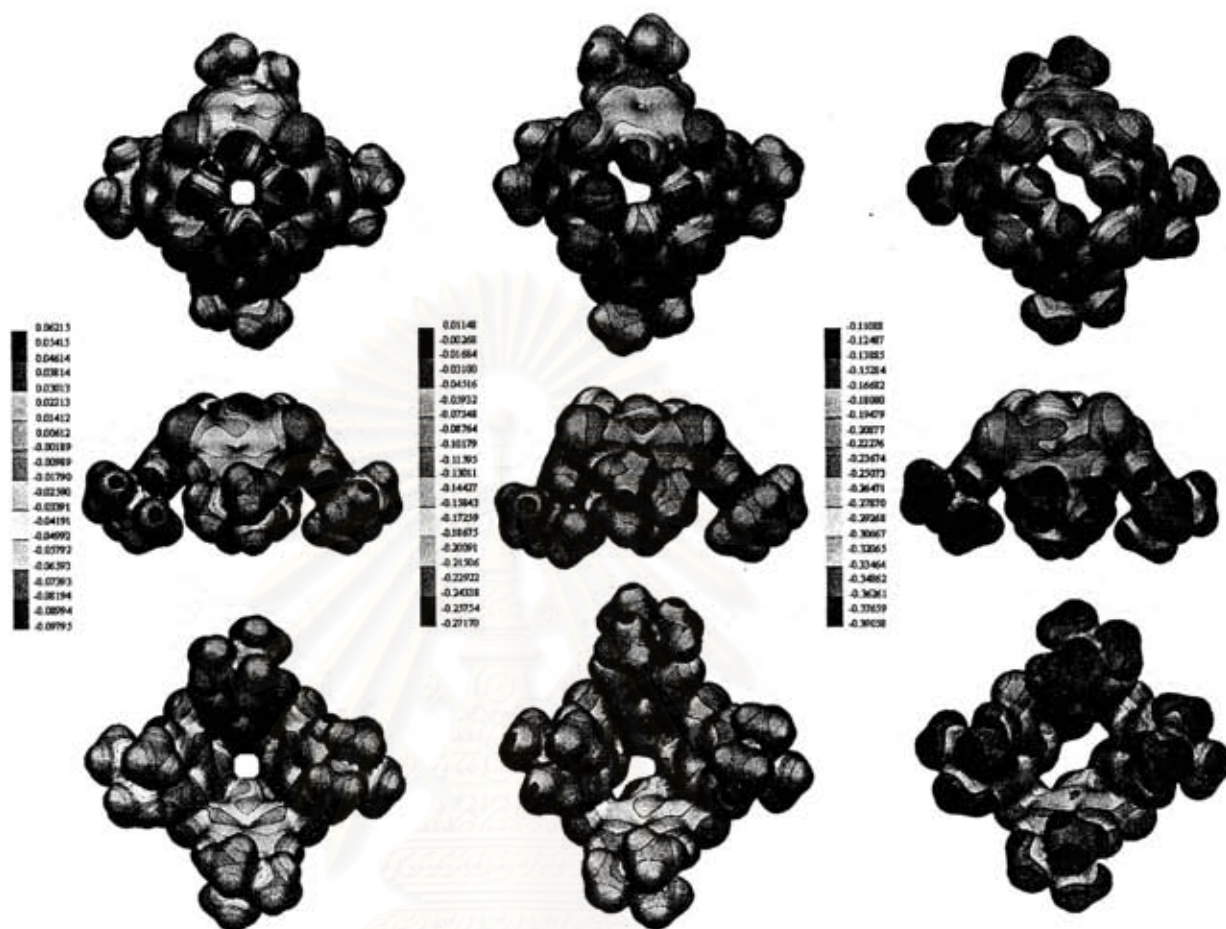


Table 4.6 Total energy and relative energy, ΔE_{rel} of the p-tert-butylthiacalix[4]arene conformers in comparison with calix[4]arene, thiacalix[4]arene, sulfonylcalix[4]arene and p-tert-butylthiacalix[4]arene conformers

	$\Delta E_{\text{rel}}^{\text{a}}$			
	Cone (0000)	partial cone (0001)	1,2-alternate (0011)	1,3- alternate (0101)
p-tert-butylthiacalix[4]arene B3LYP/6-31G* ^b	0.0 (-3446.80471287) ^c	9.05	17.05	15.18
Calix[4]arene B3LYP/6-31G* ^d	0.0	10.7	18.6	18.1
Thiacalix[4]arene B3LYP/6-31G* ^b	0.0 (-2817.80226317) ^c	9.4	17.9	17.5
B3LYP/6-31G** ^e	0.0	10.1	16.5	13.8
Sulfonylcalix[4]arene ^f B3LYP/6-31G*	8.3	10.4	0.0	5.1
p-tert-butylsulfonyl calyx[4]arene ^f B3LYP/6-31G*	0.6	2.0	0.0	4.9

^a Energies are relative to the most stable conformer, in kcal/mol. ^b AM1 geometry.

^c Total energies, in hartree. ^d Taken from ref. [29]. ^e Taken from ref. [11].

^f Taken from ref. [30].

Table 4.7 Hydrogen bond (O...H) distances for p-tert-butylthiacalix[4]arene in comparison with thiacalix[4]arene, sulfonylcalix[4]arene, p-tert-butylsulfonylcalix[4]arene and calix[4]arene

	Bond type	Bond distance ^a			
		cone	partial cone	1,2-alternate	1,3-alternate
p-tert-butylthiacalix[4]arene ^b	1 ^c	2.122 ^d	- ^e	- ^e	- ^e
		1.822 ^{d, f}			
Thiacalix[4]arene	1 ^c	2.121 ^{b, d}	- ^e	- ^e	- ^e
	1 ^c	1.82 ^g	- ^e	- ^e	- ^e
Sulfonylcalix[4]arene ^g	1 ^c	2.185 ^h	2.294 ^h	- ^e	- ^e
	2 ⁱ	2.059 ^h	2.002 ^h	1.983 ^h	2.003 ^h
p-tert butylsulfonylcalix[4]arene ^b	1 ^c	2.183 ^h	- ^e	- ^e	- ^e
	2 ⁱ	2.061 ^h	1.969 ^h	1.918 ^h	2.129 ^h
Calix[4]arene	1 ^c	1.58 ^j	- ^e	- ^e	- ^e

^a In Å. ^b AM1 geometry. ^c An interaction between phenolic proton and adjacent phenolic oxygen. ^d equivalent bond distance. ^e Not exist ^f B3LYP/6-31G* geometry ^g B3LYP/6-31G** geometry [29]. ^h AM1 geometry [30]. ⁱ An interaction between phenolic proton and adjacent sulfonyl oxygen. ^j B3LYP/6-31G* geometry [11].

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Table 4.8 Total energy, E_{total} and relative energy, ΔE_{rel} at HF/6-31G* and BLYP/6-31G* levels of the AM1 optimized conformers of p-tert-butylthiacalix[4]arene

Conformer ^a	HF/6-31G*		BLYP/6-31G*	
	E_{total}^b	ΔE_{rel}^c	E_{total}^b	ΔE_{rel}^c
Cone				
0000-AAAA	-3432.11008624	0.00	-3446.80471287	0.00
0000-AAAB	-3432.10982664	0.16	-3446.80390580	0.51
0000-AABB	-3432.10960939	0.30	-3446.80424390	0.29
0000-ABAB	-3432.10958233	0.32	-3446.80412310	0.37
0000-ABBB	-3432.10981049	0.17	-3446.80420770	0.32
0000-BBBB	-3432.10979688	0.18	-3446.80450000	0.13
Partial cone				
0001-AAAA	-3432.09366364	10.31	-3446.79028651	9.05
0001-AAAB	-3432.09348869	10.42	-3446.79014166	9.14
0001-AABA	-3432.09315493	10.62	-3446.78999921	9.23
0001-ABAA	-3432.09328914	10.54	-3446.79018450	9.12
0001-BAAA	-3432.09360390	10.34	-3446.79028651	9.05
0001-AABB	-3432.09280429	10.84	-3446.78968076	9.43
0001-ABBA	-3432.09296014	10.75	-3446.78982263	9.34
0001-BBAA	-3432.09346752	10.43	-3446.79029860	9.05
0001-BAAB	-3432.09364124	10.32	-3446.79014689	9.14
0001-ABAB	-3432.09348074	10.42	-3446.79015228	9.14
0001-BABA	-3432.09336696	10.49	-3446.79006940	9.19
0001-ABBB	-3432.09317742	10.61	-3446.78993681	9.27
0001-BBBA	-3432.09306853	10.68	-3446.78989779	9.30
0001-BBAB	-3432.09337424	10.49	-3446.79019249	9.11
0001-BABB	-3432.09317740	10.61	-3446.78995879	9.26
0001-BBBB	-3432.09306101	10.68	-3446.78984267	9.33
1,2 Alternate				
0011-AAAA	-3432.07656948	21.03	-3446.77754412	17.05
0011-AAAB	-3432.07617757	21.28	-3446.77728294	17.21
0011-AABB	-3432.07525510	21.86	-3446.77669015	17.58
0011-ABBA	-3432.07539280	21.77	-3446.77679697	17.52
0011-ABAB	-3432.07545976	21.73	-3446.77683343	17.49
0011-ABBB	-3432.07466196	22.23	-3446.77631337	17.82
0011-BBBB	-3432.07356926	22.91	-3446.77558221	18.28
1,3 Alternate				
0101-AAAA	-3432.08334870	16.78	-3446.78052766	15.18
0101-AAAB	-3432.07979023	19.01	-3446.77770953	16.94
0101-AABB	-3432.07883870	19.61	-3446.77746599	17.10
0101-ABAB	-3432.08252538	17.29	-3446.78033840	15.30
0101-ABBB	-3432.07927541	19.33	-3446.77755922	17.04
0101-BBBB	-3432.08027240	18.71	-3446.77927400	15.96

^a the first four digits indicate the characteristic conformers and each letter indicates the arrangement of each tert-butyl group in p-tert-butylthiacalix[4]arene.

^c energy are relative to the most stable conformer, in kcal/mol.

Table 4.9 Data for the structure of p-tert-butylthiacalix[4]arene 0000-AAAA conformer

	AMI	B3LYP/6-31G*	Exp. ^a		AMI	B3LYP/6-31G*	Exp. ^a			
Bond distances (Å)				C13-C12-C11				118.90	119.77	119.4
S3-C10	1.712	1.800	1.781	C13-C12-S4	118.95	119.06	120.0			
S3-C9	1.709	1.800	1.791	C11-C12-S4	122.04	120.66	120.5			
S4-C12	1.709	1.800	1.773	C12-C13-C14	121.66	123.02	122.9			
S4-C1	1.712	1.800	1.791	C15-C14-C13	118.23	116.82	116.3			
S1-C4	1.712	1.800	1.776	C15-C14-C16	119.23	120.01	122.8			
S1-C3	1.709	1.800	1.789	C13-C14-C16	122.54	123.10	120.7			
S2-C7	1.712	1.800	1.774	C10-C15-C14	122.19	123.41	122.2			
S2-C6	1.709	1.800	1.776	C2-C1-S4	123.39	119.03	120.0			
C10-C15	1.395	1.390	1.395	O1-C2-C3	122.18	122.66	120.5			
C10-C11	1.412	1.410	1.403	O1-C2-C1	117.17	118.30	120.7			
C11-O4	1.364	1.350	1.357	C3-C2-C1	120.65	119.03	118.7			
C11-C12	1.411	1.400	1.395	C20-C3-C2	118.90	119.76	119.7			
C12-C13	1.397	1.400	1.388	C20-C3-S1	118.94	118.99	120.1			
C13-C14	1.397	1.390	1.398	C2-C3-S1	122.06	120.74	119.8			
C14-C15	1.402	1.400	1.396	C5-C4-S1	123.36	120.86	120.0			
C14-C16	1.505	1.530	1.537	O2-C5-C6	122.18	122.76	120.3			
C1-C2	1.412	1.410	1.398	O2-C5-C4	117.17	117.65	120.3			
C2-O1	1.364	1.350	1.360	C6-C5-C4	120.65	119.58	119.3			
C2-C3	1.411	1.400	1.396	C5-C6-C24	118.90	119.92	119.1			
C4-C5	1.412	1.410	1.397	C5-C6-S2	122.04	120.87	120.5			
C5-O2	1.364	1.350	1.352	C24-C6-S2	118.95	118.69	120.0			
C5-C6	1.411	1.400	1.390	C8-C7-S2	123.39	120.81	121.8			
C7-C8	1.412	1.400	1.385	O3-C8-C9	122.18	122.75	120.0			
C8-O3	1.364	1.350	1.370	O3-C8-C7	117.17	117.70	119.9			
C8-C9	1.411	1.400	1.383	C9-C8-C7	120.65	119.53	119.9			
C16-C17	1.524	1.540	1.499	C8-C9-C28	118.90	119.92	119.6			
C16-C19	1.527	1.540	1.504	C8-C9-S3	122.06	120.86	120.2			
C16-C18	1.527	1.540	1.529	C28-C9-S3	118.94	118.70	119.9			
O1...H4 ^b	2.122	1.822	2.314	C17-C16-C19	108.19	108.21	108.3			
O2...H1 ^b	2.122	1.822	2.084	C17-C16-C18	108.14	108.16	109.5			
O3...H2 ^b	2.122	1.822	2.275	C17-C16-C14	112.35	112.15	112.0			
O4...H3 ^b	2.122	1.822	2.257	C19-C16-C18	109.25	109.34	108.3			
Bond angles (°)				C19-C16-C14	109.46	109.40	109.4			
C10-S3-C9	104.63	104.33	103.02	C18-C16-C14	109.40	109.51	109.2			
C12-S4-C1	104.65	104.28	100.59	Dihedral (°)						
C4-S1-C3	104.63	104.40	104.16	C3-C2-O1-H1	-1.87	-17.45	-1.7			
C7-S2-C6	104.65	104.28	103.60	C6-C5-O2-H2	-1.73	-17.39	-1.8			
C15-C10-C11	118.33	119.55	119.57	C9-C8-O3-H3	-1.87	-17.44	-1.7			
C15-C10-S3	118.21	119.58	119.68	C12-C11-O4-H4	-1.73	-17.40	-1.9			
C11-C10-S3	123.36	120.45	120.59	C20-C21-C22-C23	-0.92	0.85	-0.8			
O4-C11-C12	122.18	122.73	120.07	C24-C25-C26-C27	-0.91	0.89	-0.8			
O4-C11-C10	117.17	117.71	120.57	C28-C29-C30-C31	-0.92	0.85	-0.8			
C12-C11-C10	120.64	119.54	119.36	C13-C14-C16-C17	-0.91	0.89	-0.8			

^a taken from [32]. ^b hydrogen bond.

Table 4.10 Data for B3LYP/6-31G* optimized structures related to hydrogen bonding for the p-tert-butylthiacalix[4]arene cone, as deprotonated (LH_2^{2-} and LH_3^-), neutral (LH_4) and protonated (LH_5^+) species

Structural data	LH_2^{2-} , ^a	LH_3^- , ^b	LH_4 , ^c	LH_5^+ , ^b
Bond distances (Å)				
O1-H1	1.064	1.013	0.988	0.979
H1...O2	1.420	1.590	1.820	1.970
O2-H2	-	-	0.988	0.970
H2...O3	-	-	1.820	-
O3-H3	-	1.030	0.988	0.982
O2...H3	-	1.530	-	1.690
H3...O4	-	-	1.820	-
O3...H4	-	-	-	1.690
O4-H5	1.064	0.980	0.988	1.060
O4-H4	-	-	-	1.010
H5...O1	-	-	1.820	1.510
H5...O3	1.420	1.900	-	-
Bond angles (°)				
O1-H1-O2	-	160.92	153.20	125.71
H1-O2-H2	-	-	113.38	110.66
O2-H2-O3	-	-	153.20	92.36
H2-O3-H3	-	-	113.38	68.91
O3-H3-O4	-	-	153.20	-
H3-O4-H5	-	-	113.38	-
O4-H5-O1	99.03	-	153.20	171.78
H5-O1-H1	-	-	113.38	110.86
O3-H5-O4	168.43	150.87	-	-
O2-H3-O3	-	166.13	56.68	109.42
O3-H4-O4	-	-	-	165.52
H4-O4-H5	-	-	-	112.62
H1-O2-H3	-	98.15	80.84	109.37
H3-O3-H4	-	-	-	119.77
H3-O3-H5	-	107.04	-	-

^a in C_s symmetry. ^b in C_1 symmetry. ^c in C_4 symmetry.

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Table 4.11 Total energies of deprotonated, protonated species of p-tert-butylthiacalix[4]arene cone conformer, its zinc complex with B3LYP/6-31G**/B3LYP/6-31G* calculations and their reaction energies

Reactions	Reaction Energies ^a
Proton Affinities :	
$\text{LH}_2^{2-} + \text{H}^+ \xrightarrow{\text{PA}(1)^b} \text{LH}_3^-$ (-3445.68282691) ^c	411.12
$\text{LH}_3^- + \text{H}^+ \xrightarrow{\text{PA}(2)^b} \text{LH}_4$	329.03
$\text{LH}_4 + \text{H}^+ \xrightarrow{\text{PA}(3)^b} \text{LH}_5^+$	208.44
Deprotonation :	
$\text{LH}_4 \xrightarrow{\Delta E_{\text{deprod}}} \text{LH}_2^{2-} + 2 \text{H}^+$ (-3446.86232640) ^c	740.15
Preorganization :	
$\text{LH}_2^{2-} \xrightarrow{\Delta E_{\text{preorg}}} [\text{LH}_2^{2-}]$ (-3445.64350351) ^c	24.68
Complexation :	
$\text{LH}_2^{2-} + \text{Zn}^{2+} \xrightarrow{\Delta E_{\text{binding}}} \text{Zn}(\text{LH}_2)$ (-5224.82216590) ^c	-647.79
$[\text{LH}_2^{2-}] + \text{Zn}^{2+} \xrightarrow{\Delta E_{\text{complex}}} \text{Zn}(\text{LH}_2)$	-627.47

^a in kcal/mol. ^b PA stands for Proton Affinity. ^c in hartree.

CHAPTER V

CONCLUSIONS

We have determined the structures of sulfonylcalix[4]arene and p-tert-butylsulfonylcalix[4]arene conformers and found that the sulfonylcalix[4]arene 1,2-alternate conformer is the most stable conformer within four typical conformers. The p-tert-butylsulfonylcalix[4]arene conformers of six for cone, twelve for partial cone, seven for 1,2-alternate and three for 1,3-alternate conformers have been found and the most stable conformer is the 0011-AAAA 1,2-alternate. The optimized structure of p-tert-butylsulfonylcalix[4]arene complex with zinc(II) included by tetracyclononane is in good agreement with x-ray geometry data. The zinc complexes whether with sulfonylcalix[4]arene or p-tert-butylsulfonyl calix[4]arene, their deprotonated cone conformer are the most stable species and the stabilization energies of these complexes are -632.21 and -648.62 kcal/mol, respectively.

This research can be concluded that six cone, sixteen partial cone, seven 1,2-alternate and six 1,3-alternate conformers of p-tert-butylthiacalix[4]arene have been found. The relative stabilities of p-tert-butylthiacalix[4]arene conformers are in following order : cone (most stable series) > partial cone > 1,3-alternate > 1,2-alternate. The most stable conformers of p-tert-butylthiacalix[4]arene are of the AAAA conformational type. The LH_2^{2-} species of p-tert-butylthiacalix[4]arene cone conformer likely form complex with Zn^{2+} . The AM1 and B3LYP/6-31G* optimized structures of the most stable conformer of p-tert-butylthiacalix[4]arene show good agreement with the X-ray crystallographic data.

REFERENCES

- [1] C.D. Gutsche, in: J.F. Stoddart (Ed.) *Calixarenes Revisited*, The Royal society of Chemistry, Cambridge, 1998.
- [2] A. Ikeda, S. Shinkai, *Chem. Rev.* 97(1997) 1713.
- [3] V. Bohmer, *Angew. Chem. Int. Ed. Engl.* 34(1995) 717.
- [4] P.D.J. Grootenhuis, P.A. Kollman, L.C. Groenen, D.N. Reinhoudt, G.J. van Hummel, F. Ugozzoli, G.D. Andreotti, *J. Am. Chem. Soc.* 112 (1990) 4165.
- [5] J. Royer, F. Bayard, C. Decoret, *J. Chim. Phys.* 87 (1990) 1695.
- [6] T. Harada, J.M. Rudziński, E. Osawa, S. Shinkai, *Tetrahedron* 49 (1993) 5941.
- [7] S. Fischer, P.D.J. Grootenhuis, L.C. Groenen, W.P. van Hoorn, F.C.J.M. van Veggel, D.N. Reinhoudt, M. Karplus, *J. Am. Chem. Soc.* 117 (1995) 1611.
- [8] T. Harada, S. Shinkai, *J. Chem. Soc., Perkin Trans. 2* (1995) 2230.
- [9] F. Bayard, B. Fenet, R. Lamartine, M. Petit-Ramel, J. Royer, *J. Chim. Phys.* 92 (1995) 13.
- [10] E. Brouyère, A. Persoons, J.L. Brédas, *J. Phys. Chem.* 101 (1997) 4142.
- [11] R.J. Bernardino, B.J. Cabral, J.L.C. Pereira, *J. Mol. Struct. (Theochem)* 455 (1998) 23.
- [12] R.J. Bernardino, B.J. Cabral, *J. Phys. Chem. A* 103 (1999) 9080.
- [13] H. Kumagai, M. Hasegawa, S. Miyamari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kaniyama, S. Miyano, *Tetrahedron Lett.* 38 (1997) 3971.
- [14] N. Iki, F. Narumi, T. Fujimoto, N. Morohashi, S. Miyano, *J. Chem. Soc. Perkin Trans. 2* (1998) 2745.
- [15] N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyamari, S. Miyano, *Tetrahedron Lett.* 39 (1998) 7559.
- [16] N. Iki, N. Morohashi, F. Narumi, S. Miyano, *Bull. Chem. Soc. Jpn.* 71 (1998) 1597.
- [17] H. Akdas, L. Bringel, E. Graf, M.W. Hosseini, G. Mislin, J. Pansanel, A. De Cian, J. Fischer, *Tetrahedron Lett.* 39 (1998) 2311.
- [18] P. Lhoták, M. Himl, S. Pakhomova, I. Stibor, *Tetrahedron Lett.* 39 (1998) 8915.
- [19] N. Iki, N. Morohashi, F. Narumi, T. Fujimoto, T. Suzuki, S. Miyano, *Tetrahedron Lett.* 40 (1999) 7337.

- [20] H. Akdas, L. Bringel, V. Bulach, E. Graf, M.W. Hosseini, A. De Cian, *Tetrahedron Lett.* 41 (2000) 3601.
- [21] R.J. Bernardino, B.J. Cabral, *J. Mol. Struct. (Theochem)* 549 (2001) 253.
- [22] H. Akdas, G. Mislin, E. Graf, M.W. Hosseini, A. De Cian, J. Fischer, *Tetrahedron Lett.* 40 (1999) 2113.
- [23] H. Akdas, W. Jaunky, E. Graf, M.W. Hosseini, J.-M. Planeix, A. De Cian, J. Fischer, *Tetrahedron Lett.* 41 (2000) 3601.
- [24] P. Lhoták, M. L. Kaplanek, I. Stibor, J. Lang, H. Dvoráková, R. Hrabal, J. Sykor, *Tetrahedron Lett.* 41 (2000) 9339.
- [25] A. Casnati, *Gazz. Chim. Ital.* 127 (1997) 637.
- [26] G. Mislin, E. Graf, M.W. Hosseini, A. De Cian, J. Fischer, *Tetrahedron Lett.* 40 (1999) 1129.
- [27] N. Morohashi, N. Iki, A. Sugawara, S. Miyano, *Tetrahedron Lett.* 41 (2000) 5557.
- [28] T. Kajiwarra, S. Yokozowa, T. Ito, *Angew. Chem. Int. Ed.* 41 (2002) 2070.
- [29] T. Sone, Y. Ohba, K. Moriya, H. Kumada, K. Ito, *Tetrahedron* 53 (1997) 10689.
- [30] B. Wannu, W. Sang-aroon, T. Tuntulani, B. Pulpoka and V. Ruangpornvisuti, *J. Mol. Struct. (Theochem)* 629 (2003) 137.
- [31] N. Iki, N. Morohashi, C. Kabuto, S. Miyano, *Chem. Lett.* 8 (1999) 219.
- [32] N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi, S. Miyano, *Tetrahedron* 56 (2000) 1437.
- [33] N. Morohashi, N. Iki, C. Kabuto, T.A. Sugawara, S. Miyano, *Tetrahedron* 57 (2001) 5557.
- [34] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [35] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 385.
- [36] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J.

- Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian 94, Gaussian, Inc., Pittsburgh PA, 1995
- [37] MOLDEN 3.7 : G. Schaftenaar, CAOS/CAMM Center Nijmegen, Toernooiveld, Nijmegen, Netherlands, 1991.
- [38] HyperChem, Tools for Molecular Modeling, Release 7 for Windows, Hypercube, 2002.
- [39] P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, MOLEKEL 4.3: Swiss Center for Scientific Computing, Manno (Switzerland), 2000.
- [40] C.D. Gutsche, Pro. Macrocyclic Chem. 3 (1987) 93.
- [41] R. Ungaro, A. Pochini, G.D. Andreotti, V. Sangermano, J. Chem. Soc., Perkin Trans. 2(1984) 1979.
- [42] A. Bilyk, A. K. Hall, J. H. Harrowfield, M.W. Hosseini, B. W. Skelton, A. H. White, Inorg. Chem. 40 (2001) 672.

