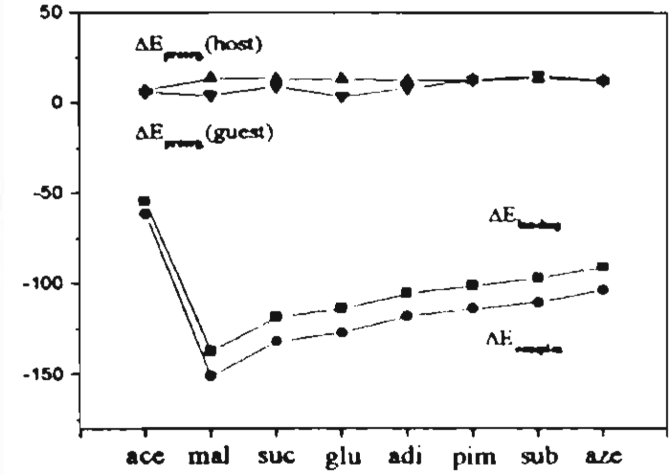

g. 8. Plot of preorganization energies of receptor 2 (host), carboxylates uest), their complexation and binding energies against sizes of rboxylate guests.

he reaction between receptor **2** and oxalate is an termolecular proton transfer process and gives a stable nic species of $[(\mathbf{2}^{-})(\text{oxalate}\;)]^{2-}$ complex. Binding teractions of the azophenol–thiourea receptor **1**, **2** and rboxylate guests are described as multipoints hydrogen onding. It is concluded that the receptors **1** and **2** are finally ble to be developed as carboxylate chemosensor.

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ภาคผนวก B: Manuscript บทความเรื่อง "An ONIOM study of host-guest interaction of tetraamino-*tert*-butylthiacalix[4] arene and tetraamino-*tert*-butylcalix[4]arene receptors with carboxylate and dicarboxylate guests"

An ONIOM study of host-guest interaction of tetraamino-*tert*-butylthiacalix[4] arene and tetraamino-*tert*-butylcalix[4]arene receptors with carboxylate and dicarboxylate guests

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Abstract. Geometry optimizations of tetraamino-*tert*-butylthiacalix[4]arene (tatbtc4a) and tetraamino-*tert*-butylcalix[4]arene (tatbc4a) complexes with acetate, oxalate, malonate, succinate, glutarate, adipate and pimelate were carried out using the integrated MO:MO method. Thermodynamic quantities, preorganization energies and complexation energies of these complexes were obtained at the ONIOM(B3LYP/6-31G(d):AM1) level of theory. The relative stabilities of the tatbtc4a and tatbc4a complexes with carboxylate guests are reported. The complexes tatbtc4a/malonate and tatbc4a/oxalate were found to be the most stable species. Selectivities of the receptors tatbtc4a and tatbc4a toward to malonate with respect to oxalate, in terms of selectivity coefficient, $K^{oxalate}_{malonate}$ are 9.90×10^2 and 1.09×10^2, respectively.

Keywords: Calix[4]arenes–Carboxylate–Host-guest–Recognition–Selectivity–ONIOM

Introduction

The organic anion receptors which contain chromophore part are basically used for chromogenic sensors for detection of biological anions. An excellent anion receptor such as thiourea-based chromophores with p-nitrophenyl groups is an excellent chromogenic anion receptor for monocarboxylate such as acetate.[1] Anion recognition of two binding-sites receptors lead to discovery of useful sensors not only for dicarboxylates but also monocarboxylates. Chromogenic azophenol-thiourea based anion sensors were developed for the selective colorimetric detection of acetate and other anions [2-4]. Furthermore chromogenic indoaniline-thiourea-based receptors were studied for fluoride detection sensors [5]. Anthracen urea and thiourea compounds were synthesized and investigated for their effective chromogenic anion sensors [6]. For fluorescent and luminescent chemosensors for detection of anions have been developed for dicarboxylate recognition [7]. Tripodal urea derivative such as aromatic carboxylate receptor was investigated for its association constant by NMR titration method [8]. The urea or thiourea groups incorporated receptors as anion recognition were studied in system of various solvents [9-11]. Previous theoretical work, the recognition of carboxylate and dicarboxylates by azophenol-thiourea derivatives were first investigated by the integrated MO:MO method and the oxalate is the most favorite ion to form complexes with both receptors of azophenol-thiourea derivatives [12]. Since determination of the binding and complexation energies of the complexes of the p-*tert*-butylsulfonylcalix[4]arene [13], p-*tert*-butylthiacalix[4]arene [14] and tetraamino-*tert* -butylthiacalix[4]arene [15] derivatives with zinc(II) cation were theoretically carried out, the complexes of these receptors with organic anions should be therefore investigated, particularly the calix[4]arene derivative functionalized by amino group.

As amino nitrogen atoms of the tetraamino-*tert*-butylthiacalix[4]arene derivatives have ability to bind to the zinc (II) cation [15], their amino protons have to be able to bind with anion. As the complex formation of tetraamino-*tert*-butylthiacalix[4]arene derivatives with anions is expected and their anion recognition leads to development of anion sensors, binding interactions between detected anions and their receptors are therefore very important information for discovering colorimetric and other detecting sensors. As organic anions such as acetate, oxalate, malonate and succinate are important biological anions, detection of these species is very useful data for medical and biological topics. In this work, binding interaction between carboxylates and different chromophore receptors have been therefore theoretically investigated in order to obtain their binding energies and thermodynamic properties of their interactions. The receptors of tetraamino-*tert*-butylthiacalix[4]arene derivatives and anionic guests of acetate, oxalate, malonate, succinate, glutarate, adipate and pimelate have been investigated in this work.

Computational Methods

Geometries of the tested host-guest complexes and its host, guest components were optimized using the hybrid density functional B3LYP [16-17] methods and the two-layered ONIOM(MO:MO) approach (ONIOM2) [18-19] using B3LYP/6-31G(d) as high model and semiempirical AM1 [20], PM3 [21] and MNDO [22] as low models. The reliability of the ONIOM2 calculations at the integrated level [23], ONIOM2(B3LYP/6-31G(d):AM1), ONIOM2(B3LYP/6-31G(d):PM3) and ONIOM2(B3LYP/6-31G(d):MNDO) approaches were examined by being employed in the geometrical optimizations of the tetraamino-*tert*-butylthiacalix[4]arene (tatbtc4a) receptor and its complex with oxalate. Their geometrical data were compared to the data of the target geometry optimized at B3LYP/6-31G(d) level of theory as listed in Table 1. Energies and geometries of oxalate/tatctb4a system as the examined host-guest complex carried out using the ONIOM2(B3LYP/6-31G(d):AM1), ONIOM2(B3LYP/6-31G(d):PM3) and ONIOM2 (B3LYP/6-31G(d):MNDO) methods were also compared with the target B3LYP/6-31G(d) geometry. The ONIOM2(B3LYP/6-31G(d):AM1) calculation of the examined system provides reasonable result with relatively lower cost for the present host-guest interaction. The two-layered ONIOM2(B3LYP/6-31G(d):AM1) for geometry optimization of the present host-guest investigation was therefore employed through out this work. The reliability of the ONIOM2(B3LYP/6-31G(d):AM1) of the similar system was discussed in references [24,25]. The real and model systems used in the two-layer ONIOM2(MO:MO) calculations for the hosts and host-guest interaction models are shown in Figs. 1 and 2, respectively. The geometrical structures of carboxylate guests and their total energies were optimized and computed at the B3LYP/6-31G(d) level of theory. All calculations were performed using the GAUSSIAN 03 program [26] and their structures were visualized using the MOLEKEL 4.3 program [27].

Energies of binding ($\Delta E_{\text{binding}}$), preorganization ($\Delta E_{\text{preorg.}}$) of host, guest and complexation ($\Delta E_{\text{complex}}$) of the ONIOM2 calculations of the present system are evaluated using the following formulas :

$$\begin{aligned}
\Delta E_{\text{binding}}\,[(\text{B3LYP/6-31G(d):AM1})](\text{host/guest}) = {} & \\
& E\,[(\text{B3LYP/6-31G(d):AM1})]\,(\text{host/guest}) \\
& - E\,[(\text{B3LYP/6-31G(d):AM1})]\,(\text{host}) \\
& - E\,[\text{B3LYP/6-31G(d)}]\,(\text{guest}) && (1)
\end{aligned}$$

$$\begin{aligned}
\Delta E_{\text{preorg.}}\,(\text{host}) = {} & E\,[(\text{B3LYP/6-31G(d):AM1})]\,(\text{complexed host}) \\
& - E\,[(\text{B3LYP/6-31G(d):AM1})]\,(\text{isolated host}) && (2)
\end{aligned}$$

$$\begin{aligned}
\Delta E_{\text{preorg.}}(\text{guest}) = {} & E\,[\text{B3LYP/6-31G(d)}]\,(\text{complexed guest}) \\
& - E\,[\text{B3LYP/6-31G(d)}]\,(\text{isolated guest}) && (3)
\end{aligned}$$

$$\begin{aligned}
\Delta E_{\text{complex}} = {} & E[(\text{B3LYP/6-31G(d):AM1})]\,(\text{host/guest}) \\
& - E\,[(\text{B3LYP/6-31G(d):AM1})]\,(\text{complexed host}) \\
& - E\,[\text{B3LYP/6-31G(d)}]\,(\text{complexed guest}) && (4)
\end{aligned}$$

$$\Delta E_{\text{binding}} = \Delta E_{\text{preorg.}}(\text{host}) + \Delta E_{\text{preorg.}}(\text{guest}) + \Delta E_{\text{complex}} \qquad (5)$$

The enthalpy ΔH^{298} and Gibbs free energy changes ΔG^{298} of all complexation reactions have been derived from the frequency computations at ONIOM(B3LYP/6-31G(d):AM1) level of theory. The entropy ΔS^{298} of their corresponding reactions were evaluated using a thermodynamic relation of $\Delta S^{298} = (\Delta H^{298} - \Delta G^{298})/T$ [28]. The equilibrium constant, K of binding process at 298.15 and 1 atmosphere was computed using thermodynamic relation of $\Delta G^{298} = -RT \ln K$.

The binding selectivity of calix[4]arene receptor to guest B with respect to guest A has been derived from the selectivity coefficient (K_B^A) [29] which is defined as an equilibrium constant of ion exchange between ions A and B. Since exchange is a chemical reaction as eq. (6), it can be treated like any other mass action expression.

$$AX + B \rightleftharpoons BX + A \qquad (6)$$

Therefore, the selectivity coefficient can be defined as $K_B^A = \frac{[BX][A]}{[AX][B]}$. If the complexations of BX and AX are observed, their stability constants due to eqs. (7) and (8) can be expressed as $K_A = \frac{[AX]}{[X][A]}$ and $K_B = \frac{[BX]}{[X][B]}$.

$$X + B \rightleftharpoons BX \tag{7}$$

$$X + A \rightleftharpoons AX \tag{8}$$

The selectivity coefficient can be therefore written as $K_B^A = \frac{K_B}{K_A}$. If the value of the selectivity coefficient K_B^A is larger than one, this implies that B is preferred over A and if K_B^A is smaller than one then A is preferred over B.

Results and discussion

According to examine the reliability of the two-layered ONIOM2(MO:MO) method, the geometries of the tatbtc4a/oxalate complex were optimized at four different levels of theory. Its geometries optimized at the B3LYP/6-31G(d), ONIOM2(B3LYP/6-31G(d):AM1), ONIOM2(B3LYP/6-31G(d):PM3) and ONIOM2(B3LYP/6-31G(d):MNDO) levels of theory are shown in Fig. 3 and their corresponding geometrical data are tabulated in Table 1. The ONIOM2(B3LYP/6-31G(d):AM1)-optimized geometry of the complex tatbtc/oxalate is very similar to the target B3LYP/6-31G(d)-optimized geometry (Fig. 3) and its geometrical data are correspondingly confirmed (Table 1). As the reliability test of the ONIOM2(MO:MO) approach for this host-guest system, the ONIOM2(B3LYP/6-31G(d):AM1) is the most reliable one with respect to the B3LYP/6-31G(d) level of theory.

Complexation of tetraamino-tert-butylthiacalix[4]arene (tatbtc4a)

The tetraamino-*tert*-butylthiacalix[4]arene (tatbtc4a) can form stable complexes with all guests (acetate, oxalate, malonate, succinate, glutarate and pimelate) except adipate. The most stable complex is the complex with malonate of which energy is stabilized by -117.60 kcal mol^{-1}. The stability of the tatbtc4a/carboxylate complex system in decreasing order is: malonate > oxalate > succinate > pimelate > glutarate > acetate, see Table 2. The ONIOM(B3LYP/6-31G(d):AM1)-optimized geometries of the tatbtc4a complexes with carboxylate guests are show in Fig. 4. Fig. 4 shows that the geometries of malonate/tatbtc4a and succinate/tatbtc4a complexes are in C_2 symmetry. The selectivity coefficient of the tatbtc4a towards malonate with respect to acetate also confirms that the tatbtc4a is favorable to form complex with the malonate. As the selectivity coefficient of the tatbtc4a toward malonate with respect to oxalate (the secondly most stable complex with tatbtc4a), $K^{oxalate}_{malonate}$ is quite big (9.90 x 10^2), the receptor tatbtc4a may well recognizes the malonate. Table 3 shows small changes of preorganization energies for host molecules and small changes for all guests excepts adipate ($\Delta E^{guest}_{preorg.}$ = 83.27 kcal mol^{-1}). Adipate can hardly ever form complex with the tatbtc4a host because the free energy of its binding reaction is the non-spontaneous process (ΔG^{298}= 13.18 kcal mol^{-1}). The change of preorganization entropy of malonate to form complex with the tatbtc4a is a remarkably high positive value (203.84 cal/mol K) as compared to the negative changes of other guest molecules, see Table 4.

Complexation of tetraamino-tert-butylcalix[4]arene (tatbc4a)

The tetraamino-*tert*-butylcalix[4]arene (tatbc4a) can form stable complexes with oxalate, malonate, succinate and glutarate, and low stable complex with acetate and pimelate as indicated by the binding and Gibbs free energies as tabulated in Table 4. The most stable complex is the complex with oxalate of which energy is stabilized by -67.61 kcal mol^{-1}. The stability of the tatbtc4a/carboxylate complex system in decreasing order is: oxalate > malonate > succinate > glutarate > pimelate >> acetate. The ONIOM(B3LYP/6-31G(d):AM1)-optimized geometries of the tatbc4a complexes with carboxylate guests are show in Fig. 5. Fig. 5 shows that the geometries of malonate/tatbc4a and succinate/tatbc4a complexes are in C_2 symmetry. The selectivity coefficient of the receptor tatbt4a toward oxalate with respect to acetate is quite big but smaller than the malonate (the secondly most stable complex with tatbc4a, $K^{oxalate}_{malonate}$ = 1.09 x 10^2). Table 5 shows big changes of preorganization energies for host molecules (> 30 kcal mol^{-1} except acetate ion, which energy is 19.17 kcal mol^{-1}), and small changes for all guests excepts adipate and pimelate. The total preorganization energies of all tatbc4a complexes are higher than 45 kcal mol^{-1}

except acetate ion (19.94 kcal mol^{-1}). Due to the high preorganization energy ($\Delta E^{guest}_{preorg}$ = 76.28 kcal mol^{-1}) of adipate and the free energy change of its binding process (ΔG^{298}= 33.32 kcal mol^{-1}), the tatbc4a/adipate complex has been never formed. The change of preorganization entropy of malonate to form complex with the tatbtc4a is a remarkably high positive value (204.04 cal mol^{-1} K^{-1}) as compared to negative changes of other guest molecules, see Table 5. Nevertheless, the receptor tatbc4a should be selective to the malonate with respect to the oxalate.

Their electronic potential surfaces

Electrostatic potential surfaces of the tatbtc4a and tatbc4a were generated from the Gaussian output files of their B3LYP/6-31G(d) computation with GFPRINT and POP=FULL keywords using the MOLEKEL 4.3 software [27]. The electrostatic potential (in au) presented over electronic isodensity (ρ=0.015 e $Å^{-3}$) of surface of volume, V_s=404.60 $Å^3$, minimum (ψ_-) and maximum (ψ_+) potentials of ψ_- = -0.1180 and ψ_+ = 0.1172 for the tatbtc4a and V_s=398.20 $Å^3$, ψ_- = -0.1206 and ψ_+ = 0.1069 for the tatbc4a are shown in Fig. 7. The color maps of electronic isodensity surfaces of tatbtc4a and tatbc4a in Fig. 7 show strong positive charge on amino protons of two opposite amino groups and strong negative charges on amino nitrogen atoms on the other amino groups. The positive charges of the amino protons on the tatbtc4a are stronger than that on the tatbc4a. Due to the positive charges on amino protons, both of the tatbtc4a and tatbc4s are therefore able to form complex with appropriate carboxylate anions such as malonate and oxalate. Although, the localization of the LUMO and HOMO orbitals in the receptors tatbtc4a and tatbc4a as shown in Fig. 8 are almost the same shape, their HOMO-LUMO energy gaps are significantly different; the HOMO-LUMO energy gaps of the tatbtc4a and tatbc4a are 4.48 and 4.66 eV, respectively. As the HOMO-LUMO energy gap of the tatbtc4a is smaller than the tatbc4a, the tatbtc4a is therefore able to form complex more stable than the tatbc4a. This has been indicated by the binding energies of the complexes with the malonate ($\Delta E^{298}_{binding}$ = -117.60 and -64.09 kcal mol^{-1} for the tatbtc4a and tatbtc4a, respectively).

Atomic charges of the binding atoms of three most stable complexes of the tatbtc4a and tatbc4a with carboxylate guests and their hydrogen bond distances computed at the

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Table 1. Geometrical data for B3LYP/6-31G(d), ONIOM(B3LYP/6-31G(d):AM1), ONIOM(B3LYP/6-31G(d):PM3) and ONIOM(B3LYP/6-31G(d):MNDO)-optimized geometries of tetraamino-*tert*-butylthiacalix[4]arene (tatbtc4a) complex with oxalate

Parameter [a]	B3LYP/6-31G(d)	ONIOM (B3LYP/ 6-31G(d):AM1)	ONIOM (B3LYP/ 6-31G(d):PM3)	ONIOM (B3LYP/ 6-31G(d):MNDO)
Host :				
Bond distance (Å)				
N1-H1	1.015	1.018	1.040	1.027
N1-H2	1.024	1.031	1.007	1.030
N2-H3	1.011	1.017	1.006	1.027
N2-H4	1.044	1.084	1.040	1.024
N1-C2	1.378	1.406	1.392	1.353
N2-C5	1.333	1.360	1.388	1.360
C1-C2	1.426	1.422	1.425	1.440
C2-C3	1.422	1.419	1.424	1.438
C3-C13	1.397	1.392	1.391	1.400
C13-C14	1.398	1.396	1.390	1.417
C14-C15	1.401	1.400	1.397	1.421
C1-C15	1.392	1.389	1.385	1.398
C14-C16	1.539	1.504	1.513	1.538
C16-C17	1.540	1.524	1.531	1.558
C4-C5	1.439	1.437	1.425	1.435
C5-C6	1.434	1.434	1.426	1.433
C6-C20	1.395	1.385	1.385	1 401
S1-C3	1.815	1.732	1.787	1.731
S1-C4	1.805	1.725	1.787	1.733
S2-C6	1.804	1.724	1.785	1.733
S2-C7	1.816	1.729	1.778	1.732
Bond angle (°)				
H1-N1-H2	107.1	103.9	110.0	107.3
H3-N2-H4	110.0	109.6	110.3	107.1
H5-N3-H6	107.8	106.8	110.8	107.4
H7-N4-H8	110.8	111.6	110.8	107.1
C1-C2-C3	116.1	117.2	118.5	117.9
C3-S1-C4	102.2	99.3	97.5	104.7
C4-C5-C6	115.6	115.8	118.4	118.7
C6-S2-C7	102.2	100.2	101.0	104.6
Dihedral angle (°)				
N1-C2-C3-C13	-173.3	-172.6	-172.9	-163.1
C3-C13-C14-C16	179.0	-179.4	-176.4	175.9
C13-C14-C16-C17	0.2	-1.0	26.0	-5.8
C2-C3-S1-C4	113.7	111.8	93.5	95.6
C3-S1-C4-C5	-88.2	-91.4	-91.5	-107.8
N2-C5-C6-C20	-168.8	-162.5	-173.7	-164.0
C6-C20-C21-C23	177.7	179.7	-176.1	177.3
C20-C21-C23-C24	-1.0	-2.1	-33.2	-10.7
C5-C6-S2-C7	88.8	98.1	114.2	106.0
C6-S2-C7-C8	-116.2	-118.0	-112.0	-95.0
H2-N1-C2-C3	-49.2	-59.1	-6.0	-9.4
H4-N2-C5-C6	-7.4	-28.4	-38.9	-14.7
H6-N3-C8-C9	-22.6	-24.6	-5.6	-9.5
H8-N4-C11-C12	3.5	-22.6	-16.4	-14.7
Guest :				
Bond distance (Å)				
C27-C28	1.550	1.553	1.557	1.592
O1-C27	1.241	1.239	1.239	1.264
O2-C27	1.292	1.292	1.294	1.267
O3-C28	1.278	1.288	1.271	1.264
O4-C28	1.268	1.258	1.270	1.268
Bond angle (°)				
O1-C27-O2	126.6	126.9	126.7	125.5
O3-C28-O4	125.7	125.3	126.8	125.5
Dihedral angle (°)				
O1-C27-C28-O3	96.1	93.9	90.6	-176.4

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[a] Atomic labeling is shown in Fig. 1.

Table 2. Binding energies, enthalpies, free energies and entropies of association of tetraamino-tert-butylthiacalix[4]arene (tatbtc4a) and various anionic guests

Guest	$\Delta E_{binding}$ [a]	ΔH^{298} [b]	ΔG^{298} [b]	ΔS^{298} [c]	$K_B^{acetate}$ [d]
acetate	-43.32	-43.61	-28.03	-52.26	1.00×10^{00}
oxalate	-103.77	-104.26	-80.92	-78.29	8.12×10^{38}
malonate	-117.60	-41.35	-84.99	146.38	8.04×10^{41}
succinate	-86.91	-87.71	-68.80	-63.41	9.83×10^{29}
glutarate	-75.06	-75.64	-58.19	-58.54	1.54×10^{22}
adipate	-4.93	-5.00	13.18[e]	-60.98	-[e]
pimelate	-58.98	-60.26	-42.38	-59.95	3.62×10^{10}

[a] In kcal mol^{-1}, derived from the ONIOM (B3LYP/6-31G(d):AM1) energies with zero-point vibrational energy corrections (ZPVE).

[b] In kcal mol^{-1}.

[c] In cal mol^{-1} K^{-1}.

[d] Selectivity coefficient of guests with respect to acetate.

[e] Non spontaneous process.

Table 3. Preorganization energies, corresponding thermodynamics of tatbtc4a receptor (host), carboxylates (guest) and their complexation energies derived from the ONIOM (B3LYP/6-31G(d):AM1) calculations

Host:guest	Host				Guest				$\Delta E^{total}_{preorg}$ [a]	$\Delta E_{complex}$
	ΔE^{host}_{preorg} [a]	ΔH^{298} [b]	ΔG^{298} [b]	ΔS^{298} [c]	$\Delta E^{guest}_{preorg}$ [d]	ΔH^{298} [e]	ΔG^{298} [f]	ΔS^{298} [f]		
tatbtc4a/acetate	10.65	10.67	10.99	-1.06	0.86	0.26	2.79	-8.49	11.51	-54.83
tatbtc4a/oxalate	22.54	21.56	25.01	-11.58	1.54	1.03	8.66	-25.60	24.08	-127.85
tatbtc4a/malonate	1.84	1.53	2.10	-1.92	2.47	64.59	3.81	203.84	4.31	-138.72
tatbtc4a/succinate	18.06	16.55	22.32	-19.35	13.07	12.91	13.69	-2.61	31.13	-118.04
tatbtc4a/glutarate	17.75	16.31	20.27	-13.27	17.05	15.87	19.24	-11.31	34.8	-109.86
tatbtc4a/adipate	17.54	16.74	19.03	-7.70	83.28	83.02	85.53	-8.41	100.82	-105.75
tatbtc4a/pimelate	17.87	17.04	19.85	-9.40	26.49	25.00	27.93	-9.83	44.36	-103.34

[a] In kcal mol^{-1}, derived at the ONIOM (B3LYP/6-31G(d):AM1) level with (ZPVE) corrections.

[b] In kcal mol^{-1}.

[c] In cal mol^{-1} K^{-1}.

[d] In kcal mol^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.

[e] In kcal mol^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.

[f] In cal mol^{-1} K^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.

Table 4. Binding energies, enthalpies, free energies and entropies of association of tetraamino-tert-butylcalix[4]arene (tatbc4a) and various anionic guests

Guest	$\Delta E_{binding}$ [a]	ΔH^{298} [b]	ΔG^{298} [b]	ΔS^{298} [c]	$K_{B}^{acetate}$ [d]
acetate	-13.60	-8.28	-7.73	-1.86	1.00×10^{00}
oxalate	-67.61	-62.58	-54.28	-27.86	1.76×10^{34}
malonate	-64.09	3.78	-57.05	204.04	1.93×10^{36}
succinate	-49.77	-44.56	-42.66	-6.36	5.00×10^{25}
glutarate	-43.71	-39.01	-36.58	-8.14	1.69×10^{21}
adipate	25.78 [e]	31.05	33.32	-7.59	- [f]
pimelate	-26.72	-22.79	-18.41	-14.68	7.27×10^{7}

[a] In kcal mol^{-1}, derived from the ONIOM (B3LYP/6-31G(d):AM1) energies with ZPVE corrections.

[b] In kcal mol^{-1}.

[c] In cal mol^{-1} K^{-1}.

[d] Selectivity coefficient of guests with respect to acetate.

[e] Destabilized complex.

[f] Non-spontaneous process.

Table 5. Preorganization energies, corresponding thermodynamics of tatbc4a receptor (host), carboxylates (guest) and their complexation energies derived from the ONIOM (B3LYP/6-31G(d):AM1) calculations

Host:guest	Host				Guest				$\Delta E^{total}_{preorg.}$ [a]	$\Delta E_{complex}$
	$\Delta E^{host}_{preorg.}$ [a]	ΔH^{298} [b]	ΔG^{298} [b]	ΔS^{298} [c]	$\Delta E^{guest}_{preorg.}$ [d]	ΔH^{298} [e]	ΔG^{298} [f]	ΔS^{298} [f]		
tatbc4a/acetate	19.27	18.64	19.96	-4.42	0.67	0.08	2.61	-8.49	19.94	-33.54
tatbc4a/oxalate	68.05	71.96	62.11	33.05	1.31	0.80	8.44	-25.61	69.36	-136.98
tatbc4a/malonate	51.76	55.83	44.66	37.47	2.19	64.31	3.52	203.91	53.95	-118.04
tatbc4a/succinate	49.79	54.49	41.22	44.50	11.97	11.82	12.48	-2.21	61.76	-111.53
tatbc4a/glutarate	38.64	43.21	31.02	40.86	8.60	7.44	10.81	-11.28	47.24	-90.95
tatbc4a/adipate	37.62	42.23	30.03	40.89	76.28	75.10	79.97	-16.36	113.9	-88.13
tatbc4a/pimelate	61.35	65.27	55.77	31.85	21.83	19.78	24.21	-14.88	83.18	-109.89

[a] In kcal mol^{-1}, derived at the ONIOM (B3LYP/6-31G(d):AM1) level with (ZPVE) corrections.
[b] In kcal mol^{-1}.
[c] In cal mol^{-1} K^{-1}.
[d] In kcal mol^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.
[e] In kcal mol^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.
[f] In cal mol^{-1} K^{-1}, derived at the B3LYP/6-31G(d) level with ZPVE corrections.

Table 6. Atomic charges of binding atoms (treated as high layer) of three most stable complexes of tatbtc4a and tatbc4a with carboxylate guests and hydrogen bond distances obtained by the ONIOM(B3LYP/6-31G(d):AM1) calculations

Properties/host-guest	tatbtc4a			tatbc4a		
	acetate	oxalate	malonate	acetate	oxalate	malonate
Host's atomic charges[a]						
S1	-	-	-	-0.084	-0.089	-0.074
S2	-	-	-	-0.079	-0.054	-0.067
S3	-	-	-	-0.056	-0.052	-0.074
S4	-	-	-	-0.043	-0.102	-0.067
N1	-0.622	-0.650	-0.648	-0.677	-0.577	-0.678
N2	-0.676	-0.741	-0.805	-0.602	-0.797	-0.782
N3	-0.621	-0.778	-0.649	-0.660	-0.718	-0.678
N4	-0.675	-0.776	-0.805	-0.737	-0.780	-0.782
H1	0.170	0.243	0.233	0.307	0.195	0.267
H2	0.276	0.235	0.241	0.205	0.267	0.260
H3	0.274	0.252	0.293	0.217	0.197	0.299
H4	0.200	0.292	0.288	0.216	0.364	0.301
H5	0.169	0.273	0.233	0.208	0.270	0.267
H6	0.276	0.299	0.241	0.294	0.288	0.260
H7	0.274	0.307	0.293	0.257	0.351	0.299
H8	0.177	0.263	0.289	0.292	0.230	0.301
Guest's atomic charges[a]						
O1	-0.633	-0.679	-0.636	-0.624	-0.666	-0.628
O2	-0.628	-0.637	-0.634	-0.613	-0.595	-0.630
O3	-	-0.681	-0.634	-	-0.637	-0.628
O4	-	-0.664	-0.636	-	-0.633	-0.630
Hydrogen bond distance[b]						
O1-H8 (O1-H6)	(1.876)	(1.896)	(1.963)	1.883	(1.857)	(1.955)
O1-H7(O1-H1)	2.005	1.777	1.955	(1.889)	1.732	2.003
O2-H6 (O2-H4)[O2-H2]	[1.881]	-	(1.981)	1.969	-	(1.994)
O2-H7 (O2-H5)[O2-H3]	[2.011]	-	(2.008)	2.119	-	(1.912)
O3-H1	-	2.896	2.008	-	2.685	1.912
O3-H2 (O3-H8)	-	1.976	(1.981)	-	2.039	(1.994)
O4-H3 (O4-H5)	-	(1.967)	1.955	-	(1.927)	2.003
O4-H4 (O4-H2)	-	1.631	(1.962)	-	1.566	(1.955)

[a] In au. [b] In Å, values in parenthesis and bracket belong to their bond distances in corresponding parentheses.

Captions for the illustrations

Fig. 1. Real molecule (top) and model system (bottom) of hosts (a) tatbtc4a and (b) tatca4a. The bold atoms of real molecules of hosts are treated as high level of theory in which have been used in the ONIOM(MO:MO) calculation.

Fig. 2. Atom labeling of tatbtc4a/oxalate complex as a representative of host-guest system.

Fig. 3. Geometrical structures of tetraamino-tert-butylthiacalix[4]arene (tatbtc4a) complex with oxalate optimized at (a) B3LYP/6-31G, (b) ONIOM(B3LYP/6-31G(d):AM1), (c) ONIOM(B3LYP/6-31G(d):PM3) and (d) ONIOM(B3LYP/6-31G(d):MNDO) levels of theory.

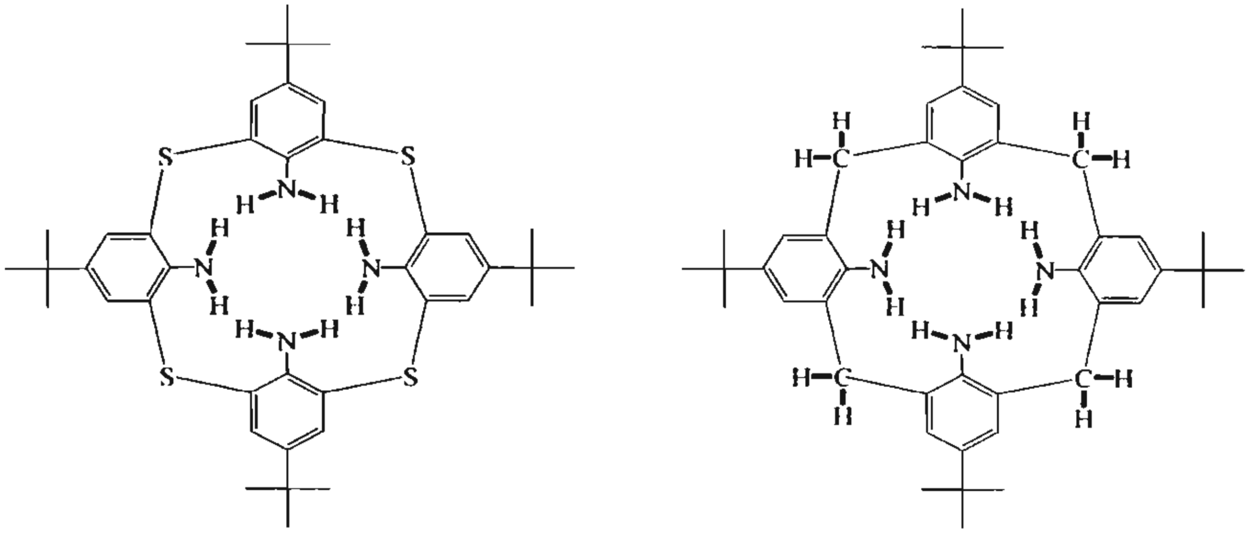
Fig. 4. ONIOM(B3LYP/6-31G(d):AM1)-optimized geometries of tetraamino-tert-butylthiacalix[4]arene (tatbtc4a) with carboxylate guests. Binding energies ΔE are in kcal mol^{-1}.

Fig. 5. ONIOM(B3LYP/6-31G(d):AM1)-optimized geometries of tetraamino-tert-butylcalix[4]arene (tatbc4a) with carboxylate guests. Binding energies ΔE are in kcal mol^{-1}.

Fig. 6. Plot of preorganization energies of (a) tatbtc4a (host) and carboxylates (guest) and (b) tatbc4a (host) and carboxylates (guest) and their complexation and binding energies against sizes of carboxylate guests, based upon the ONIOM(B3LYP/6-31G(d):AM1) method.

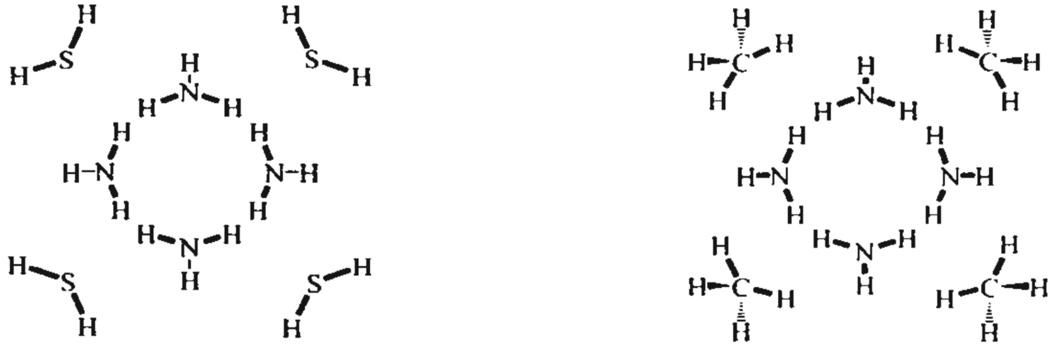
Fig. 7. Top, side and bottom views of the molecular electrostatic potential (in au) presented over electronic isodensity (ρ=0.015 e Å^{-3}) of (a) surface of volume, V_s=404.60 Å^3, minimum, ψ_- and maximum, ψ_+ potentials of ψ_- = -0.1180 and ψ_+ = 0.1172 for tetraamino-tert-butylthiacalix[4]arene (tatbtc4a) and (b) V_s=398.20 Å^3, ψ_- = -0.1206 and ψ_+ = 0.1069 for tetraamino-tert-butylcalix [4]arene (tatbc4a).

Fig. 8. Localization of the LUMO (above) and HOMO (bottom) orbitals in (a) tetraamino-tert-butylthiacalix[4]arene (tatbtc4a) and (b) tetraamino-tert-butylcalix[4]arene (tatbc4a).



Real system : tatbtc4a

Real system : tatbc4a



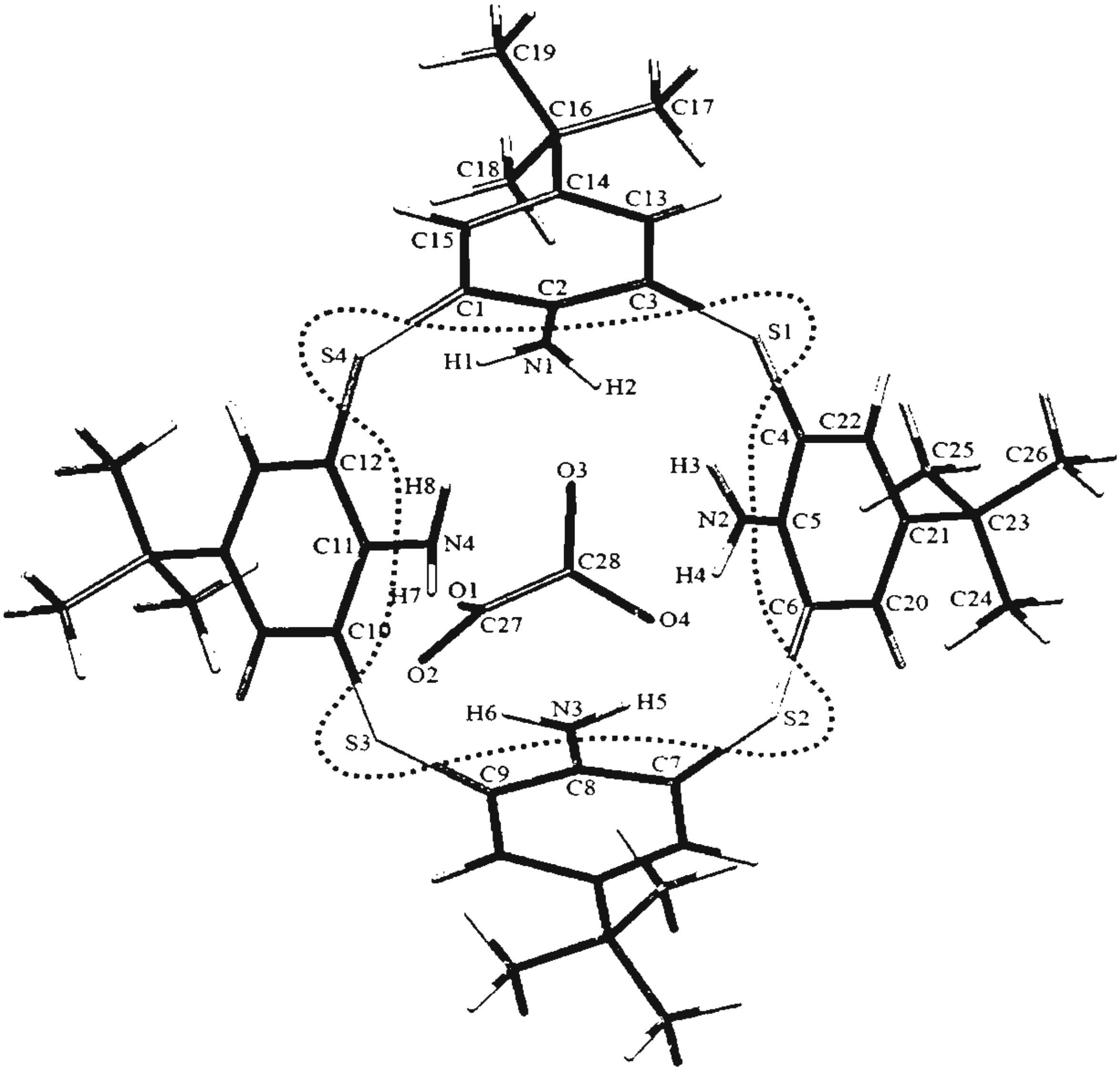
Model system : 4 H_2S and 4 NH_3

Model system : 4 CH_4 and 4 NH_3

(a)

(b)

Fig. 1.


C19
C16
C17
C18
C14
C13
C15
C2
C1
C3
S4
S1
H1
N1
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C22
C12
C25
C26
H8
O3
H3
N2
C5
C21
C23
C11
N4
C28
H4
H7
O1
O4
C6
C20
C24
C10
C27
O2
H6
N3
H5
S3
S2
C9
C8
C7

Fig. 2.

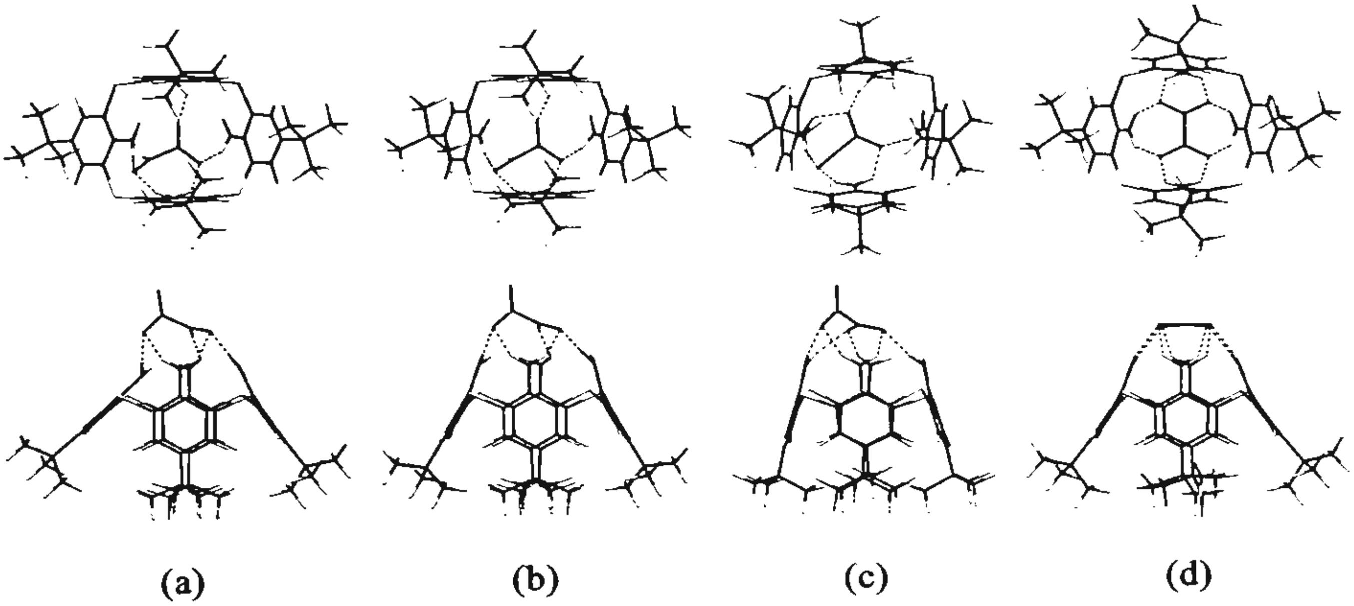
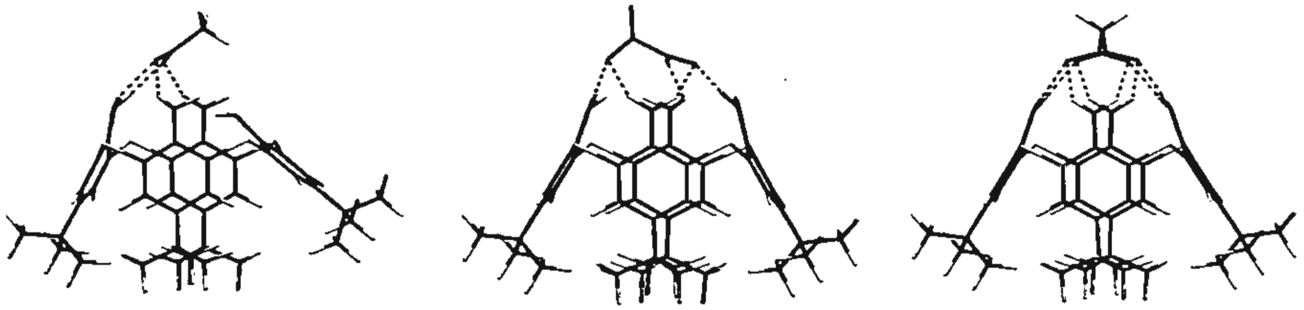
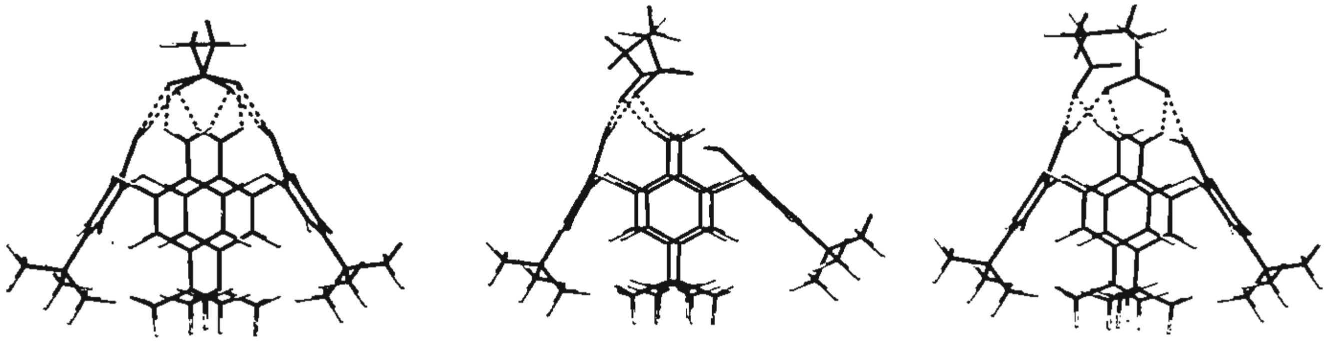


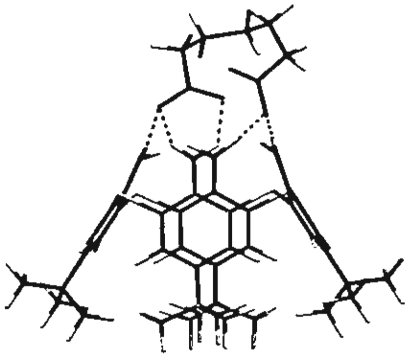
Fig. 3.



ace/tatbtc4a, ΔE = -43.32 oxa/tatbtc4a, ΔE = -103.77 mal/tatbtc4a, ΔE = -117.60

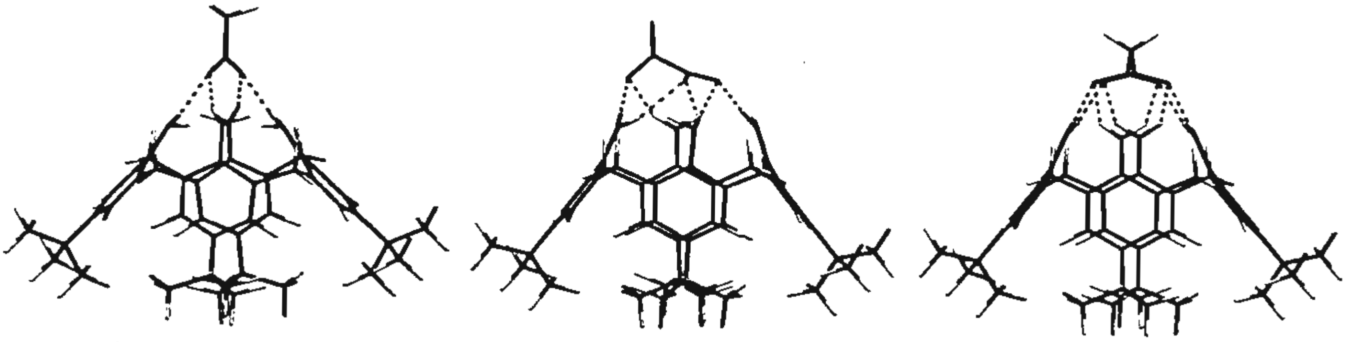


suc/tatbtc4a, ΔE = -86.91 glu/tatbtc4a, ΔE = -75.06 adi/tatbtc4a, ΔE = -4.93

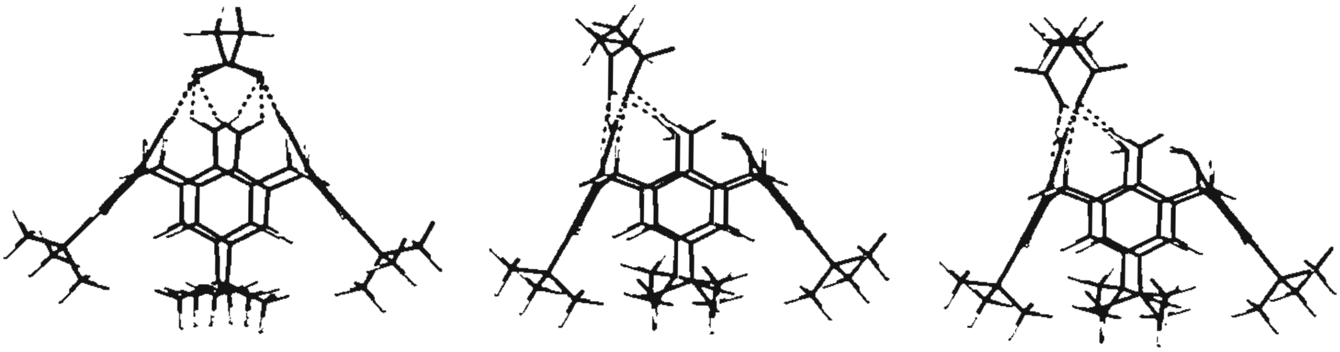


pim/tatbtc4a, ΔE = -58.98

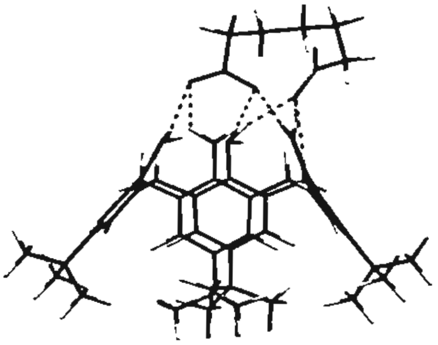
Fig. 4.



ace/tatbc4a, $\Delta E = -13.60$ oxa/tatbc4a, $\Delta E = -67.61$ mal/tatbc4a, $\Delta E = -64.09$

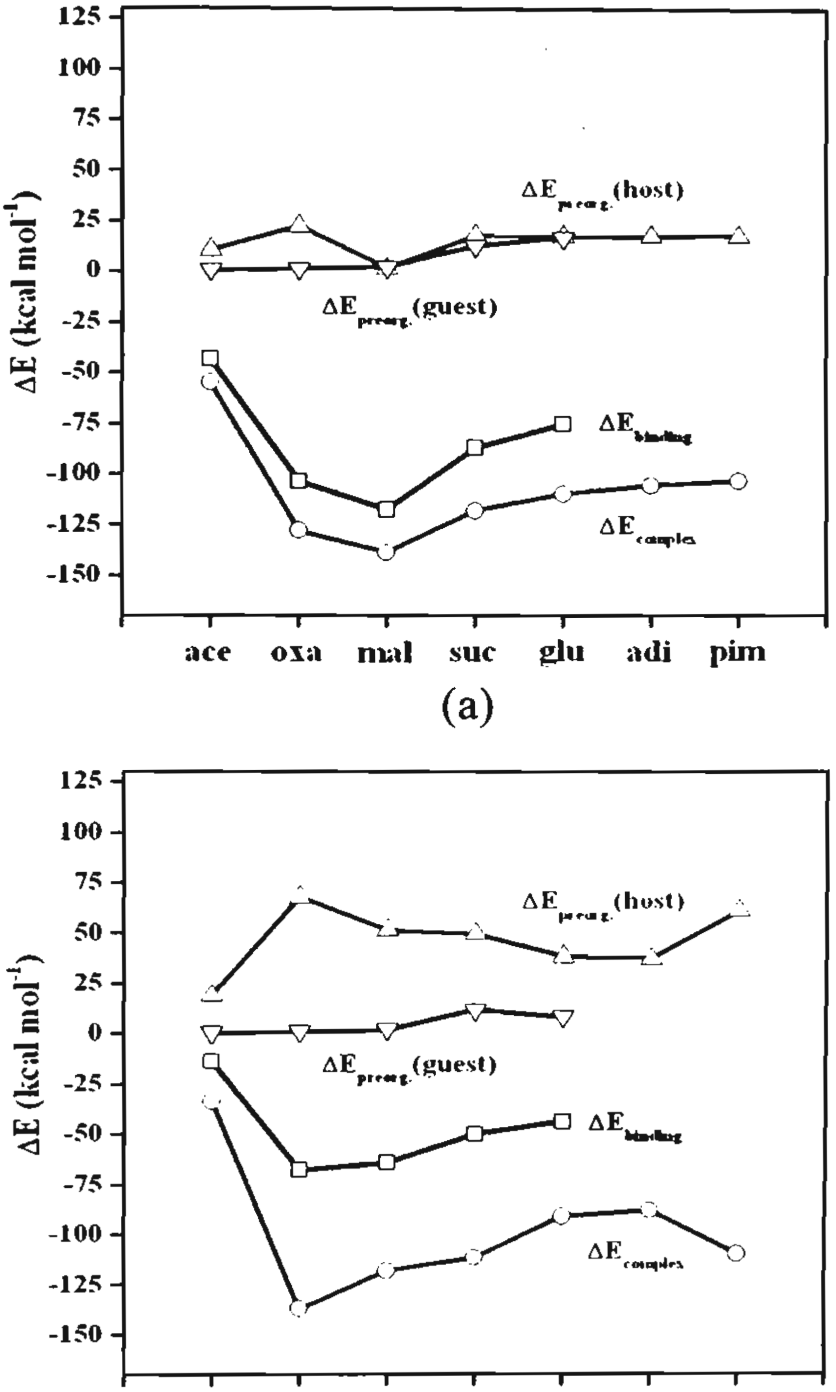


suc/tatbc4a, $\Delta E = -49.77$ glu/tatbc4a, $\Delta E = -43.71$ adi/tatbc4a, $\Delta E = 25.78$



pim/tatbc4a, $\Delta E = -26.72$

Fig. 5.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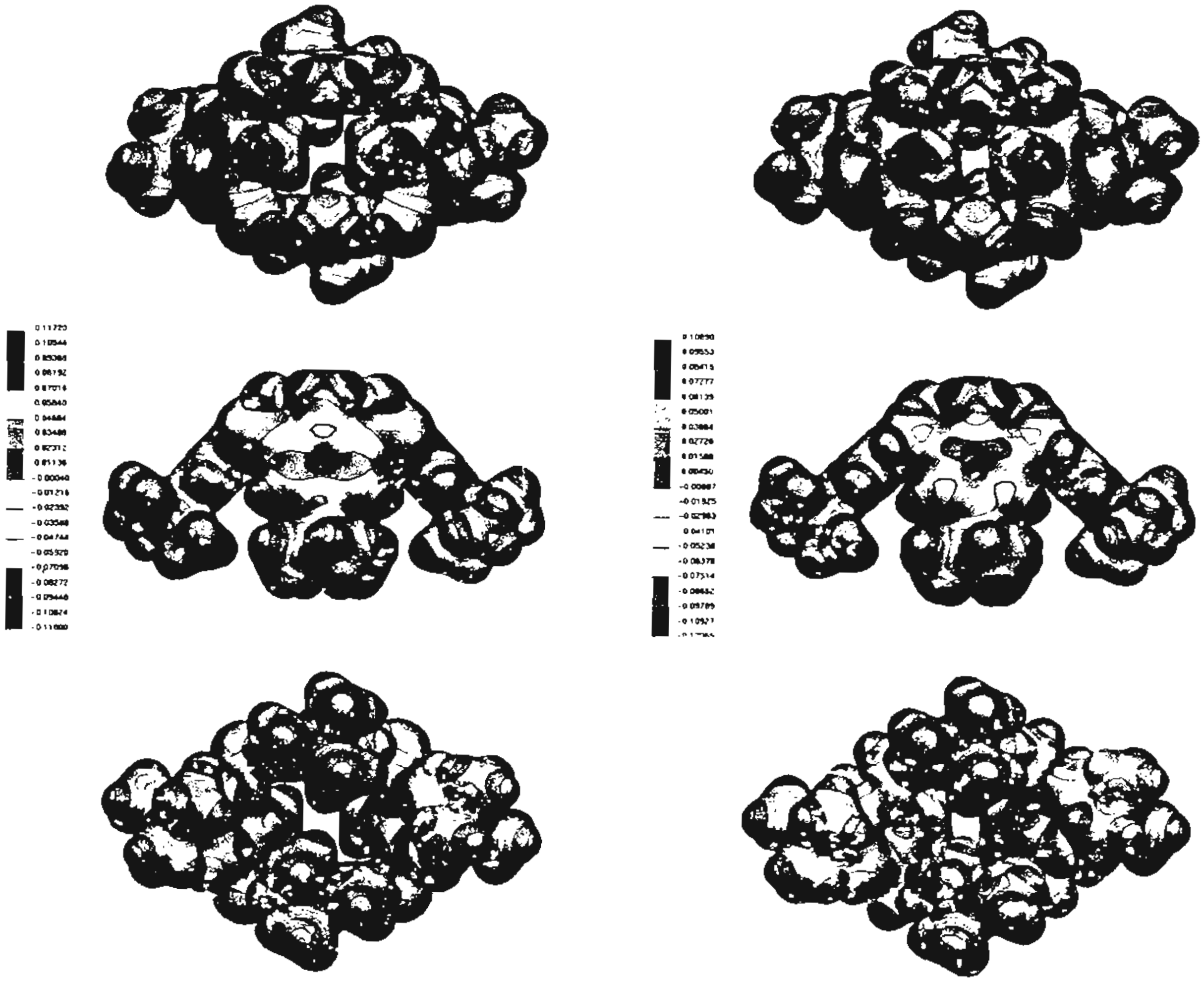
100
75
50
25
0
-25
-50
-75
-100
-125
-150
ΔE (kcal mol^{-1})
ΔE$_{preorg.}$(host)
ΔE$_{preorg.}$(guest)
ΔE$_{binding}$
ΔE$_{complex}$
ace
oxa
mal
suc
glu
adi
pim

(a)

(b)

Fig. 6.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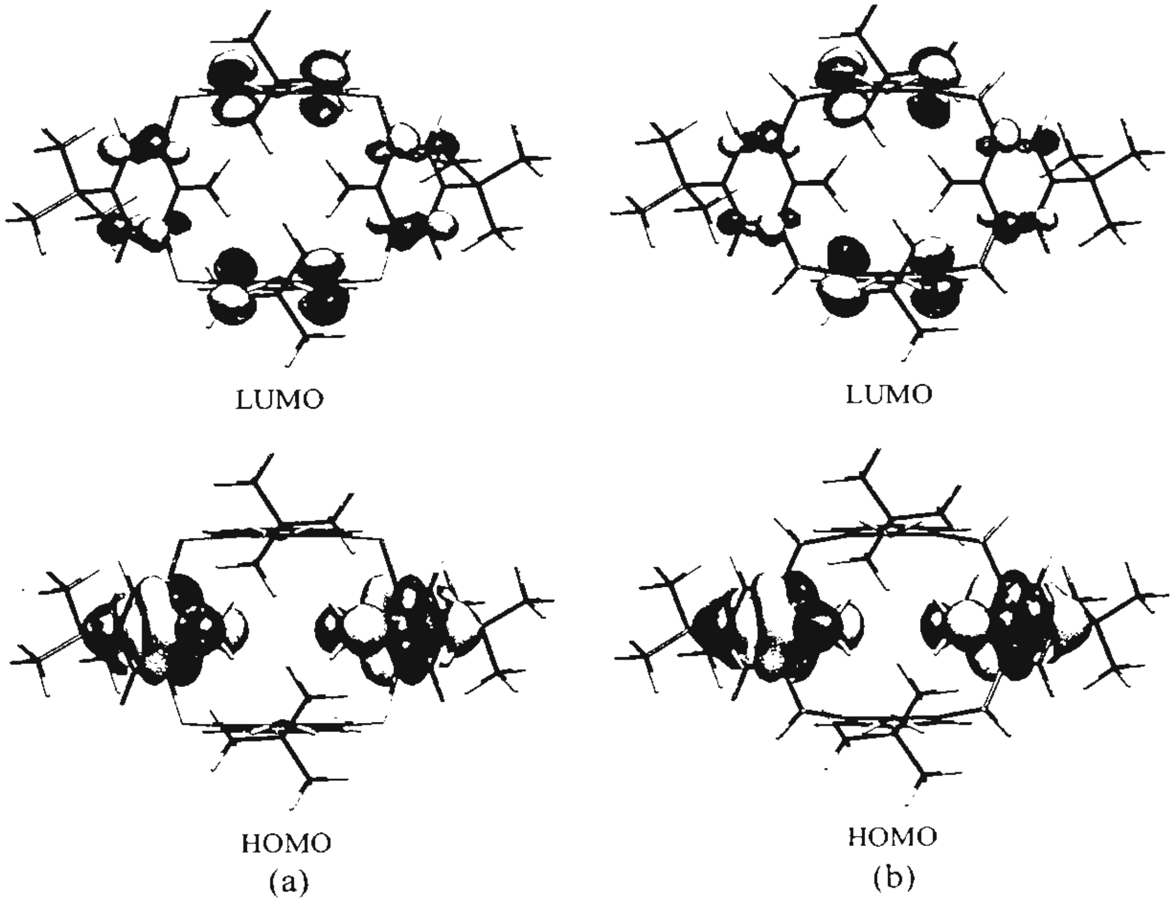
(a) (b)

Fig. 7.



LUMO LUMO

HOMO HOMO

(a) (b)

Fig. 8.

เอกสารสรุปงานวิจัยเพื่อประชาสัมพันธ์

เป็นการค้นหาโมเลกุลโฮสต์ที่สามารถจดจำแอนไอออนที่เป็นกรดคาร์บอกไซลิก โดยการหาโครงสร้างของโมเลกุลโฮสต์ เกสต์ และ สารประกอบเชิงซ้อนระหว่างสารประกอบโฮสต์กับเกสต์ จากการคำนวณโครงสร้างของสารประกอบเชิงซ้อนระหว่างสารประกอบอะโซฟีนอล-ไธโอยูเรีย (1 และ 2) สารประกอบเตตระอะมิโน-เทอร์เชียรี-บิวทิวไธอาคาลิก[4]เอรีน (tatbtc4a) และ สารประกอบเตตระอะมิโน-เทอร์เชียรี-บิวทิวคาลิก[4]เอรีน (tatbc4a) กับแอนไอออน อะซีเทต อ๊อกซาเลต มาโลเนต ซักซิเนต กลูตาเรต อะดิเพต พิมิเลต ซับเบอเรต และ อะซีเนต โดยวิธีอินทิเกรเทต MO:MO พบว่าสารประกอบ อะโซฟีนอล-ไธโอยูเรีย และสารประกอบเตตระอะมิโน-เทอร์เชียรี-บิวทิวคาลิก[4]เอรีนมีสมบัติในการจดจำแอนไอออนที่เป็นกรดคาร์บอกไซลิกบางตัวได้ดี ในการศึกษาวิจัยพลังงานรวมตัวและพลังงานการเกิดสารประกอบเชิงซ้อนระหว่างโฮสต์และเกสต์เหล่านี้ ได้รับจากการคำนวณโดยวิธี ONIOM2 (B3LYP/6-31G(d):AM1) ลำดับความเสถียรของสารประกอบเชิงซ้อนระหว่างสารประกอบ 1, 2, tatbtc4a และ tatbc4a กับแอนไอออน ได้รับการรายงาน อันตรปฏิกิริยาการรวมตัวระหว่าง สารประกอบ 1, 2, tatbtc4a และ tatbc4a กับคาร์บอซาเลต พบว่าเกิดพันธะไฮโดรเจนแบบหลายจุด ค่าเทอร์โมไดนามิกของการรวมตัวของสารประกอบเชิงซ้อน ค่าพลังงานการปรับโครงสร้าง และพลังงานการเกิดสารประกอบเชิงซ้อนได้รับการคำนวณ ค่าสัมประสิทธิ์การเลือกเฉพาะของโฮสต์ tatbtc4a และ tatbc4a ต่อไอออนมาโลเนต เทียบกับ อ๊อกซาเลต $K_{malonate}^{oxalate}$ เท่ากับ 9.90 x 10^2 and 1.09 x 10^2 ตามลำดับ