Conformational and energetical structures of sulfonylcalix[4] arene, p-tert-butylsulfonylcalix[4]arene and their zinc complexes

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Abstract

The p-tert-butylsulfonylcalix[4]arene and sulfonylcalix[4]arene conformers have been obtained by AMI 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 thincalix[4]arene. The conformational energies of p-tertbutylsulfonylcalix[4]arene have been compared with the energies of sulfonylcalix[4]arene, and p-tert-butylsulfonylcalix[4]arene. The most stable conformer of sulfonylcalix[4]arene and p-tertbutylsulfonylcalix[4]arene are 1,2-alternate and 0011-AAAA 1,2alternate 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 conformers and their complexes with zinc(III) have been computed at HF/6-31G* and B3LYP/6-31G* theoretical levels. The optimized structures of complex species of p-tert-butylsulfonylcalix[4]arene with zinc(III) is in good agreement with recent x-ray geometry data.

Introduction

Ability of recognition or selectivity of molecular systems with other molecules is very important role in host-guest chemistry. Calix[4]arena is one of the well known members of the calix[h]arena family. Calix[4]arenes have four characteristic conformations known as cone, partial cone, 1,2-alternate and 1,3-alternate conformers. 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 Fig. 1. Due to a special ability of calix[4]arene structures to include transition metal cations and neutral molecule leading to useful applications, the sulfonylcalix[4]arene structures should have also special ability to form complexes with some cations.

In the present work, we have determined the structures, conformations and energies of sulfonylealix[4]arene, p-tertbutylsulfonylealix[4]arene and their zinc complexes by theoretical approach. The main purposes of this work are to determine the sulfonylealix[4]arene and p-tert-butylsulfonylealix[4]arene conformers, their structural information, energies of their interconversion and complexation with zinc(II) in comparison with the x-ray crystallographic structure.



Fig. 1 Calix[4]arenes specified by substituted R, R' and X groups.

Methods

The conformers of sulfonylcalix[4]arene (LH4) and p-tertbutylsulfonylcalix[4] arene (L'H4) were searched using PES mode with AMI method. The energies of the conformations were obtained with the rms value of energies gradient less than 0.001 kcal/mol. The structures of complex species of sulfonylcalix[4]arene and p-tertbutylsulfonylcalix[4] arene with Zn(II) and all related species were optimized by semi-empirical AMI method. The energies of AMIoptimized structures were computed by single point HF/6-31G* and B3LYP/6-31G* methods. Four typical conformers of the sulfonylcalix[4]arene nolecule as cone, partial cone, 1,2-alternate and 1,3-alternate are firstly generated using standard geometry parameters and optimized using semi-empirical AMI method. All conformations of p-tert-butylsulfonylcalix[4]arene have been defined by a methyl group in tert-butyl group attached to each aromatic ring pointing against aromatic hydroxyl group as type A and an another one pointing against aromatic hydroxyl group as type A and an another one pointing against aromatic hydroxyl group as type A and an domward aromatic hydroxyl groups are defined as the number 1 and 0, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers ser, therefore, denoted as four digits : 0000, 0001, 0011 and 10101, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers are, therefore, denoted as four digits : 0000, 0001, 0011 and 10101, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers are, therefore, denoted as four digits : 0000, 0001, 0011 and 10101, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers are, therefore, denoted as four digits : 0000, 0001, 0011 and 10101, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers are, therefore, denoted as four digits : 0000, 0001, 0011 and 10101, respectively (cone, partial cone, 1,2-alternate and 1,3-alternate conformers are, therefore, denoted as four digits : 0000, 0001, 0011 and 10101,

Results and discussion

Determination of the four sulfonylealix[4]arene conformers, cone, partial cone, 1,2-alternate and 1,3-alternate have been carried out by the AM1 geometry optimizations (Fig. 2). Hydrogen bonding presented in sulfonylealix[4]arene (a) cone, (b) partial cone, (c) 1,2-alternate and (d) 1,3-alternate conformers are shown in Fig.3. 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. 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* S10* [12] by 8.6 kcal/mole. Stabilities of the sulfonylcalix[4]arene conformers are in the order : 1,2-alternate > [1,2-alternate > cone> partial cone and the most stable conformer of sulfonylcalix[4]arene, n,2-alternate, is different from the thiacalix[4]arene and calix[4]arene conformers of which cone conformers are the most stable species.



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







Fig. 4. 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



Fig. 5. Structures of p-tert-butylsulfonylcalix[4]arene as (a) LH2²⁻, (b) (LH2)Zn and (c) (LH2)Zn(tacn) species. Structures above and below are the molecular top and side views.



We found that all the sulfonylcalix[4]arene conformers are able to form stable complexes with zinc(II) ion, except the 1,3alternateconformer. The zinc complex with deprotonated sulfonylcalix[4]arene cone conformer, LH2(cone)Zn, is the most stable complex. The energy differences between the sulfonylcalix[4]arene cone and 1,2-alternate conformers, AEq6form.(LH4) and between the deprotonated and neutral forms of sulfonylcalix[4]arene cone conformers, AEq6prot.(LH2) are 8.2 and 710.3 kcal/mole at B3LYP/6-316⁴ energy/devel, respectively (Table 1). The energy of complexation between the depronated sulfonylcalix[4]arene 1,2-alternate conformer and Zn(II), AE_{complex}(LH2/Zn), is -632.21 kcal/mole as shown in Table 1. 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 tret-butyl groups in 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 are shown in Fig. 4.

The reaction pathway of complexation between the deprotonated form of p-tert-butylsulfonylcalix[4]aren cone conformer, L'H2²⁻ (cone) and zinc(II) ion is proposed as shown in Scheme I. The structures of ptert-butylsulfonylcalix[4]arene as deprotonated form L'H2²⁻, (L'H2)Zn and (L'H2)Zn(tacn) complex species as shown in Fig. 5 are 6000-AABB cone conformers. According to the x-ray crystallographic structure of synthesized (L'H2)Zn(tacn) crystalline, the complex of p-tert-butylsulfonylcalix[4]arene cone conformer with inc(II) included by the tetracyclononane (tacn) is therefore proposed in the complexation process as shown in Scheme 1.



Fig. 6. 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.

Table 1. Total energies, ΔE_{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	ΔE_{total}^{b}	Reaction energies c		
sulfonylcalix[4]arene				
LH ₄ (1,2-alternate)	-3419.236519		-	
LH4(cone)	-3419.223378	ΔE_{deform}	=	8.25
LH2 ²⁻	-3418.091383	ΔE_{deprot}	=	710.34
LH2 2- (preorg.)	-3418.039473	ΔE_{preorg}	=	32.54
Zn ²⁺	-1778.107014	1.0	-	
(LH ₂)Zn	-5197.153976	$\Delta E_{complex}$	=	-632.21
p-tert-butylsulfonylcalix[4]arene L'H4 (0011-AAAA) ^d	-4048.231842			
L'H4 (0000-ABAB) °	-4048.230935	ΔE deform	=	0.57
L'H4 (0000-AABB) f	-4048.229697	ΔE _{nerorg}	=	0.78
L'H2 ²⁻	-4047.094992	ΔE deprot.	=	712.04
L'H2 2- (preorg.1)	-4047.018237	ΔE' preorg.	=	48.16
(L'H ₂)Zn	-5807.005983	ΔE complex	=	-648.62
tacn 8	-398.208416			
(L'H ₂)Zn(tacn) ^h	-6206.957330	$\Delta E_{inclusion}$	=	-101.56
L'H2 ²⁻ (preorg.2)	-4047.072376	ΔE" preorg.	=	14.19
Zn(tacn)2+	-2176.255587	1.0	-	
(L'H2)Zn(tacn) h	-6206.957330	$\Delta E'_{complex}$	=	-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 tetrazazychoomane. ^h the same structures

Conclusions

The structures of sulfonylcalix[4]arene and p-tertbutylsulfonylcalix[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, sixteen for partial cone, seven for 1,2-alternate and three for 1,3alternate 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 sulfonylealix[4]arene or p-tertbutylsulfonyl 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.

References

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