

DFT Study of Hydrogen Bonding on Calix[8]arene as Nanostructure Compound

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ABSTRACT

An azobenzene bridge was introduced into the lower (or smaller) rim of p-tert-butylcalix[8]arene to form 1,5-singly bridged calix[8]arene derivatives, respectively. Bridged calix[8]arene of conformationally rigid were isolated. The stability of the two structures of bridged calix[8]arenes have been compared. The study of organic structure to form nanoporous structures is a well known in chemistry phenomena to finding crystal structure of calix[8]arene as supramolecular chemistry. The effect of hydrogen bonding on calix[8]arene was reported at Density Functional Theory by Gaussian 98 of program package. The self assembled nanotubes in solid state through network hydrogen bonds between the chains of this structure were investigated.

Keywords: Calix[8]arene; DFT; HF; Hydrogen bonding; Nanostructure

INTRODUCTION

Porous materials are Crystalline or amorphous solids that permit the inclusion of small molecules through holes in their structures. Structural chemists and materials scientists have been interested in building these formworks not only to understand their design principles [1-5] but also because of their diverse commercial applications [6,7] chemical separation, asymmetric synthesis, selective catalysis, data storage, optical lasers. The investigation of the hydrogen bonding has attracted considerable attention over the year.

Much research has been done examining hydrogen bonding by studying weakly bound complexes hydrogen bonding belongs to the important weak interactions in nature being intimately involved in the structure and properties of water in its various phases, in large molecules such as proteins, nucleic acids and calix[8]arenes. Most hydrogen bonds are of YH...H type, where Y is an electronegative atom having one or more lone electron pairs or a raising of excess electron density like atomic π -system [4]. In addition to these well-known type of HB, other characteristic, although weaker, interaction may appear between C-H

hydrogen and an X acceptor [9,10] the C-H...X interaction follow the properties of the more conventional YH...X ones, although to a lesser degree. The most common structural and spectroscopic changes such as the lengthening of the Y-H bond and the red-shift in the YH stretching frequency have been observed in most CH...X systems [9] the calixarenes which present the advantage of both crown ethers and cyclodextrins [11-13] are macro cyclic products of phenol, formaldehyde condensations. They offer different sizes on plat forms for a wide choice of chemical modifications at the upper or lower rims. Different substituted functional groups at the both rims form different properties of calixarenes subsequently, different applications. As a result, calixarenes have been widely applied in ionic and molecular recognition [14 - 16] during the last two decades.

About the hydrogen bonding properties of calixarenes, we would like to pay our attentions

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on hydrogen bonding properties of calix[8]arene by density functional theory methods .

Recently density functional theory (DFT) has been accepted by the quantum chemistry community as a cost-effective approach for the computation of molecular structure, vibration frequencies, and energies of chemical reactions. Many studies have shown that molecular structures and vibration frequencies calculated by DFT methods are more reliable than MP2 methods [17-19]. While there is sufficient evidence that DFT provides an accurate description of the electronic and structural properties of solids, interfaces and small molecules, relatively little is known about the symmetric performance of DFT applications to molecular associates. To further assess the reliability of DFT methods applied to this field of chemistry. In this paper we discuss the structure and bonding of the calix[8]arene as obtained by high level ab initio calculations. The role of basis set size and basis set superposition effects are analyzed in detail. The stable new and in fact it has been obtained previously by explicit calculations. However, in the present paper, we put forward what we believe are now the most accurate result for the hydrogen bond. In calix[8]arene molecule, as obtained from high-level calculations and systematic analysis of the theoretical result obtained.

MATERIALS AND METHODS

The geometry optimization of the calix[8]arene has been carried out using the GAUSSIAN 98 programs package [20] at the HF level and 6-31G, 3-21G and STO-3G basis sets. For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis set. In order to confirm the superiority of the DFT methods, we simultaneously adopted HF method at the 6-31G, 3-21and STO-3G basis set along with analytic vibration frequency calculations.

The popular hybrid density functional B3LYP method, namely Beck's [21] three – parameter non- local exchange functional with the non-local correlation functional of Lee et al [22] .

RESULT AND DISCUSSION

As shown in Fig. 1 types bond interactions: H...O and H...N are compared by HF methods differed between two structure of calix[8]arene consist of oxygen and nitrogen bridge, selected computed data, bond distance, is compiled in Table 1. To assess the quality of the theoretical data, experimental geometrical parameters available for calix[8]arene. From the differences in the physical meaning of the computed and experimental result the theoretical results are in good agreement with experimental geometries.

Table 1. Selected bond distance of calix[8]arene at HF/6-31 level (Distance in $^{\circ}\text{A}$)

Parameters	Y		
	H	N	O
Computational $r_{\text{C-Y}}$	1.108	1.355	1.202
Experimental $r_{\text{C-Y}}$	1.108	1.338	1.206

*Note: The experimental data were taken from the following reference: [4]

In the compound, the frequency of C-H stretch is decreasing from 3092 to 3041 cm^{-1} , which indicates the increasing acidity of the C-H hydrogen from CH...N to CH...O. This phenomenon may be attributed to the induce effect of the electronegative element. In addition, the charge distribution in this compound is of primary importance from the point of view of the CH...Y [4].

We found two stable structures of the calix[8]arene which are shown in fig.1. Taking

the calculated result of the first structure compared with the geometries of the another structure, it can be found that the second structure formation induces a small stretch of the N-N bond a very small contraction of the C-N bond. Other bond lengths involved in the hydrogen bonding slightly lengthen. First structure exhibits a cyclic conformation, N accepting a proton forms and H denoting a proton to C.

In second structure O accepting a proton from C and H donating a proton to C. Furthermore, the linearity being 78.0 for the CH...N hydrogen bond and 78.0 for the CH...O at HF level and 6-31G. Actually, the two structures are similar to

each other, while in second structure, the two planes of the calix[8]arene nearly parallel to each other. Surveying the calculated results, the interaction energy of structure *I* is more than structure *II*.

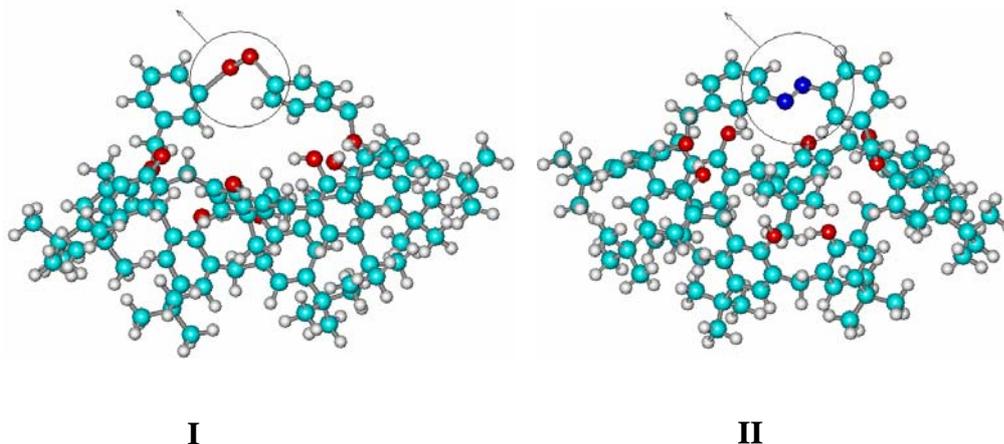


Fig. 1. The optimized geometries structures of calix[8]arene.

Since the optimized geometries of calix[8]arene are similar to each other from structure *I* to structure *II*, we do not analysis the calix[8]arene for simplicity. Finally, a few additional points are worth mentioning concerning the structure of compounds. It is interesting to note that the optimized geometries of calix[8]arene are similar to other types of hydrogen bonding interactions: H...O and H...N. Interaction energies are calculated by taking the energy differed between the structures.

To analysis in more detail the role of methods effects on the binding energy between to structures, we use Table 2, which gives a detailed analysis of the binding energy obtained with tree methods.

Table 2. Binding energies of the calix[8] arene (kJ/mol)

Basis sets	Str. I	Str. II
6-31G	9.1 (8.1)	9.2 (8.9)
3-21G	15.5 (7.1)	10.8 (8.4)
STO-3G	10.2 (9.6)	10.7 (11.1)

As expected method sensitivity exists, the interaction energy computed with 3-21G is much higher. However, for 3-21G method at this basis

set level, the basis set superposition error (BSSE) correction is larger than that of 6-31G and STO-3G (the numbers shown in parenthesis). The relative stability order of the structures of calix[8]arene is in good agreement with the experimental calculations.

Vibration spectroscopy is one of the most useful experimental tools for study of the H-bonded compound, so the information on calculated harmonic vibrational frequencies can be useful. In table3, we give the HF level and 6-31G, 3-21G and STO-3G basis sets values for both vibration frequencies and IR intensities of the complexes.

Since the frequency shifts are relatively stable with respect to theoretical methods, one can estimate the IR spectrum for the compound by combining the observed fundamental vibration frequency of its moieties and the frequency shift in table 3 .The C-H stretching frequency shows a slight change in its value on hydrogen bonding .This structure have large intensities and predicted IR spectral characteristics might be of great interest in the analysis of the experimental spectral features. It is considering more difficult to predict accurate shifts in absorption intensities, which is unfortunate. For in this system, there is an extremely large increase in

the intensity of the stretching vibration of the hydrogen donor.

Table 3. Vibrational Frequencies (ν) and IR intensities (I) of calix[8]aren at HF/6-31g

Structure	Hydrogen bonding	$\nu(\text{cm}^{-1})$	I (km/mol)
Str. I	CH	2895	23
Str. II	CH	1261	14

CONCLUSION

The hydrogen bond interaction in structure *I* has been analyzed by ab initio, HF method employing different basis set levels.

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