

Full Length Research Paper

Computational study of hydrogen bonding on calix[8]arene as nanostructure compound

Monajjemi M.¹, Sayadian M.², Zare K.¹, Ilkhani A. R.³ and F. Mollaamin^{1*}

¹Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.

²Ph.D student, Science and Research Branch, Islamic Azad University, Tehran, Iran.

³Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran.

Accepted 2 March, 2011

The study of organic structure to form nanoporous structures is well known in chemistry phenomena to finding crystal structure of calix[8]arene as supra molecular chemistry. The effect of hydrogen bonding on calix[8]arene was reported at Hartree Fock by Gaussian 98 program package. The self assembled nanotubes in solid state through network hydrogen bonds between the chains of this structure were investigated.

Key words: Calix [8]arene, 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 (Nangia, 2001; Bong et al., 2001; Hosseini and De Cian, 1998; Baldini et al., 2002; Mac Gillivery and Atwood, 1999) but also because of their diverse commercial applications (Langley and Hulliger, 1999; Barton et al., 1999), chemical separation, asymmetric synthesis, selective catalysis, dates storage, optical lasers. The investigation of the hydrogen bonding has attracted considerable attention over the years. Much research has been done in 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 raging of excess electron density like atomic π -system (Baldini et al., 2002). In addition to these well-known types of HB, other characteristic, although weaker, interaction may appear between C-H hydrogen and an X acceptor (Monajjemi et al., 2008, 2006). The CH...X interaction

follows 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 Y-H stretching frequency have been observed in most CH...X systems (Monajjemi et al., 2008). The calixarenes which present the advantage of both crown ethers, and cyclodextrins (Hu et al., 2000; Baur et al., 2001; Takaya et al., 2003) are macro cyclic products of phenol, formaldehyde condensations. They offer different sizes on platforms 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 and subsequently, different applications. As a result, calixarenes have been widely applied in ionic and molecular recognition (Pailleret and Arrigan, 2001; Schatz and Schildbach, 1998; Mislin et al., 1999; Monajjemi and Chahkandi, 2004) during the last two decades. About the hydrogen bonding properties of calixarenes, we would like to pay our attentions on hydrogen bonding properties of calix[8]arene by density functional theory methods .

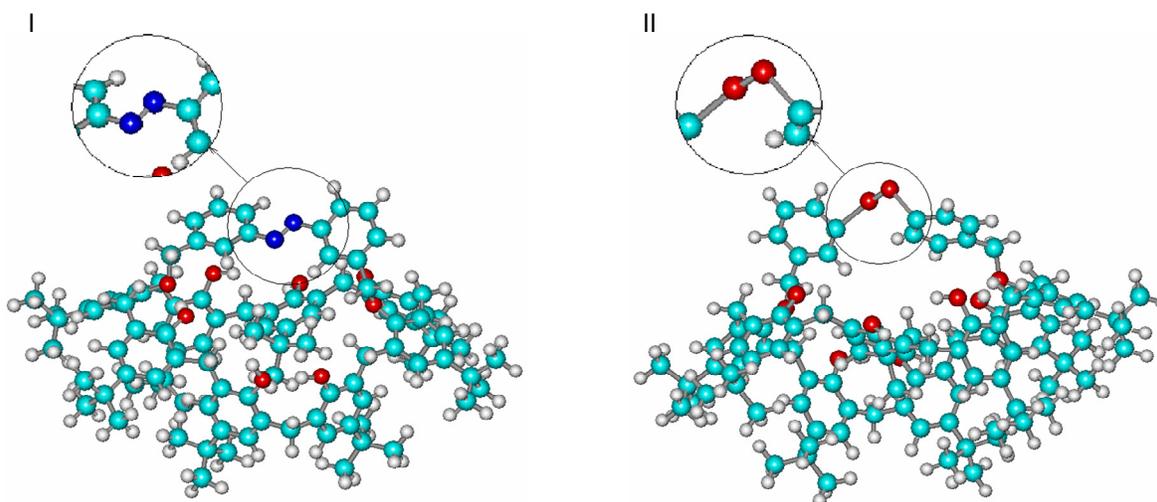
Recently, density functional theory (DFT) has been accepted by the quantum chemistry community as a cost-effective approach for the computation of molecular structure, vibration frequencies, and energies of chemical reactions. Many studies have shown that molecular structures and vibration frequencies calculated by DFT methods are more reliable than MP2 methods (Monajjemi and Chahkandi, 2004; Monajjemi et al., 2007). While there

*Corresponding author. E-mail: smollaamin@gmail.com.

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

Parameter	Y		
	H	N	O
Computed $^{\text{R}}\text{C-Y}$	1.108	1.355	1.202
Experimental $^{\text{R}}\text{C-Y}$	1.108	1.338	1.206

*Note: The experimental data were taken from Baldini et al. (2002).

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

is sufficient evidence that DFT provides 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 access 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 is 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 bound in calix[8]arene molecule, as obtained from high- level calculations and systematic analysis of the theoretical result obtained (Monajjemi et al., 2008).

MATERIALS AND METHODS

The geometry optimization of the calix[8]arene has been carried out using the GAUSSIAN 98 programs package (Meng et al., 2005; Zhou and Liu 1997; Aiping et al., 2003; Monajjemi et al., 2010) 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, 3-21G and STO-3G basis set along with analytic vibration frequency calculations (Becke and Cheill, 1993). Our computational model consists of geometries for calix[8]arene that were fully optimized by restricted Hartree Fock (RHF) with STO-3G, 3-21G and 6-31G levels (Monajjemi et al., 2010).

RESULTS AND DISCUSSION

Selected computed data and bond distance, is compiled in Table 1. To assess the quality of the theoretical data, experimental geometrical parameters were available for calyx [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. In the compound, the 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 induced 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. We found two stable structures of the calix[8]arene which are shown in Figure 1. Taking the calculated result of the first structure compared with the geometries of the other

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

Basis sets	Structure I	Structure 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)

Table 3. Vibrational frequencies (ν) and IR intensities (I) of calix[8]arene at HF/6-31G.

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

structure, it can be found that the second structure formation induces a small elongation of the N-N bond by a very small contraction of the C-N bond. Other bond lengths involved in the hydrogen bonding slightly lengthens. The first structure exhibits a cyclic conformation, N, accepting a proton forms and H, denoting a proton to C. In the second structure, O is 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 the second structure, the two planes of the calix[8]arene are nearly parallel to each other. Surveying the calculated results, the interaction energy of structure I is more than structure II. Since the optimized geometries of calix[8]arene are similar to each other from structure I to structure II, we do not analyze 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 each other. Types of hydrogen bonding interactions: H...O and H...N, and the interaction energies are calculated by taking the energy differed between the structures.

To analyze in more details, the role of methods effects on the binding energy between the structures, we use Table 2, which gives a detailed analysis of the binding energy obtained with three methods. As expected, method sensitivity exists and 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 Table 3, 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 has large intensities and predicted IR spectral characteristics might be of great interest in the analysis of the experimental spectral features. It is considered more difficult to predict accurate shifts in absorption intensities, which is unfortunate. For this system, there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor.

Conclusion

The hydrogen bond interaction in structure I and II have been analyzed by ab initio, HF method employing different basis set levels. Two stable structures are considered. Of which, structure I is more stable than the other structure and their stabilities depend on the values of the interactions between CH...N and CH...O. Moreover, the infrared spectrum frequencies, IR intensities and the vibrational frequency shifts have been investigated and we found that the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the two structures and there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor.

REFERENCES

- Aiping F, Dongmei D, Zhengyu Z (2003). Density functional theory study of vibrational spectra of acridine and phenazine. *Spectrochimica Acta Part A*. 59: 245-/253.
- Baldini L, Sansone F, Casnati A, Ugozzoli F, Ungaro R (2002). Peptidocalix[4]arene self-assembled nanotubes. *J. Upram. Chem.*, 2: 219-226.

- Barton TJ, Bull LM, Klemperer WG, Loy DA, McEnaney B, Misono M, Monson PA, Pez G, Scherer GW, Vartuli JC, Yaghi OM (1999). Tailored porous materials. *Chem. Mater.*, 11:2633-56.
- Baur M, Frank M, Schatz J, Schildbach F (2001). Water-soluble calix[n]arene as receptor molecules for non-polar substrates and inverse phase-transfer catalyst. *Tetrahedron*, 57: 6985.
- Becke AD, Cheill J (1993). Density-functional thermochemistry. III. The role of exact exchange. *Phys.*, 98: 5648.
- Bong DT, Clark TD, Granja JR, Ghadiri MR (2001). Self-assembling organic nanotubes. *Angew. Chem. Int. Ed.*, 40: 988-1011.
- Hosseini MW, De Cian A (1998). Molecular Tectonics: An Approach to Organic Networks. *Chem. Commun.*, 3: 727-733.
- Hu S, Xu C, He Y, Meng L, Cui D (2000). Electrocatalytic reduction of dioxygen at the surface of glassy carbon electrodes modified by calix[6]arene-methyl viologen. *Microchem. J.*, 65: 311.
- Langley PJ, Hulliger J (1999). Nanoporous and mesoporous organic structures: new openings for materials research. *Chem. Soc. Rev.*, 28: 279-91.
- Mac Gillivery LR, Atwood JL (1999). Structural classification and general principles for the design of spherical molecular hosts. *Angew. Chem. Int. Ed.*, 38: 1018-77.
- Meng Y, Zhou Z, Duan C, Wang B, Zhong Q (2005). Non-conventional hydrogen bonding interaction of BH₃NH₃ complexes: a comparative theoretical study. *J. Molecular Struct. THEOCHEM*. 713: 135-144.
- Mislin G, Graf E, Hosseini MW, Cian A De, Fischer J (1999). Tetrasubstituted calix[4]arenes: Synthesis and Solid State Structural Analysis. *Tetrahedron Lett.*, 40:1129-1132.
- Monajjemi M, Saedi L, Najafi F, Mollaamin F (2010). Physical properties of active site of tubulin-binding as anticancer nanotechnology investigation. *Int. J. Phys. Sci.*, 5(10): 1609-1621.
- Monajjemi M, Chahkandi B (2004). Study of the hydrogen bond in different orientations of adenine-thymine base pairs: an ab initio study. *J. Mol. Struct. (THEOCHEM)*, 714: 43.
- Monajjemi M, Chahkandi B, Zare K, Amiri A (2005). Study of the Hydrogen Bond in Different Orientations of Adenine-Thymine Base Pairs: an ab initio Study. *Biochemistry (Moscow)*, 70(3): 366 - 376.
- Monajjemi M, Heshmat M, Aghaei H, Ahmadi R, Zare K (2007). Solvent effect on ¹⁴N NMR shielding of glycine, serine, leucine, and threonine: comparison between chemical shifts and energy versus dielectric constant. *Bull. Chem. Soc. Ethiopia*. 21: 111-116.
- Monajjemi M, Ketabi S, Hashemian MZ, Amiri A (2006). Simulation of DNA Bases in Water: Comparison of the Monte Carlo Algorithm with Molecular Mechanics Force Fields. *Biochemistry (Moscow)*, 71: 1.
- Monajjemi M, Lee VS, Khaleghian M, Honarparvar B, Mollaamin F (2010). Theoretical Description of Electromagnetic Nonbonded Interactions of Radical, Cationic, and Anionic NH₂ BHNBNH₂ Inside of the B₁₈N₁₈ Nanoring. *J. Phys. Chem. C.*, 114: 15315-15330.
- Monajjemi M, Mahdavian L, Mollaamin F (2008). Characterization of nanocrystalline silicon germanium film and nanotube in adsorption gas by monte carlo and langevin dynamic simulation. *Bull. Chem. Soc. Ethiop.*, 22: 1-10.
- Monajjemi M, Rajaeian E, Mollaamin F, Naderi F, Saki S (2008). Investigation of NMR shielding tensors in 1,3 dipolar cycloadditions: solvents dielectric effect. *J. Phys. Chem. Liquids*. 46(3): 299-306.
- Nangia A (2001). Organic nanoporous structures. *Current Opinion in Solid State Mat. Sci.*, 5: 115-122.
- Pailleret A, Arrigan DWM (2001). Electrochemical oxidation of a tetraester calix[4]arene. *Elect. Commun.*, 3: 24.
- Schatz J, Schildbach F (1998). Thermal Gravimetry, Mass Spectrometry, and Solid State ¹³C NMR Spectroscopy - Simple and Efficient Methods to Characterise the Inclusion Behaviour of p-tert-Butylcalix[n]arenes. *J. Chem. Soc. Perkin Trans.*, 2:75.
- Takaya M, Buhlmann P, Umezawa Y (2003). Ion-Channel - Mimetic Sensors Based on Self-Assembled Monolayers of Phosphate Esters: High Selectivity for Trivalent Cations. *Micro. Acta.*, 132: 55-60.
- Zhou XF, Liu RF (1997). Density functional theory study of vibrational spectra. 6: assignment of fundamental vibrational frequencies of propene isomers: Dewar benzene, benzvalene, trimethylenecyclopropane, prismane, and 3,4-dimethylenecyclobutene. *Spectrochim. Acta Part A*. 53:259.