



Investigation of Basis set Effects on the NMR Chemical Shielding Tensors Data on (10, 10) SWCNTs Calixarene Complexes

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<http://dx.doi.org/10.13005/ojc/310465>

(Received: August 17, 2015; Accepted: September 23, 2015)

ABSTRACT

Density functional theory calculations (DFT), as well as hybrid methods (B3LYP) and HF method for CNT-Calixarene complexes have been carried out to study structural stability. The geometry of the Calixarene has been optimized at DFT methods such as M062x B3LYP and HF methods with 6-31G, 6-31G* and 6-31G** basis sets. According to GIAO method, NMR parameters have been evaluated. The Gaussian quantum chemical package is used for all calculations. The gauge including atomic orbital (GIAO) approach was applied for chemical shielding calculations for an isolated calix aren and a complex of Calix-SWCNTs.

Key words: Calixarene, CNT

INTRODUCTION

Calixarenes are macrocyclic vases which are easily available through the cyclocondensation of Para substituted phenols with formaldehyde. Calixarenes are widely used as molecular platforms for the construction of specific receptors capable of highly selective recognition between fairly similar substrates. Apparently, the outstanding receptor properties of functional Calixarenes make them highly promising materials for sensor technology, radioactive waste management, pharmaceutical science, and analytical application¹⁻⁴.

Calixarene and their analogs can be applied as a basic skeleton for molecular device units in molecular nanotechnology^{1,2}. The larger Calixarene are more flexible than the smaller ones and are conformational dynamic. Smaller oligomers, such as calix⁴ arenes, are relatively rigid and conformational stable, although the dynamics are affected in all cases by substituents. In this work, we report angle and bonding properties, structural stability of the Calixarene and basis set effects have been calculated.

A Calixarene is a macrocycle based on a hydroxy-alkylation product of a phenol and an

aldehyde^{3,4}. Calixarene are characterized by a three-dimensional basket, cup or bucket shape. In calixarene the internal volume is around 10 cubic nanometers. Calixarene are characterized by a wide upper rim and a narrow lower rim and a central annulus. With phenol as a starting material the 4 hydroxyl groups are intra mural on the lower rim. Calixarene exist in different chemical conformations because rotation around the methylene bridge is not difficult. One of the characteristic properties of Calixarene is a conformational variety. For example, calyx⁴ arenes can assume four types of conformations, namely, cone, partial-cone, 1,3-alternate, and 1,2-alternate; 1,3-alternate isomers of calyx [4]arenes derivatives can then be used for a heterobimolecular complexation³. By using their conformational variety and design possibilities,. For further structural information, NMR parameters and vibrational frequencies calculations have been reported to explore the ability of the system. All computations were done using the Gaussian 98 software.

The carbon nanotube (CNT) is a representative nano-material. CNT is a cylindrically shaped carbon material with a nano-metric-level diameter⁵⁻¹⁵.

SWCNTs have considered as the leading candidate for nano-device applications because of their one-dimensional electronic bond structure, molecular size, and biocompatibility, controllable property of conducting electrical current and reversible response to biological reagents hence SWCNTs make possible bonding to polymers and biological systems such as DNA and carbohydrates¹²⁻³⁵.

Although it is a commonplace material using in pencil leads, its unique structure causes it to present characteristics that had not found with any other materials. CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite²²⁻⁴².

Its structure, which is in the form of a hexagonal mesh, resembles a graphite sheet and it carries a carbon atom located on the vertex of each mesh. The sheet has rolled and its two edges

have connected seamlessly³²⁻⁵⁰.

The type attracting most attention is the single-wall CNT, which has a diameter deserving the name of "nanotube" of 0.4 to 2 nanometers. The length is usually in the order of microns, but single-wall CNT with a length in the order of centimeters has recently released⁴²⁻⁵⁹.

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The length is usually in the order of microns, but single-wall CNT with a length about centimeters have recently released. The extremities of the CNT have usually closed with lids of the graphite sheet⁷¹⁻⁸¹.

The lids consist of hexagonal crystalline structures (six-membered ring structures) and a total of six pentagonal structures (five-membered ring structures) placed here and there in the hexagonal structure⁷⁹⁻⁹⁵. The first report by Iijima was on the multiwall form, coaxial carbon cylinders with a few tens of nanometers in outer diameter. Two years later single walled nanotubes were reported.

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In the NBO analysis, the interaction arising from electron delocalization are analyzed by selecting a number of natural bonding and anti-bonding orbitals that distort from the idealized Lewis structure, caused by interactions among them through hyper-conjugative or electrostatic interactions. In NBO analysis, the input atomic orbital basis set is transformed via natural atomic orbitals

(NAOs) and natural hybrid orbital (NHOs) into NBO. In the present theoretical study, particular attention has been paid to the structural properties of The Si6O12-CNTs and Si7O14-CNTs systems. So, the NBO analysis gives supplementary information of the relative structural properties. It should be noted that conjugated systems, such as benzene and p-conjugated linear molecules, have been well studied with NBO analysis.

Computational details

The geometry of the Calixarene have been optimized by Becke's hybrid three-parameter exchange functional and the non-local correlation functional of Lee, Yang and Parr (B3LYP) method [99,100] with 6-31G basis set and HF method with 6-31G, 6-31G* and 6-31G** basis sets. Using ab initio Gaussian quantum chemical package¹⁰¹. The term ab initio is given to calculations that are obtained exactly from theoretical principles, without adding any experimental data¹⁰². The most common category of ab initio calculation is called Hartree-Fock (HF), in which the initial approximation is called the mean field approximation. This means which the coulombic electron- electron repulsion is not clearly included; although, its average effect is contained in the calculations¹⁰¹. In computational chemistry, energy minimization or geometry optimization methods are used to compute the equilibrium configuration of molecules. Stable states of molecular systems correspond to global and local minima on their potential energy surface. The geometry will be adjusted until a stationary point on the potential surface is found. In addition, we have obtained dipole moments as the coefficients of a series expansion of a potential due to continuous or discrete sources such as an electric charge distribution. If we consider a molecule consisting of N particles with charges eZ_i , the particle i has spherical polar coordinates r_i , θ_i , and ϕ_i . The electrostatic dipole operator is:

$$Q_i^j = \sum_{i=1}^N eZ_i R_i^m(r_i) \quad \dots(1)$$

Where $R_i^m(r_i)$ is a regular solid harmonic function¹⁰³⁻¹⁰⁵.

Vibrational frequencies are computed by

determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. This transformation is only valid at a stationary point. Thus, it is meaningless to compute frequencies at any geometry other than a stationary point for the method used for frequency determination. Nuclear magnetic resonance (NMR) allows the observation of specific quantum mechanical magnetic properties of the atomic nucleus. NMR is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation. It might appear from the above that all nuclei of the same nuclide would resonate at the same frequency. This is not the case. The most important perturbation of the NMR frequency for applications of NMR is the shielding effect of the surrounding shells of electrons. Electrons, similar to the nucleus, are also charged and rotate with a spin to produce a magnetic field opposite to the magnetic field produced by the nucleus. In general, this electronic shielding reduces the magnetic field at the nucleus. As a result the energy gap is reduced, and the frequency required to achieve resonance is also reduced. This shift in the NMR frequency due to the electronic molecular orbital coupling to the external magnetic field is called chemical shift, and it explains why NMR is able to probe the chemical structure of molecules, which depends on the electron density distribution in the corresponding molecular orbitals. If a nucleus in a specific chemical group is shielded to a higher degree by a higher electron density of its surrounding molecular orbital, then its NMR frequency will be shifted upfield (that is, a lower chemical shift), whereas if it is less shielded by such surrounding electron density, then its NMR frequency will be shifted downfield (that is, a higher chemical shift). Unless the local symmetry of such molecular orbitals is very high (leading to isotropic shift), the shielding effect will depend on the orientation of the molecule with respect to the external field. In solid-state NMR spectroscopy, magic angle spinning is required to average out this orientation dependence in order to obtain values close to the average chemical shifts. This is unnecessary in conventional NMR investigations of molecules, since rapid "molecular tumbling" averages out the chemical shift anisotropy (CSA). In this case, the term "average" chemical shift (ACS)

is used. To study the structural stability and others properties in the Calixarene molecule, optimization, Vibrational frequencies and NMR calculations of Calixarene molecule have been evaluated with two methods and three basis sets to get a deeper insight about the respective parameters.

RESULT AND DISCUSSION

There are three types of QMC: variation, diffusion and Green's functions. These methods act with an openly correlated wave function and calculate integrals numerically utilizing a Monte Carlo integration. These calculations are very time consuming, but they are the most correct methods known to date. On the whole, ab initio calculations provide perfect quantitative results and can donate increasingly accurate quantitative results as the molecules under consideration become smaller. We selected low-energy structures found on each surface and exposed them to unrestrained quantum mechanical minimization using.

To evaluate the methods effects, we calculated the optimized energies of the Calixarene molecule at DFT-B3LYP and HF levels of theory with three levels including low (4-31g), medium(6-311g**) and high (ccpvtz) basis sets. So, to determination the effects of basis sets, we calculated the energies of the Calixarene molecule with this basis sets that the NMR data are given in Table 1 and 2. It can be seen from the Tables, that three basis sets in different levels have significant effects on the calculated parameters. The schema of Calixarene molecule has been shown in figure 1.

There are some methods for determination Ab initio NMR parameters such as Gauge-Including atomic orbitals (GIAO), Individual gauge for localized orbitals (IGLO), and Localized orbitals local origin (LORG) and Continuous set of gauge transformations (CSGT). According to GIAO method, NMR parameters of Calixarene molecule such as δ , ζ and α have been reported in Table1 and 2 and. The calculation of NMR parameters using ab initio techniques has become a major and powerful tool in the investigation to look at how variations in the molecular structure occur. The ability to quickly evaluate and correlate the magnitude and orientation of the chemical shielding anisotropy

tensor with variations in bond length, bond angles and local coordination has seen a number of recent applications in the investigation of molecular structure.

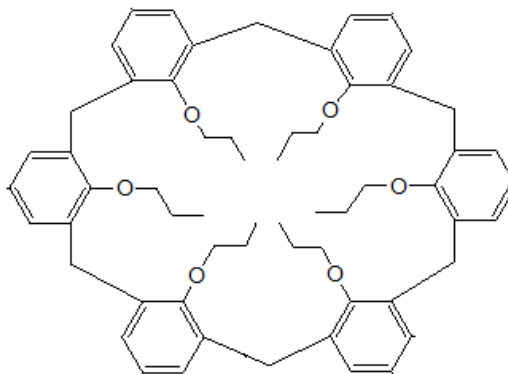


Fig. 1: Calixarene

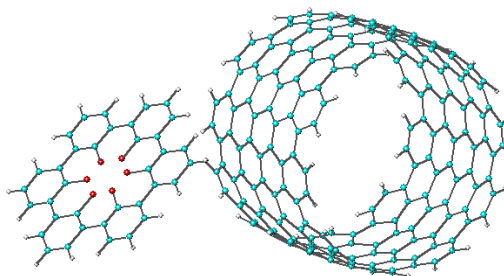


Fig. 2: Calix-(10,10)CNTs in b3lyp/6-311g**

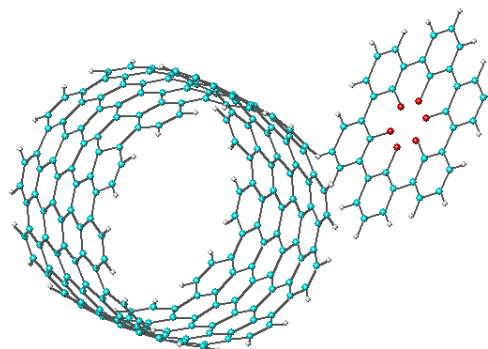


Fig. 3: Calix-(10,10)CNTs in HF/4-31g

Table 1: NMR chemical shielding tensors data of isolated Calixarene

Atom number	Methods																	
	B3LYP									HF								
	4-31g			6-311G*			ccpvtz			4-31g			6-311G**					
η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	
1	0.72	268.2	402.3	0.19	25.9	-118.2	0.75	295.6	443.4	0.68	272.4	408.6	0.68	272.5	408.8	0.68	272.5	408.8
2	0.72	268.2	402.3	0.501	154.1	154.1	0.75	295.6	443.4	0.68	272.4	408.6	0.68	272.5	408.8	0.68	272.5	408.8
3	0.51	85.6	128.5	0.55	122.5	122.5	0.70	107.0	160.5	0.69	101.2	151.9	0.69	101.3	152.0	0.69	101.3	152.0
4	0.59	80.6	121.0	0.13	126.7	126.7	-43.8	-94.02	-141.0	-41.9	-93.12	-139.6	-42.2	-93.5	-140.2	-42.2	-93.5	-140.2
5	0.45	107.4	161.2	0.22	93.7	93.79	0.57	87.7	131.6	0.56	74.9	112.4	0.61	75.9	113.9	0.61	75.9	113.9
6	0.59	80.6	121.0	0.57	100.2	100.2	-43.8	-94.0	-141.0	-41.9	-93.1	-139.6	-42.2	-93.5	-140.2	-42.2	-93.5	-140.2
7	0.59	80.68	121.0	0.46	123.0	-220.9	0.27	83.84	125.7	0.24	80.8	121.2	0.24	81.2	121.8	0.24	81.2	121.8
8	0.51	85.7	128.5	0.07	12.5	-112.3	0.70	107.0	160.5	0.69	101.2	151.9	0.69	101.3	152.0	0.69	101.3	152.0
9	0.83	83.17	124.7	0.16	23.754	-119.8	0.94	94.6	141.9	-43.7	-88.40	-132.6	-43.59	-89.15	-133.7	-43.59	-89.15	-133.7
10	0.51	85.6	128.5	0.28	35.7	-123.0	0.94	77.8	116.7	-34.8	-75.5	-113.3	-34.94	-75.78	-113.6	-34.94	-75.78	-113.6
11	0.83	83.18	124.7	0.17	47.9	-237.9	-32.7	-84.4	-126.7	-27.3	-78.3	-117.5	-27.09	-79.2	-118.9	-27.09	-79.2	-118.9
12	0.83	83.1	124.7	0.05	11.3	-113.7	-32.7	-84.4	-126.7	-27.3	-78.3	-117.5	-27.0	-79.2	-118.9	-27.0	-79.2	-118.9
13	0.45	107.4	161.2	0.29	35.5	-120.8	0.54	129.1	193.7	0.57	119.1	178.7	0.60	119.8	179.7	0.60	119.8	179.7
14	0.59	80.67	121.0	0.27	73.3	-249.2	0.27	83.8	125.7	0.24	80.809	121.2	0.24	81.2	121.8	0.24	81.2	121.8
15	0.83	83.18	124.7	0.17	24.5	-119.6	0.94	94.63	141.9	-43.7	-88.4	-132.6	-43.5	-89.15	-133.7	-43.5	-89.15	-133.7

Table 2: NMR chemical shielding tensors data of Calixarene in binding to SWCNNTS

Atom number	Methods																	
	B3LYP									HF								
	4-31g			6-311G*			ccpvtz			4-31g			6-311G**					
η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	η	δ	$\Delta\sigma$	
1	0.32	145.8	145.8	0.34	75.5	145.5	0.79	159.7	443.4	0.68	272.4	-16.9	0.74	272.5	18.3			
2	0.48	155.1	155.1	0.48	73.6	155.3	0.23	153.9	443.4	0.68	272.4	-39.6	0.17	272.5	22.9			
3	0.65	133.6	133.6	0.63	90.4	134.9	0.37	149.7	160.5	0.69	101.2	-26.1	0.31	101.3	26.1			
4	0.48	119.3	119.3	0.48	81.2	119.0	0.24	148.9	-141.0	-41.9	-93.12	-23.7	0.37	-93.5	14.2			
5	0.14	96.5	96.5	0.14	63.4	96.20	0.72	46.8	131.6	0.56	74.9	-142.0	0.73	75.9	163.4			
6	0.48	99.1	99.1	0.48	66.4	98.4	0.82	50.8	-141.0	-41.9	-93.1	-125.1	0.83	-93.5	114.2			
7	0.06	12.1	-114.2	0.97	157.4	-64.1	0.87	65.7	125.7	0.24	80.8	-127.8	0.86	81.2	137.7			
8	0.06	11.9	-112.7	0.99	160.7	-62.7	0.87	51.4	160.5	0.69	101.2	-134.4	0.86	101.3	124.4			
9	0.20	26.5	-117.8	0.41	151.8	126.1	0.57	163.2	141.9	-43.7	-88.40	-10.5	0.48	-89.15	13.9			
10	0.28	36.5	-124.2	0.29	119.4	136.2	0.14	159.8	116.7	-34.8	-75.5	-7.82	0.23	-75.78	14.6			
11	0.17	50.0	-240.5	0.65	245.6	248.5	0.70	119.1	-126.7	-27.3	-78.3	-17.3	0.75	-79.2	25.0			
12	0.18	88.7	-226.0	0.17	251.1	237.0	0.24	64.0	-126.7	-27.3	-78.3	-19.8	0.71	-79.2	29.5			
13	0.29	34.9	-120.0	0.18	122.4	135.0	0.19	63.3	193.7	0.57	119.1	-15.8	0.89	119.8	8.7			
14	0.25	67.2	-245.5	0.32	292.3	273.2	0.88	139.0	125.7	0.24	80.809	-43.7	0.23	81.2	32.0			
15	0.09	18.4	-120.2	0.55	144.5	125.3	0.88	62.7	141.9	-43.7	-88.4	-14.4	0.19	-89.15	26.0			

CONCLUSION

This article presents a HF and DFT study on Calixarene that investigated oxygen and atoms as active sites of an organic structure. The most chemical shift and the least isotropic chemical shift is related to oxygen atoms but the total charge decrease for them ; that is because of conjugated bonds and aromaticity of the rings configuration and the resonance occurs between non-planar sheets .

Nuclear magnetic resonance (NMR) spectroscopy is a valuable technique for obtaining chemical information. Chemical shift anisotropy asymmetry (ζ), isotropy (δ iso), anisotropy (δ aniso), and $\Delta\sigma$ and chemical shift tensor ($\tilde{\alpha}$) are observed for the atoms are characterized in Table 2 and 3 for Calixarene molecule. Our obtained results yielded strong evidence that intermolecular interaction effects such as electron transfer interactions play very important role in determining NMR chemical shielding tensors of the atoms are characterized in Calixarene molecule and some systematic trends appeared from the analysis of the calculated values.

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