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# Investigation of NMR Parameters of para-Sulfonato-calix[4]arene by HF Calculation

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### ABSTRACT

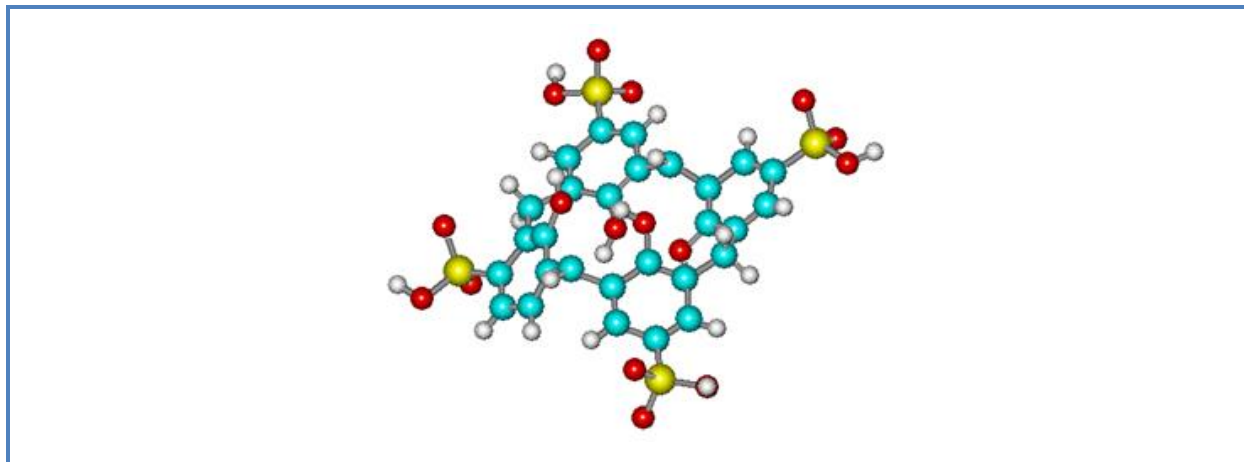
Conformationally-rigid para-sulfonato-calix[4]arene (C<sub>28</sub>H<sub>24</sub>O<sub>16</sub>S<sub>4</sub>) was isolated. The NMR parameters of the structure of calix[4]arenes have been compared. The study of organic structures to form nanoporous materials is a well-known chemical phenomena (supramolecular chemistry) that is necessary for finding the crystal forms of calix[4]arenes. We investigated and compared the hydrogen bonding, oxygen, and sulfur atom effects on calix[4]arene via Hartree-fock(HF) theory by the Gaussian 98 of program package.

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## Graphical Abstract



## Introduction

Porous material is crystalline or amorphous solids that let the inclusion of small molecules through holes in their structures. Structural and materials scientists have been interested in building these frameworks not only to understand their design principles but also because of their diverse commercial applications, chemical separation, asymmetric synthesis, selective catalysis, data storage, optical lasers [1, 2]. The investigation of the hydrogen bonding has attracted considerable attention over the year from the variety of macro cyclic compounds, calixarenes are preferable for metal extraction because of the easy synthesis of a great number of derivatives, which allows to compare the impact of cavity size, conformation, functional groups, and other factors on the extraction behavior, and the flexibility to design a proper ligand to selectively recognize a metal ion [3, 4]. Calixarenes have received much attention recently as one of the most widely employed molecular frameworks for the construction of many versatile macromolecular systems [5]. The large computational resources required to evaluate the energy and structure of calix[n]arenes have prevented extensive ab initio and density functional treatments until recently [6]. 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 calixarenes [7]. Most hydrogen bonds are of YH...H type, where Y is an electronegative atom having one or more lone electron pairs or a region of excess electron density like atomic  $\pi$ -system [8]. About the hydrogen bonding properties of calixarenes, we would like to pay our attentions on hydrogen bonding properties of calix[4]arene by density functional theory methods. Density functional quantum chemical calculations have recently provided a relatively consistent

picture on base pair interaction energies and geometries [9]. This can lead to more detailed information on structure, charge distribution, and energetic of the base pair.

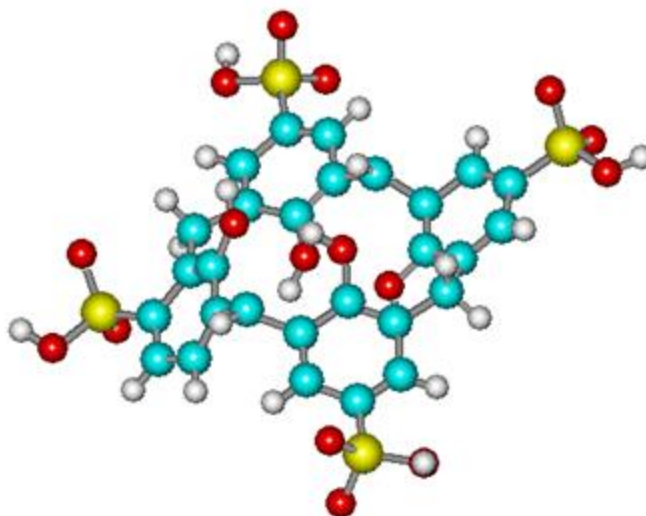
Recently density functional theory (DFT) has been accepted by the quantum chemistry community as a cost-effective approach for the computation of molecular structure, vibration frequencies, and energies of chemical reactions [10]. At present, quantum chemistry is almost universally applicable to the interpretation of physical and chemical properties of various compounds. Recent improvements in ab initio quantum chemical methodologies, when combined with similar improvements in computer software, have recently permitted the first successful predictions nuclear magnetic resonance spectra of materials [11-30]. Successful interpretation of nuclear magnetic resonance (NMR) data requires an accurate knowledge of the chemical shifts anisotropy (CSA).

### **Materials and methods**

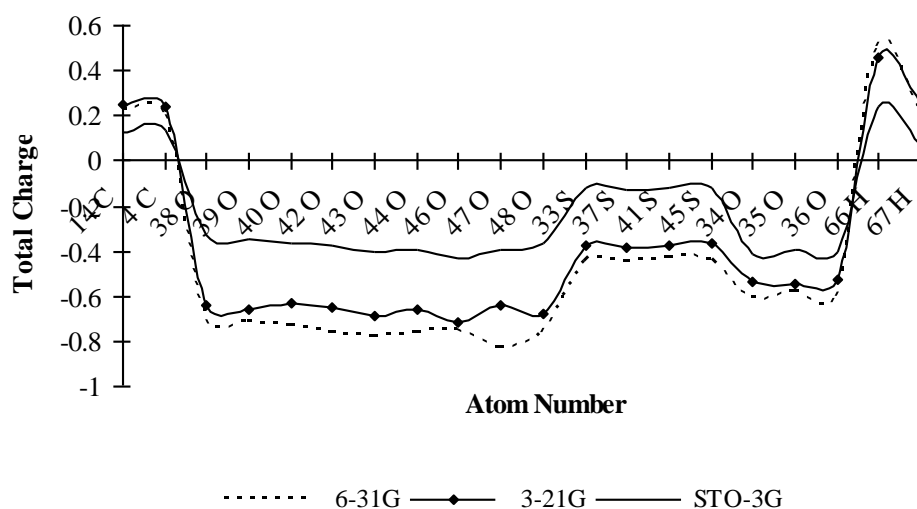
The geometry optimization of the calix[4]arene has been carried out using the GASSIAN 98 programs package. Our computational model consists of geometries for calix[8]arene were fully optimized by restricted Hartree-Fock (RHF) with STO-3G, 3-21G and 6-31G levels. For hydrogen bonding, it is expected that 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 STO-3G, 3-21G and 6-31G basis set along with analytic NMR shielding tensors calculations.

### **Results And Discussion**

Selected computed data, total charge, is compiled in table 1. To assess the quality of the theoretical data, geometrical parameters available for calix[4]arene. From the differences in the physical meaning of the computed result, the theoretical results are in good agreement with geometries. In the compound, the C-H stretch is decreasing total charge, which indicates the increasing acidity of the CH hydrogen from CH...S 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. We fund one stable structure of the calix[4]arene which are shown in figure 1. Taking the calculated result of the three basis set compared with the together, it can be found that induces a small elongation of the O-S bonds a very small contraction of the C-S bond. Other charges involved in the hydrogen bonding and sulfur bonding. In this structure exhibits a cyclic conformation, S accepts a proton from C and H donating a proton to see.



**Figure 1.** The optimized geometries structure of calix[4]arene

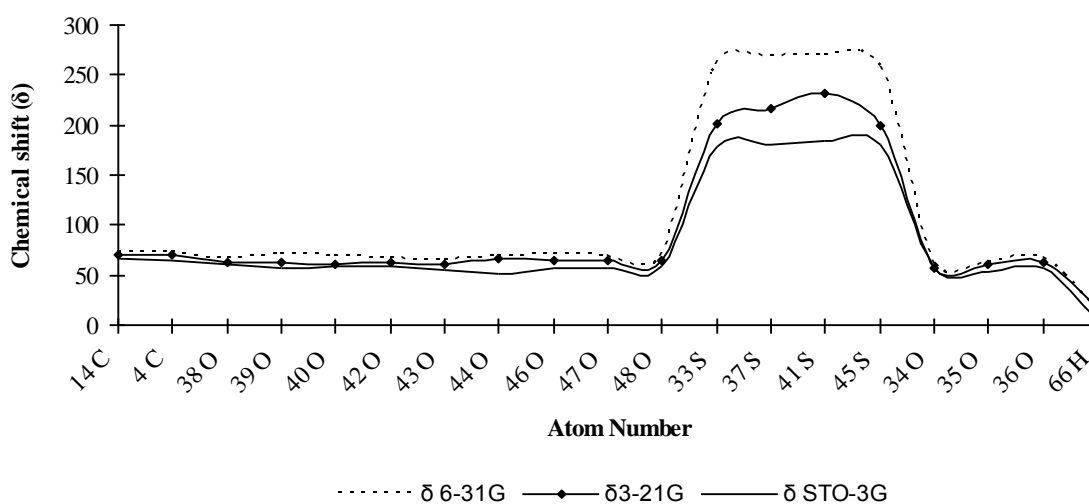


**Figure 2.** Total charge(Colomb) *via* atom number of calix[4]arene

As shown in figure 2 the most of the negative charge attached to oxygen atoms and then it attached to sulfur atoms, similarly the most of the positive charge attached to hydrogen atoms that linked to oxygen atoms and then it attached to carbon atoms that linked to sulfur atoms. To analysis in more detail the role of methods effects, we use table 1; which gives a detailed analysis of the chemical shifts obtained with three methods. As expected basis set sensitivity exists, the chemical shift computed with 6-31G is higher than of two basis sets.

**Table 1.** Total charge, Chemical shift and  $\Delta\sigma$  of calix[4]arene at HF/6-31G, 3-21G and STO-3G

No. Atom	Total charge(Coulomb)			Chemical shift ( $\delta$ ) (ppm)			$\Delta\sigma$		
	6-31G	3-21G	STO-3G	6-31G	3-21G	STO-3G	6-31G	3-21G	STO-3G
14 C	0.223745	0.24559 9	0.12882 5	72.33	69.7896	67.0919	99.9951	99.6844	88.6379
4 C	0.199199	0.24436 4	0.14025 2	71.6584	69.6946	65.3571	98.9876	100.041 9	87.5357
38 O	-0.70453	-0.63593	-0.32594	66.7484	61.8635	60.3793	72.1226	68.2952	65.0689
39 O	-0.71425	-0.66241	-0.34751	69.4126	63.1438	56.3681	76.6188	73.2157	57.5522
40 O	-0.73049	-0.63541	-0.36797	68.7444	61.5079	58.7229	79.1166	74.7619	58.0844
42 O	-0.76496	-0.65135	-0.37444	67.1154	63.2567	59.306	75.673	73.8851	58.959
43 O	-0.7799	-0.6853	-0.40723	65.3904	60.834	55.4836	77.5856	72.7511	59.2254
44 O	-0.76036	-0.65656	-0.39657	68.7416	65.7593	51.1021	79.1124	69.6389	63.6532
46 O	-0.75497	-0.71394	-0.43263	69.5813	63.6564	57.0332	74.8719	67.4846	56.0497
47 O	-0.83222	-0.63556	-0.38997	67.8571	64.576	56.1468	76.2857	69.364	58.2202
48 O	-0.76101	-0.67569	-0.36822	67.6881	63.8072	58.089	77.5321	71.7107	60.6336
33 S	-0.45095	-0.37313	-0.12211	259.518 6	200.362 8	178.960 7	634.932 9	570.044 2	518.941 1
37 S	-0.45395	-0.38563	-0.12471	268.222 4	217.171 5	180.541 3	644.838 7	587.757 3	525.811 9
41 S	-0.43579	-0.37712	-0.12268	268.989 5	232.405 8	184.298 2	670.184 2	630.608 8	560.447 3
45 S	-0.43795	-0.36663	-0.11981	257.996 9	199.758 4	179.520 9	706.375 4	609.137 5	510.781 4
34 O	-0.60892	-0.53464	-0.41045	59.9845	57.6553	56.5304	69.5268	56.483	57.7955
35 O	-0.5845	-0.54147	-0.39228	63.2528	61.0182	53.5006	67.3942	57.5273	57.7509
36 O	-0.59792	-0.53116	-0.39899	67.2321	63.3511	57.5	69.0881	60.5267	60.2499
66 H	0.509348	0.46039 6	0.23641 5	15.2997	16.6335	5.2307	22.9495	24.9504	22.846
67 H	0.209318	0.25223	0.06883 3	3.2221	3.5584	4.7845	4.8352	5.3376	7.796



**Figure 3.** Chemical shift (ppm) *via* atom number of calix[4]arene

The calculation of NMR parameters using semi-empirical and ab initio techniques has become a major and powerful tool in the investigation to look at how variations in the molecular structure occurs. 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 and nearest neighbor interactions has seen a number of recent applications in the investigation of molecular structure. In this work, we obtained the chemical shifts of calix[4]arene atoms principal values in available method. Also diffuse and polarizable functions effects in basis sets are investigated on NMR shielding tensors.

Initially, molecular structure of calix[4]arene is optimized by using HF method with 6-31G. Then,  $^{13}\text{C}$  NMR,  $^1\text{H}$  and  $^{16}\text{S}$  calculations of the title compound ( $\text{C}_{28}\text{H}_{24}\text{O}_{16}\text{S}_4$ ) have been made by HF method with 6-31G basis set. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift values have been calculated for the optimized structures of the title compound. These results are shown in table 1.

As it is elaborated in the figure 3 the most of the chemical shift attached to sulfur atoms; for find reason notice to figure 4 although compound conjugated bonds must be aromatic theoretically but the aromaticity becomes non-stable because of the spherical prohibition so that the configuration charges and the resonance occurs between non-planar sheets; hence the chemical shift on the sulfur atoms are under such more strong electrostatic field. As it has been shown in the table 1, the most  $\Delta\sigma$  is related to sulfur atoms; Also, that is because of conjugated bonds and aromaticity of the Sulfur bonds configuration and the resonance occurs between non-planar sheets; hence the  $\Delta\sigma$  on the sulfur atoms are upper than another atoms strong.

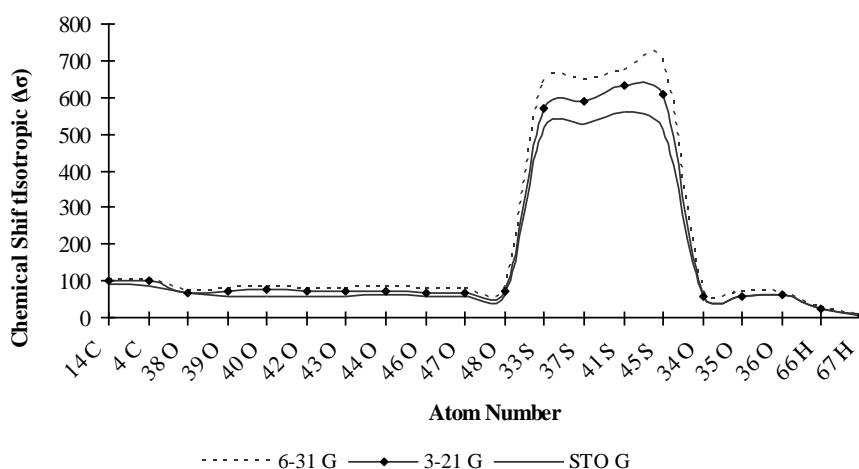


Figure 4. Chemical shift isotropic(ppm) via atom number of calix[4]arene

## Conclusion

This article presents a HF study on para-sulfonato-calix[4]arene that investigated hydrogen, oxygen and sulfur atoms as active sites of an organic structure. The most chemical shift and  $\Delta\sigma$  is related to sulfur atoms but the total charge decrease for them; that is because of conjugated bonds and aromaticity of the Sulfur bonds configuration and the resonance occurs between non-planar sheets. Also, the most of the negative charge attached to oxygen atoms and then it attached to sulfur atoms, similarly the most of the positive charge attached to hydrogen atoms that linked to oxygen atoms and then it attached to carbon atoms that linked to sulfur atoms that must considered for synthesis an organic structure as fertilizer agriculture.

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