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# NMR Analysis of Para-Sulfonato-Calix [4] arene Complex with Some of Metal Ions: A Computational Study

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**Abstract:** Calixarenes are widely used molecular scaffolds that have found broad application in supramolecular chemistry. Their derivatives are currently the object of several studies, due to their peculiar cavity, that is suitable for very specific and efficient complex of ions and small organic molecules, with a high degree of efficiency and selectivity and form host-guest systems in the solid and liquid states. In this paper we have reported the studies on the complex properties of a para-sulfonato-calix[4]arene($C_{28}H_{24}O_{16}S_4$) with some of alkali-earth and alkali cations. The complex properties of para-sulfonato- calix[4]arene were studied by means of density functional theory (DFT) calculations. The complexes showed different properties for the cations, on the base of the cations and the position of the substituent grafted on the ligand.

**Key words:** Para-sulfonatocalix [4] arene · Calixarenes · NMR · Hydrogen bonding · Chemical shift

## INTRODUCTION

The term ‘calix [*n*] arenes’ commonly refers to the cavity-shaped cyclic molecules made up of *n* phenol units linked via alkylidene groups. Calixarenes, along with cyclodextrins and crown-ethers are considered as the third generation of supramolecules [1-3]. The interest in studying these compounds is because of their host-guest properties and their selective affinity for several metal ions and small organic molecules. These macrocyclic host molecules with pre-organized cavities can be successfully use in liquid membranes and in the preparation of ion-selective electrodes to detect and separate alkali ions [4-6]. Furthermore, the study of the host-guest interactions is crucial in understanding the assembly of biological structures such as ribosome, enzymes and nucleic acids’ complexes. The tetramer calix[4]arenes show a particular binding efficiency towards alkali and alkaline earth metal ions, on the base of their stereo chemical conformation [7-12]. The rate of complex depends on the molecules pre-organization and on the desolvation of the ligand’s sites prior to complex. since 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 [8].

The large computational resources required to evaluate the energy and structure of calix[n]arenas have prevented extensive ab initio and density functional treatments until recently [13, 14]. Density functional quantum chemical calculations have recently provided a relatively consistent picture on the base of pair interaction energies and geometries. This can lead to more detailed information on structure, charge distribution and energetic of the base pair [15]. nowadays, quantum chemistry is almost universally applicable to the interpretation of physical and chemical properties of various compounds. Recently improvements in ab initio quantum chemical methodologies, when combined with similar improvements in computer hardware, have recently permitted the first successful predictions nuclear magnetic resonance spectra of materials [16, 17]. Successful interpretation of nuclear magnetic resonance (NMR) data requires an accurate knowledge of the chemical shifts anisotropy (CSA) [18, 19].

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**Computational Methods:** The geometry optimization of the calix [4] arene has been defeated using the GASSIAN 98 programs package [20, 21]. Our computational model consists of Geometries for calyx [8] arene were fully optimized by restricted B3LYP with STO-3G, 3-21G and 6-31G levels [21]. For hydrogen bonding, it has been expected that both diffuse and polarization functions that may be necessary in the basis set. In order to confirm the superiority of the DFT method, we simultaneously adopted B3LYP method at the STO-3G, 3-21G and 6-31G basis set along with analytic NMR shielding tensors calculations [21].

## RESULT AND DISCUSSION

Selected computed data, total charge, is compiled in Table 1. To assess the quality of the theoretical data, geometrical parameters are available for para-sulfonato-calix [4] arene. 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, from the point of view of the CH…Y. the charge distribution in this compound is so important.

We fund one stable structure of the calix[4]arene which has been shown in Fig.1. Taking the calculated result of the six complexes and by comparing them with each other, it can be found that induces a small elongation of the O-S bonds is a very small contraction of the C-S bond. Other charge involved in the hydrogen bonding and sulfur bonding. In these structures exhibits a cyclic conformation, S accepting a proton from C and H donoring a proton to C.

As it has shown in Fig. 2 the most of the negative charge attached to oxygen atoms and then it attached to carbon atoms, similary the most of the positive charge attached to sulfur atoms that linked to oxygen atoms and then it attached to metal atoms that linked to S-O bond. As notice, the total charge computed for Li-calix is higher than of Na-calix then K-calix complex. That is because of nuclear effective charge which is decreased from Li to K atom. To analysis in more details of the role of metal ions effects, we use Table 1; which gives a detailed analysis of the chemical shifts obtained with metal ions. The calculation of NMR parameters using DFT techniques has became a major and powerful tool in the investigation for finding out that how a variation in the molecular structure occurs. The ability to quickly evaluate, correlate the magnitude and orientation of the chemical shielding

Table 1: Total charge, chemical shift and isotropic chemical shift of para-sulfonato-calix[4]aren complexes at B3LYP level

| | Total charge(C) | | | δ ( ppm) | | | $\sigma_{iso}$( ppm) | | |
|---|---|---|---|---|---|---|---|---|---|
| No. Atom | Li | Na | K | Li | Na | K | Li | Na | K |
| 2 C | 0.1932 | 0.1821 | 0.1801 | 175.2573 | 170.3415 | 170.1109 | 195.3421 | 221.3211 | 243.7802 |
| 14 C | -0.5514 | -0.5238 | -0.5171 | 195.1432 | 189.0304 | 188.3291 | 201.3435 | 233.6591 | 252.3312 |
| 24 C | -0.4531 | -0.4327 | -0.4122 | 189.2153 | 183.3016 | 176.128 | 243.8791 | 254.2213 | 261.8932 |
| 30 O | -0.2436 | -0.2121 | -0.1932 | 125.4563 | 119.8703 | 117.4321 | 312.9231 | 345.7659 | 367.3298 |
| 31 O | -0.2161 | -0.1823 | -0.1711 | 153.0119 | 148.2311 | 140.1297 | 296.3459 | 337.9302 | 349.1197 |
| 32 O | -0.2265 | -0.1979 | -0.1793 | 169.8367 | 166.3203 | 163.0023 | 276.1238 | 312.1133 | 335.0095 |
| 33 S | 0.5632 | 0.5123 | 0.4807 | 2634.1427 | 2533.1305 | 2487.2134 | -543.023 | -562.984 | -578.234 |
| 37 S | 0.6103 | 0.5772 | 0.5122 | 2598.3821 | 2544.1781 | 2445.0305 | -345.99 | -376.81 | -398.24 |
| 41 S | 0.6345 | 0.5522 | 0.5004 | 2672.5639 | 2532.2317 | 2500.1967 | -458.32 | -462.99 | -469.12 |
| 45 S | 0.5962 | 0.5634 | 0.5203 | 2655.1131 | 2537.0121 | 2436.3211 | -589.90 | -596.17 | -600.23 |
| 34 O | -0.3439 | -0.3088 | -0.2841 | 1763.4976 | 1701.4503 | 1642.0321 | -24.7557 | -25.3369 | -27.0823 |
| 35 O | -0.3562 | -0.3104 | -0.2899 | 1801.4135 | 1721.7536 | 1658.2999 | -56.3226 | -49.1824 | -61.3118 |
| 36 O | -0.3423 | -0.3272 | -0.2821 | 1796.0515 | 1719.1519 | 1638.9023 | -49.2391 | -47.6531 | -55.9485 |
| 49 H | 0.0037 | 0.0029 | 0.0022 | 23.7048 | 22.8762 | 21.8723 | 8.9892 | 9.6209 | 10.2301 |
| 65 H | 0.0115 | 0.0106 | 0.0092 | 11.3412 | 11.03451 | 10.3955 | 11.4549 | 13.1123 | 13.9829 |
| 235 M | 0.3121 | 0.2009 | 0.1523 | 70.1232 | 113.8977 | 136.1752 | 102.1702 | 88.2821 | 71.8153 |
| | | | | Li-Calix | | Na-Calix | | | K-Calix |
| Dipole moment (Deby) | | | | 13.2164 | | 11.3782 | | | 10.4342 |
| Energy (kcal/mol) | | | | -3898.46 | | -3811.02 | | | -3781.52 |

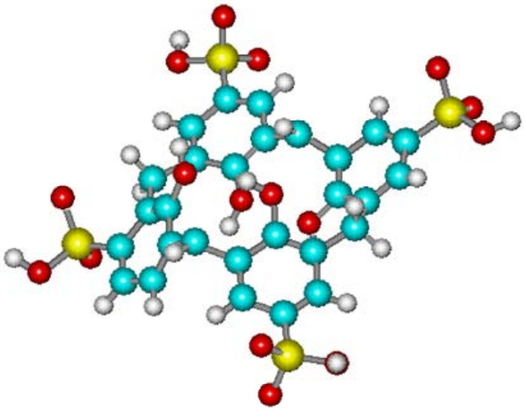

Fig. 1: The optimized geometries structure of para-sulfonato-calix [4] arene

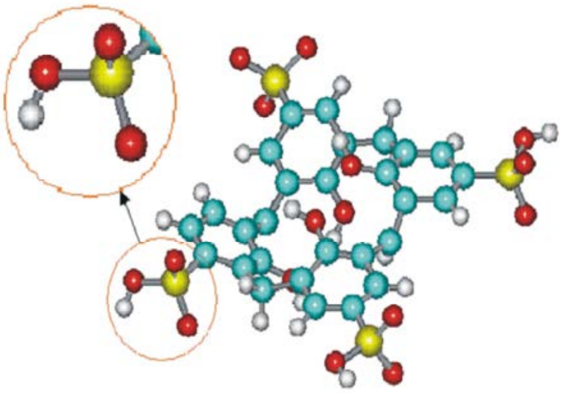

Fig. 4: The final optimization form of para-sulfonato-calix[4]arene

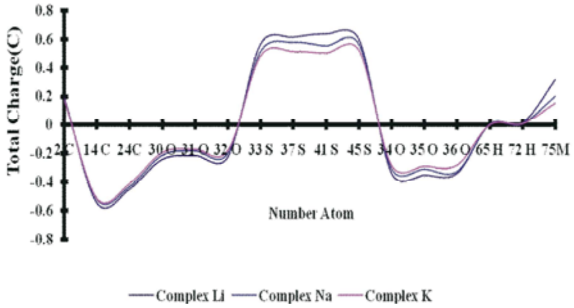

Fig. 2: Total charge (Colomb) via atom number of para-sulfonato-calix [4] arene complexes with some alkali-earth metals

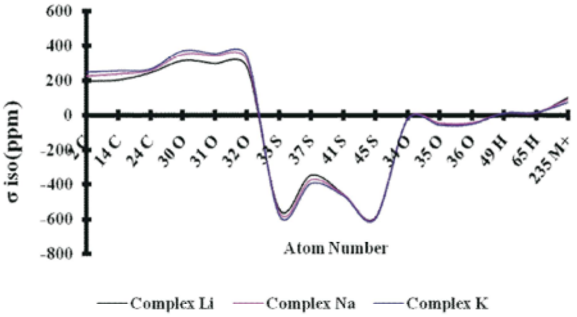

Fig. 5: Chemical shift isotropic (ppm) via atom number of para-sulfonato-calix[4]arene complexes with some alkali-earth metals

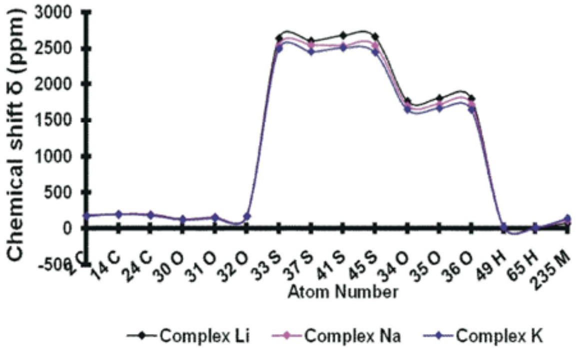

Fig. 3: Chemical shift (ppm) via atom number of para-sulfonato-calix[4]arene complexes with some alkali-earth metals

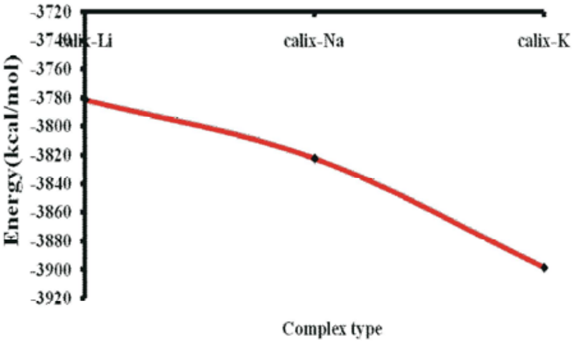

Fig. 6: Energy (kcal/mol) via para-sulfonato-calix[4]arene complexes with some alkali-earth metals

anisotropy tensor with variations in bond length, bond angles, local coordination and nearest neighbor interactions has seen a number of recent applications in the investigation of molecular structure. In this paper, we obtained the chemical shifts of calix[4]arene atoms principal values in available method. Also diffuse and polarized functions effects in basis sets are investigated on NMR shielding tensors. As expected, the chemical shift computed for Li-calix is higher than of Na-calix then K-calix complex.

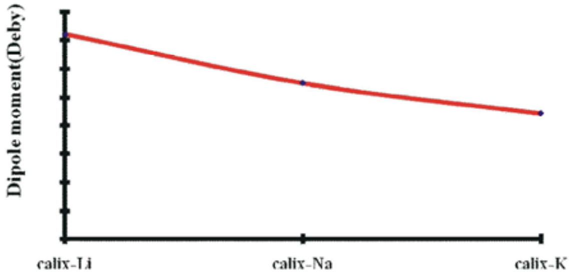

Fig. 7: Dipole moment (Deby) via para-sulfonato-calix[4]arene complexes with some alkali-earth

Initially, molecular structures of the title compound and $^{13}$C NMR, $^{1}$H and S$^{16}$ calculations have been calculated by B3LYP method. These results have been shown in Table 1. As it has been elaborated in the Fig. 3 the most of the chemical shifts attached to sulfur atoms; for finding the reason notice to Fig. 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 and Fig. 5 the least $\sigma_{iso}$(isotropic chemical shift) 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 $\sigma_{iso}$ on the sulfur atoms are lower than another atoms. As it has been shown in Fig. 5, this parameter computed for Li-calix is higher than of Na-calix then K-calix complex.

As it has been elaborated in the Fig. 6 and Table 1; the most of the energy attached to Li-calix complex; then, this complex is the most stable of the other complexes also as it has been shown in Fig. 7. The most dipole moment is related to Li-calix complex that is because of nuclear effective charge which is decreased from Li to K atom.

## CONCLUSIONS

This article presents a DFT 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 the least isotropic chemical shift 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 total charge attached to sulfur atoms and then metal atoms that are because of electronegativity of oxygen atoms that linked to them.

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