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Investigation of NMR Shielding Tensors of Para-Sulfonato-calix [4] arene Complexation with some of Alkali metal atoms

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ABSTRACT

Calixarenes are a readily available and important class of macrocycles in supramolecular chemistry. Calixarenes have generated considerable interest due to their basket shaped structure and as useful building blocks to synthesize selective receptors for the guest species, notably alkali, alkaline earth, lanthanide and transition metal cations. In this work studied on the complexing properties of a para-sulfonato-calix [4] arene ($C_{28}H_{24}O_{16}S_4$) with alkali metal cations. The complexation properties of para-sulfonato- calix [4] arene were studied by Hartree Fock method. The complexes showed different properties for the different cations, depending on the cations and the position of the substituents grafted on the ligand.

Keywords: P-sulfonatocalix [4] arene; Guest; DFT; HF; NMR; Hydrogen bonding; Nanostructure; Chemical shift

INTRODUCTION

The formulation of eqn. (1) not only requires an investigation of the composition of the complex but it also requires knowledge regarding whether the free and the complex electrolytes are predominantly in their ionic forms in solution as required by eqn. (1). Such behavior is dependent on the charge of the cation, the counter-ion present in the metal-ion salt, the working concentration and the medium. As far as the metal-ion salts are concerned much efort has been devoted to establishing their properties in different media and these data are documented in the literature [8] although this information has been often ignored. In contrast, knowledge regardingcalixarene-based electrolytes is indeed very limited [9, 10].

Therefore it can be safely stated that most thermodynamic data involving cations are based on the assumption that, if the free metal-ion salt is fully dissociated in a given medium, the same behavior will be shown by the complexed metal salt since this is formed by a large cation and as such it is unlikely to interact with the anion. Although this may be often the case, the validity of such an assumption needs to be verified experimentally to fulfill the requirements of eqn. (1), which explicitly demands that both the free and the complex cations are predominantly ionic species in solution. Complexation was studied involving p-sulfonato-calix [4] arene have been reported in the literature and the NMR parameters of these complexations by theoretical methods [11, 12].

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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 base pair interaction energies and geometries. This can lead to more detailed information on structure, charge distribution, and energetic of the base pair [15]. 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 a 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].

COMPUTATIONAL METHODS

The geometry optimization of the calix [4] arene has been carried out using the GASSIAN 98 programs package [20, 21]. 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 [21].

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[21].

RESULT AND DISCUSSION

Selected computed data, total charge, is compiled in table 1. To assess the quality of the theoretical data, geometrical parameters available for para-sulfonato-calix [4] arene.
In the compound, this 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 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 fig.1. Taking the calculated result of the six complexes compared with 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 charge involved in the hydrogen bonding and sulfur bonding. In these structures exhibits a cyclic conformation, S accepted a proton from C and H donor a proton to C.

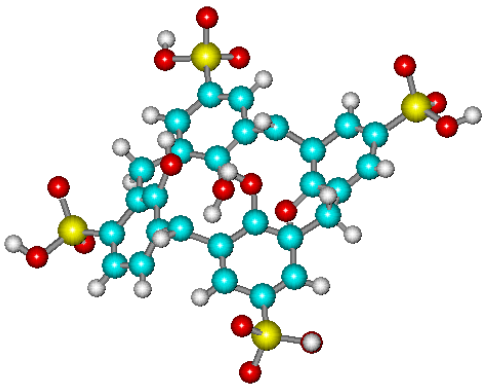

Fig. 1. The optimized geometries structure of para-sulfonato-calix [4] arene.

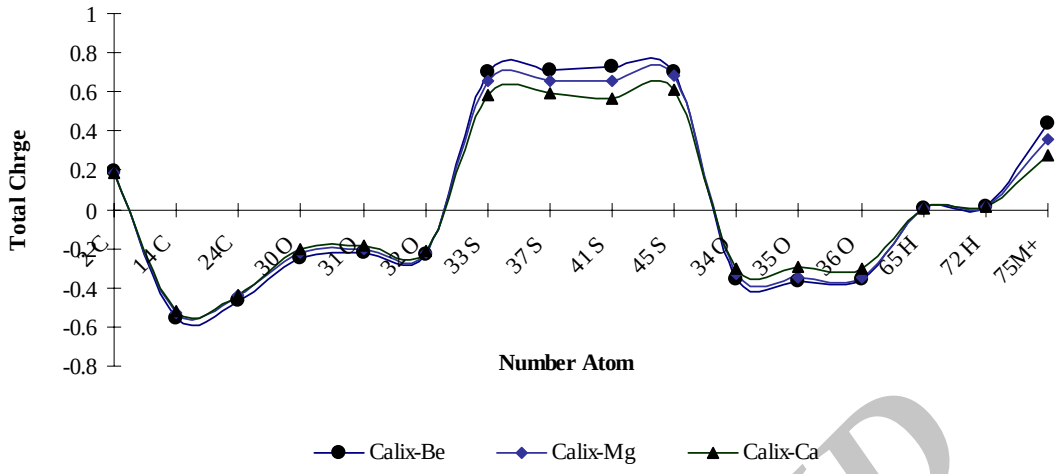

Fig. 2. Total charge (Colomb) via atom number of para-sulfonato-calix [4] arene complexes with some alkali metals.

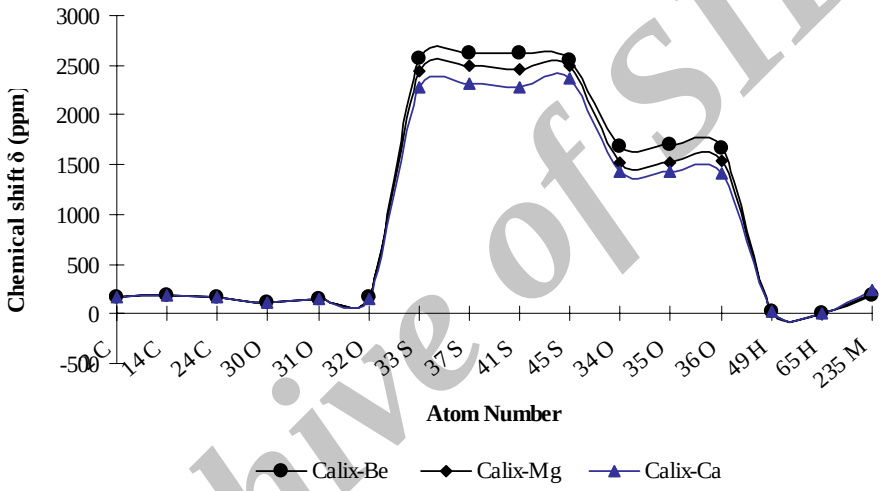

Fig. 3. Chemical shift (ppm) via atom number of para-sulfonato-calix [4] arene complexes with some alkali metals.

As 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 chrge computed for Be-calix is higher than of Mg-calix then Ca-calix complex. That is because of nuclear effective charge which is decreased from Li to K atom. To analysis in more detail the role of metal iones effects, we use Table 1; which gives a detailed analysis of the chemical shifts obtained with metal iones. The calculation of NMR parameters using ab initio techniques has become a major and powerful tool in the investigation to look at how a variation 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. As expected, the chemical shift computed for Be-calix is higher than of Mg-calix then Ca-calix complex.

Initially, molecular structures of the title compound and ^{13}C NMR, ^{1}H and ^{16}S calculations have been made by HF method. These results are shown in Table 1.

As it is elaborated in the fig. 3 the most of the chemical shift attached to sulfur atoms; for find 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 σ_{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 σ_{iso} on the sulfur toms are lower than another atoms. As shown in fig. 5, this parameter computed for Be-calix is higher than of Mg-calix then Ca-calix complex.

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

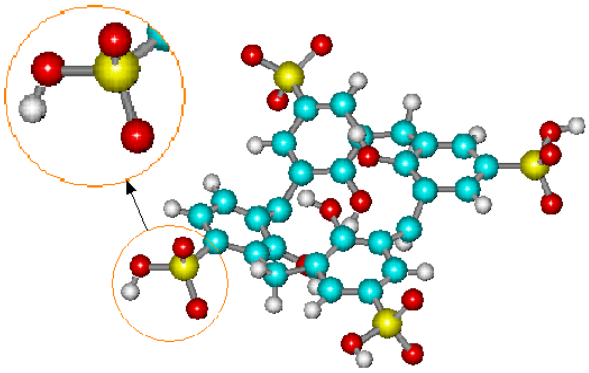

Fig. 4. The final optimization form of para-sulfonato-calix [4] arene.

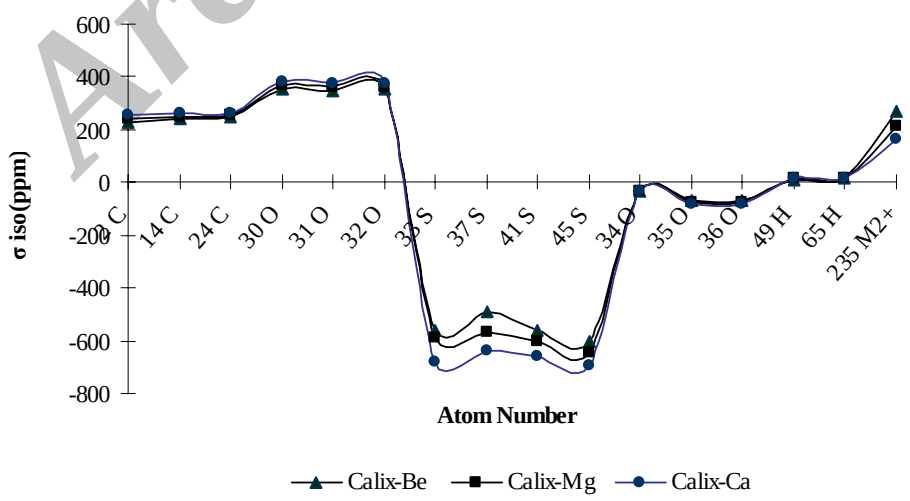

Fig. 5. Chemical shift isotropic (ppm) via atom number of para-sulfonato-calix [4] arene complexes with some alkali metals.

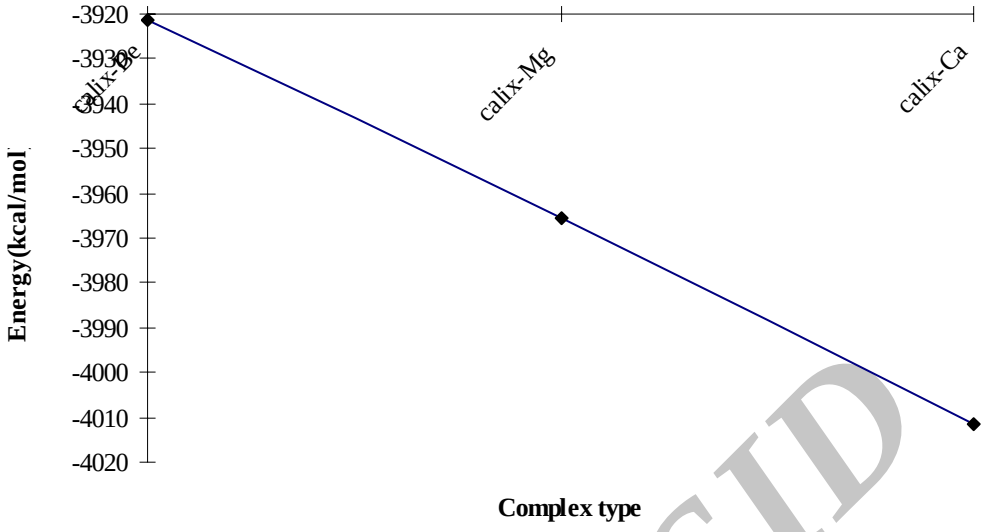

Fig. 6. Energy (kcal/mol) via para-sulfonato-calix [4] arene complexes with some alkali metals.

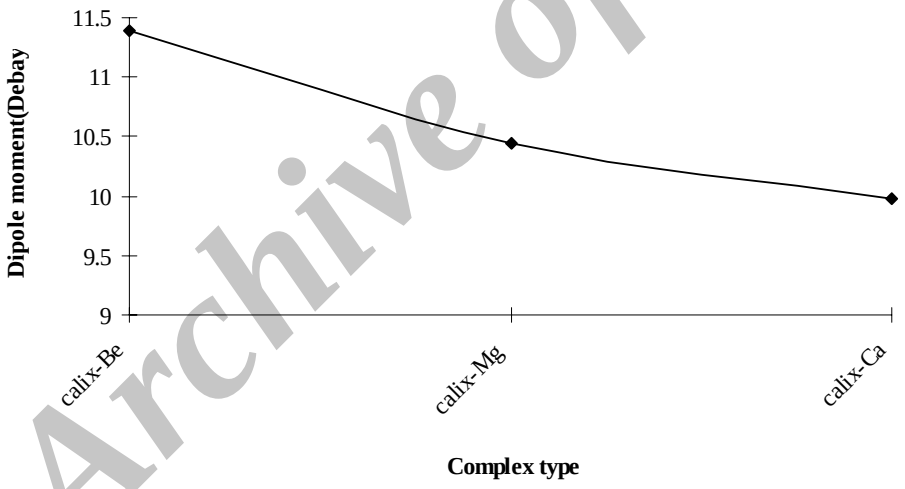

Fig. 7. Dipole moment (Deby) via para-sulfonato-calix [4] arene complexes with some alkali metals.

CONCLUSIONS

This article presents a HF study on Para-Sulfonato-Calix [4] arene that investigatied 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 is because of electronegativity of oxygen atoms that linked to them.

Table 1. Tothal charge, chemical shift and isotropic chemical shift of para-sulfonato-calix [4] aren complexes at HF level

No. Atom	Total charge(C)			δ (ppm)			σ_{iso}(ppm)		
	Be	Mg	Ca	Be	Mg	Ca	Be	Mg	Ca
2 C	0.1975	0.1899	0.1823	170.2341	169.4532	163.0096	223.6572	242.1315	256.1234
14 C	-0.5588	-0.5327	-0.5211	189.0983	190.3452	188.1713	243.1734	251.1891	260.2341
24 C	-0.4623	-0.4408	-0.4378	175.2351	170.9192	163.2219	245.1104	255.4392	263.9206
30 O	-0.2496	-0.2202	-0.2031	120.7564	115.5534	111.1723	353.3589	364.6555	379.1919
31 O	-0.2243	-0.2033	-0.1845	149.4342	145.3302	145.6502	347.2997	359.3215	374.6537
32 O	-0.2317	-0.2253	-0.2091	163.1145	162.1818	155.3311	352.8834	360.1773	374.9023
33 S	0.7023	0.6822	0.6455	2561.6958	2432.0983	2276.8093	-572.56	-589.12	-600.34
37 S	0.7112	0.6904	0.6567	2531.1187	2492.6502	2319.7345	-487.450	-501.921	-521.729
41 S	0.7312	0.6947	0.6534	2497.9623	2483.1311	2284.4362	-558.118	-571.323	-597.177
45 S	0.6982	0.6811	0.6555	2541.1205	2491.543	2365.7123	-600.14	-610.43	-632.81
34 O	-0.3581	-0.3305	-0.3009	1676.1516	1512.8753	1426.3946	-31.4893	-32.9814	-35.7992
35 O	-0.3624	-0.3476	-0.2978	1701.3714	1522.1366	1434.4429	-71.3221	-75.1193	-83.4285
36 O	-0.3606	-0.3434	-0.3023	1669.1012	1531.2213	1412.4532	-67.3112	-73.3984	-81.1458
49 H	0.0041	0.0032	0.0027	21.6534	20.8761	20.1131	12.3019	12.8985	13.1794
65 H	0.0132	0.0113	0.0099	10.7835	10.2119	9.7812	13.7722	13.8541	14.0903
235 M	0.4423	0.3609	0.2763	184.9827	211.3423	232.2199	267.1249	212.1932	164.3776

Dipole moment (Deby)	Be-Calix	Mg-Calix	Ca-Calix
	11.3913	10.4381	9.9832
Energy (kcal/mol)	-3921.33	-3965.35	-4011.32

REFERENCES

[1] C.D. Gutsche, J.F. Stoddard (Eds.), Calixarenes, The Royal Society of Chemistry, Cambridge, England, 1989.

[2] S. Shinkai, Tetrahedron 49 (1993) 8933.

[3] V. Bo¨hmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 713.

[4] L. Cecille (Ed.), Radioactive Waste Management and Disposal, Elsevier, London, 1991.

[5] W.J. McDowell, G.N. Case, J.A. McDonough, R.A. Bartsch, Anal. Chem. 64 (1992) 3013.

[6] T. Jin, M. Kinjo, T. Koyama, Y. Kobayashi, H. Hirata, Langmuir 12 (1996) 2684.

[7] P.J. Dijkstra, J.A.J. Brunink, K-E. Bugge, D.N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli, E. Ghidini, J. Am. Chem. Soc. 111 (1989) 7567.

[8] A. Ikeda, S. Shinkai, J. Am. Chem. Soc. 116 (1994) 3102.

[9] P.D. Beer, M.G.B. Drew, P.A. Gale, P.B. Leeson, M.I. Ogden, J. Chem. Soc. Dalton Trans. (1994) 3479.

[10] A. Arduini, S. Fanni, G. Manfredi, A. Pochini, R. Ungaro, F. Ugozzoli, J. Org. Chem. 60 (1995) 1448.

[11] S. Arimori, T. Nagasaki, S. Shinkai, J. Chem. Soc. Perkin Trans. 2 (1995) 679.

[12] A. Arduini, W.M. McGregor, D. Paganuzzi, A. Pochini, A. Secchi, R. Ungaro, F. Ugozzoli, J. Chem. Soc. Perkin Trans. 2 (1996) 839.

[13] A. Amiri, M. Monajjemi, S. Ketabi , J.Physics and Chemistry of Liquids , 45, (2007) 425.

[14] A. Ariafard, R. Fazaeli, H.R. Aghabozorg, M. Monajjemi, Journal of Molecular Structure (Theochem), 625, (2003) 305.

[15] M. Monajjemi, B. Chahkandi , K. Zare , and A. Amiri , Biochemistry (Moscow), 70, (2005) 366.

[16] A.C. De Dios, E. Oldfield. Sol. State NMR, 6, (1996) 101.

[17] E. Old field. J. Biomol. NMR, 5, (1995) 217.

[18] D. Fushman, D. Cowburn. J. Am. Chem. Soc., 120, 7109 (1998); J. Byed, C. Redfield. J. Am. Chem. Soc., 120, (1998) 9692.

[19] K. Pervushin, R. Riek, G. Wider, K. Wuthrich. Proc. Natl. Acad. Sci., USA, 94, (1997) 12366, R. Riek, G. Wider, K. Pervushin, K. Wuthrich. Proc. Natl. Acad. Sci., USA, 96, (1999) 4918.

[20] M.J. Frisch, et al. Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh PA (1998).

[21] M. Monajjemi, E. Rajaeian , F. Mollaamin , F. Naderi and S. Saki, J. Physics and Chemistry of Liquids ,46, (2008) 299.