One Pot Mechanochemical Synthesis of Resorcinol Based Calix[4]arene and It's *ab initio* Study

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One pot mechanochemical synthesis of calix[4]arene resorcinol with 12 OH groups has been synthesized and confirmed on the basis of IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. *Ab initio* molecular orbital calculations at HF/3-21G*, HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization are reported for the synthesized resorcinol based calix[4]arene.

Key Words: Synthesis, Calix[4]arene, *ab initio*.

INTRODUCTION

Calixarenes and their derivatives have drawn tremendous interest because of their application in diverse areas such as host-guest chemistry[1-4], selective ion transport[5,6], sensors[7] and catalysis[8,9]. In the calixarene family, calix[4]arenes are the most popular because of their rigid structures, which make them ideal candidates for complexation studies with ions and neutral molecules[1,2]. This chemistry has become even more versatile because of the ease with which calix[4]arene can be modified with functional groups at either lower or upper rims or both, depending on the requirement. These modified calixarenes provide a highly preorganized architecture for the assemblage of converging binding sites[7]. Here in we reported the mechanochemical way for the synthesis of 2,8,14,20-*tetrakis*(4-hydroxyphenyl)-calix[4]resorcinarene and it's characterization, spectroscopic studies and *ab intio* study Hartree-Fock calculations at the HF/3-21G*, HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization.

EXPERIMENTAL

The ^{1}H, ^{13}C{1H} NMR spectra were recorded at 300 and 75.4 MHz, respectively at 295 K, using a Brocker 300 NMR spectrometer. ^{1}H NMR and ^{13}C{1H} NMR chemical shifts are reported in ppm downfield from TMS. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents and in ^{13}C{1H} NMR the ^{13}C signal of the deuterated solvents was used as a reference.

Synthesis of 2,8,14,20-*tetrakis*(4-hydroxyphenyl)calix[4]resorcinarene: 4-Hydroxybenzaldehyde (10 mmol, 1.22 g) and resorcinol (10 mmol, 1.10 g) were loaded into a porcilain bowl (100 mL). The sample hand milled for 1 h and then it charged with 5 mL phosphoric acid. The colour of the sample changed to red and the sample hand milled again for another 1 h. After this time the sample washed with water and methanol, filtered and dried in vacuum to give the sample as a red powder (2.04 g, 9.5 mmol, 95 % yield). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 5.4-5.5 (s, 4H, CH), 5.9-6.6 (m, 24 H, ArH), 8.4-8.9 (12H, OH). ^{13}C{1H} NMR: δ 41.7(CH), 102.2, 102.5, 114.3, 121.2, 121.4, 122.3, 128.9, 130.0, 130.3, 132.0, 134.9, 136.4, 152.7, 153.0, 154.7, 154.9 (Ar).

Computational methods: In the present work, the geometries of the 2,8,14,20-*tetrakis*(4-hydroxyphenyl)calix[4]- resorcinarene was fully optimized at both the restricted Hartree-Fock (RHF) and DFT (B3LYP)[10] levels of theory using the Gaussian 98 program[11] on a Pentium-PC computer with a 1.8 MHz processor. At first, calix was optimized using the standard HF/3-21G**basis set; second the resulting structure was used for further calculations using the standard HF/ 6-31G** basis set and third, the obtained structure in second step was used for calculation in higher level B3LYP/6-31G**[10]. Therefore, calix was optimized step by step through three different methods.

RESULTS AND DISCUSSION

Calixarenes have been used in a large and various number of chemical modification during the last two decades[1,12]. These modifications, intended to either their properties or general shape, usually have been based on the functionalization of the calix macrocycle at uper rim or lower rim positions[13]. Yamakawa and co-workers[14] reported the synthesis and using of calix[4]resorcinarene in the preparation of dendrimers as core molecules. Multi-step synthesis of calixarenes are often long and the yields sometimes modest. In present studies, the synthesis of calix[4]-resorcinarene in one step and high yield are reported. The *ab initio* study of the calix[4]-resorcinarene on the different bases set is also reported. Figs. 1 and 2 shows the structure obtained from *ab initio* study based on B3LYP/6-31G** and also bond lengths and angles of the core in calix[4]arene.

A simple and efficient synthesis method, solvent mediated milling and hydrogenation, was employed in order to prepare the calix[4]arene from the basic materials, 4-hydroxybenzaldehyde and resorcinol in the presence of phosphoric acid in a porcelain bowl. The obtained structure was confirmed by ^{1}H, ^{13}C NMR and CHN analysis which are in agreement with the proposed structure in Figs. 1 and 2. The spectrum showed peaks at 5.4-5.5 ppm, 5.9-6.6 ppm, 8.4-8.9 ppm, which are attributed to methine, aromatic and phenolic protons, respectively.
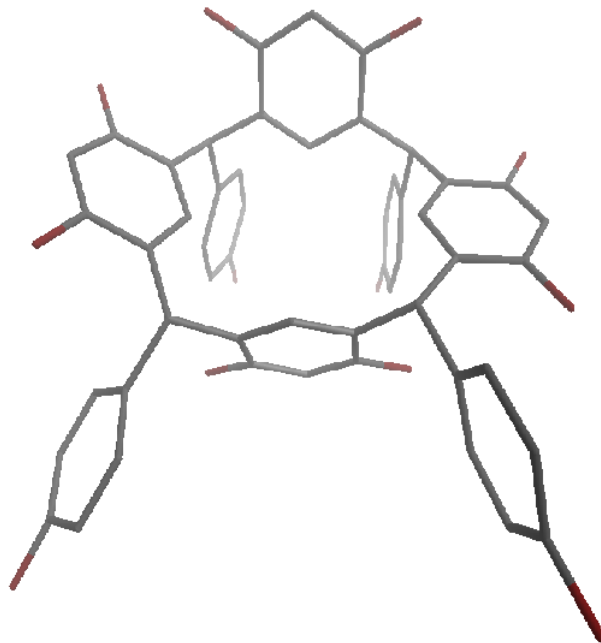
Fig. 1.   Obtained structure of 2,8,14,20-*tetrakis*(4-hydroxyphenyl)calix[4]resorcinarene
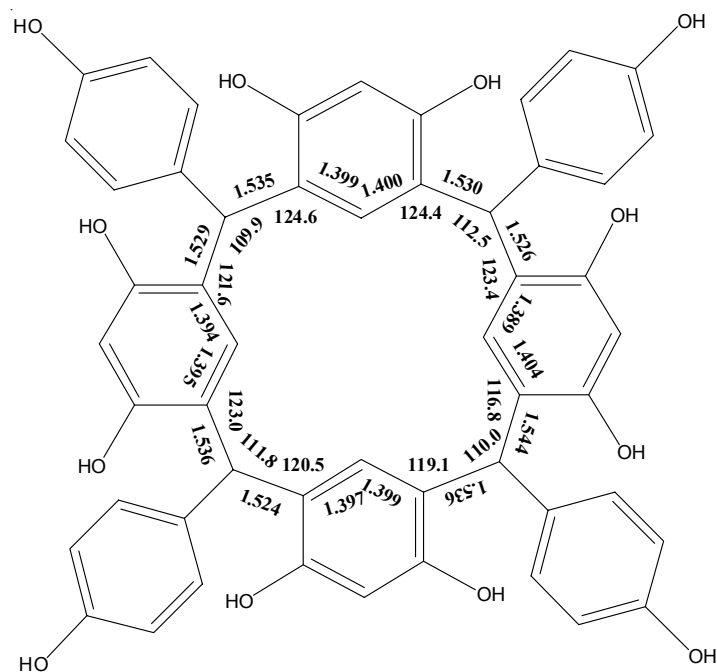using the B3LYP/6-31G** basis set

Fig. 2.   B3LYP/6-31G** calculated bond lengths (in Å) and bond angles (in °) for 2,8,14,20-
tetrakis(4-hydroxyphenyl)calix[4]resorcinarene

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