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Vibrational Spectroscopic, 13C NMR, DFT Studies on Chlorofullerene ($C_{60}C_{l6}$): A Potential Bioactive Agent

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Abstract

The present work comprises the systematic computational chemical findings on Chlorofullerene ($C_{60}C_{l6}$). The molecular arrangement of $C_{60}C_{l6}$ was augmented by density function theory DFT model B3LYP principle through 6-31G(d,p) basis set using Gaussian 09 program. The infrared and Raman spectra were simulated and assigned for C60Cl6 molecule. Carbon – chlorine stretching vibrations are found to be in the range 150-900 cm^{-1} and the chains are strongly affected with the radial vibrations of the carbon sphere. The augmented geometries at ground-state of the molecules are calculated without any geometrical restriction and the molecules are found to be minima on their respective potential energy surfaces. The augmented structures have been subjected to Gauge including atomic orbital (GIAO), the chemical shielding tensors applying B3LYP principle through 6-31G(d,p) in solvent phase in order to calculate 13C chemical shift values with respect to trimethylsilane (TMS) as computational reference. Molecular acuteness and constancy were examined using the Frontier molecular orbitals (FMO) examination. The molecular electrostatic potential (MEP) mapping provides a valuable information regarding the net electrostatic effect produced by net charge distribution of the molecule. Chlorofullerenes are considered to be promising compounds for the investigation of biological action which show pronounced anti-HIV action and low toxicity. Hence, these results set goal in scheming the biocompatible molecules which will be beneficial in the field of carbon nano medicine and drug delivery application.

Keywords: DFT, GIAO, Chemical Shift, Electrostatic Potential.

Introduction

Fullerenes were recently discovered carbon allotropic after graphite and diamond. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of icosahedral symmetry for closed sphere structure [1]. Halogenation was among the first reactions discovered for fullerenes. The reaction of C60 with fluorine, chlorine and bromine are important because the resulting halide products can be useful precursors to a variety of substituted derivatives [2-5]. The reason of higher selectivity of halogenation reactions is likely to be electrostatic effects caused by electron-removing property of halogen atoms [4]. In the present exploration, firm molecular structure of $C_{60}C_{16}$ was accessed and the vibrational frequencies were calculated. GIAO uses magnetic shield tensor to simulate 13C NMR spectra and chemical shifts were calculated. Frontier molecular orbitals related molecular properties were analyzed. The even molecular electrostatic potential surface was simulated computationally by total electron density mapping and visualized in order to probe the molecular acuteness.

Computational Details

The molecular structure of the chlorofullerene was augmented by DFT model B3LYP principle through 6-31G(d,p) basis set level of theory using Gaussian 09 program [5]. The C-C hexagon, C-C pentagon and C-Cl bond lengths in $C_{60}C_{16}$ molecule were calculated as 1.52 Å, 1.49 Å and 1.96 Å, respectively. The magnetic shield simulator GIAO is employed to compute the chemical shifts (δ ppm). The structural parameters were calculated for $C_{60}C_{16}$ molecule. Frequency calculations were performed on all optimized structures to ensure stable minima. The infrared and Raman frequencies, FMOs related molecular properties were calculated for firm molecular structure. GaussView 05 program [6] was used to visualize the

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optimized structure, vibrational spectra and frontier molecular orbitals of the molecule.

Results and Discussion

The augmented molecular structure of $C_{60}Cl_6$ molecule was shown in figure 1 (a). The computed IR and Raman spectra were shown in figure 1(b). The $C_{60}Cl_6$ molecule has C_s symmetry with 192 normal modes of vibrations. The predicted vibrational wavenumbers specifying that the steady geometry is located at the minima point on the potential energy surface. The observed active vibration around region 830 cm^{-1} parallels to of C-Cl vibrations. From the FT-RAMAM spectrum the presence of C_{60} Ag mode with little shifting indicates that the icosahedral symmetry is relatively unperturbed. The normal-mode analysis yields, $\Gamma_{vib}(C_{60}Cl_6)$ = 99A'+93A" [2,3] indicating 192 IR and RAMAN active modes. The strong IR modes were observed in the region 750-850 cm^{-1} which is caused by the deformations due to the carbon-chlorine in $C_{60}Cl_6$ molecule. It indicates the symmetry of the molecule.

Table 1: The 13C NMR spectra calculated chemical shift

Site numbers of atom	Nuclei	Isotropic chemical potential (δ ppm)	TMS shielding value (δ ppm)
16, 44	13C	22.13	182.46
10, 50	13C	19.32	182.46
47, 1	13C	18.30	182.46
49, 59	13C	135.15	182.46
45, 7	13C	150.26	182.46

Figure 2 shows the simulated NMR spectra of $C_{60}Cl_6$ in solvent phase using DMSO as solvent. The polarizable continuum model (PCM) is generally used in computational chemistry in order to model solvation effects. The GIAO models the shielding tensor and 13C nuclei of $C_{60}Cl_6$ shows splits in region 180 to 20 ppm [7,8] with two degeneracies. The carbon atom bonded to chlorine atoms shows a sudden change in chemical shift (δ ppm) from 150 ppm to 20 ppm. The values are tabulated in Table 1.
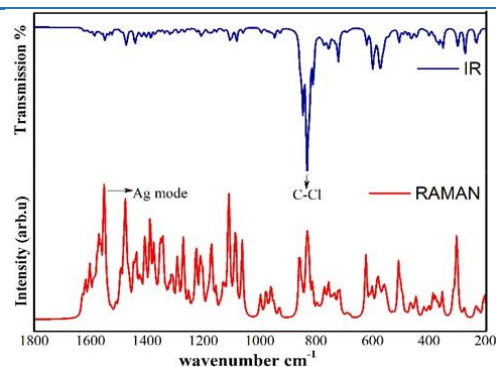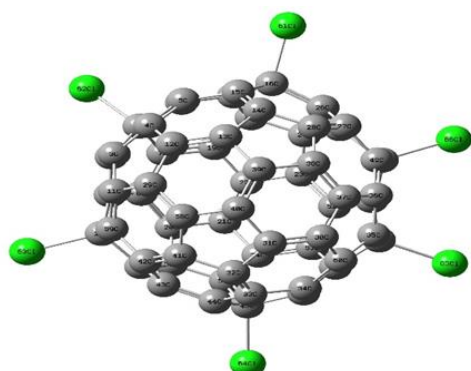

Figure 1: (a) The augmented structure of $C_{60}Cl_6$ molecule (b) vibrational spectra of $C_{60}Cl_6$ molecule
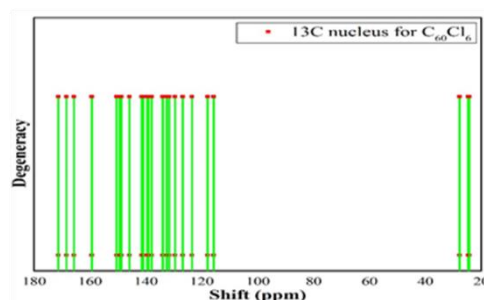

Figure 2: The 13C NMR spectra of $C_{60}Cl_6$

Figure 3 indicates that the occurrence of the delocalization of electron density within the molecule. The charge delocalization reveals the biological activity of the molecule. The band gap energy has an indispensable role in determining the constancy and acuteness of the molecule. The ionization potential and electron affinity of the molecule were calculated as 5.01 eV and 6.14 eV, respectively. The electronegativity, global hardness, softness, chemical potential and electrophilicity index values of the molecule were calculated as -5.57, 0.56, 1.76, 5.57 and 27.45eV respectively.
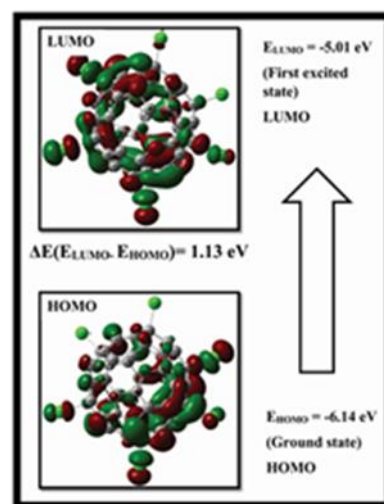

Figure 3: The FMOs of $C_{60}Cl_6$ molecule

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The band gap value was calculated as 1.13 eV, the lower value compared with C_{60} molecule, which leads to the stability and bio-compatibility of the molecule [9].

The molecular electrostatic potential diagram of the $C_{60}C_{l6}$ molecule is shown in figure 4. Simulating and accessing molecular electrostatic potential provides a visual method to understand the standards polarity of the molecule. The region around the chlorine atom bonded to C_{60} is found to be neutral and crystal clear which indicates that chlorofullerene can act as a substrate for the preparation of water-soluble fullerene derivatives, promising compounds for investigation of the biological action [10]. The central region located inside hallow sphere of fullerene designates presence of positive charge which specifies nucleophilic site of the molecule.
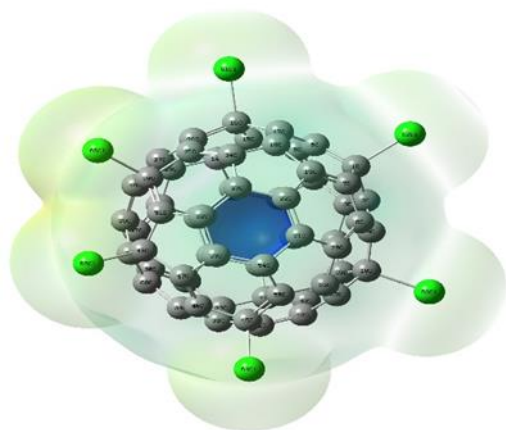

Figure 4: The molecular electrostatic potential of the $C_{60}C_{l6}$ molecule

Conclusions

In the present exploration, the $C_{60}C_{l6}$ molecule was augmented by DFT model B3LYP principle through 6-31G(d,p) basis set. The vibrational frequencies of the molecule and 13C NMR chemical shifts were evaluated with computational efficacy. The FMOs analysis was performed and the related molecular properties calculations were carried out. The calculated energy gap value of the molecule agrees well with the reported bio-active molecules. The clear MEP plot indicates the possibility for preparing water soluble C_{60} which shows anti-HIV agent and low toxicity. Hence, it is hoped that the $C_{60}C_{l6}$ molecule can be used as a promising candidate in the field of carbon nano medicine and pharmaceutical applications.

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