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Molecular Spectroscopic Study of Fulleropyrrolidine Carbodithioic Acid

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This work is conducted to calculate the electronic properties of fulleropyrrolidine carbodithioic acid. This system is subjected to optimization and vibrational frequency calculations at B3LYP/STO-3G. To minimize the computational time, the active part of the structure is recalculated at HF/3-21G*, HF/3-21G**, HF/6-31G**, B3LYP/3-21G*, B3LYP/3-21G**, B3LYP/6-31G** and MP2/6-31G**. A comparison between active structure and total structure indicate a shift in the calculated bands. These may be attributed not only for the modification of the structure, but also for the effect of basis set.

Keywords: Fulleropyrrolidine, HF, B3LYP, MP2 and Vibrational Frequency.

1. INTRODUCTION

Fullerene-based systems are the third allotropic form of carbon (unlike graphite or diamond) which was discovered in 1985 by Kroto.[1] Fullerene [C_{60}] is the most abundant representative of the fullerene family. It is an aromatic structure with a soccer-ball-like shape and also known as buckyball or buckminsterfullerene. Unlike graphite or diamond, C_{60} has high symmetry (icosahedral I_h), and is predicted to be stable due to geodesic and electronic properties inherent in the truncated icosahedral cage structure.[2] In solution, C_{60} is capable of bonding chemically with other organic molecules without changes in their electronic properties which it could reversibly accept up to six electrons.[3–5] Unfortunately, C_{60} is hydrophobic and has poor solubility in common organic solvents so that it needed optimization for its physicochemical properties in addition to a study of its interaction with the biological system in order to use of their potential biological activities.[6, 7]

The unique physical and chemical properties of fullerene-based systems lead many scientists to predict several technological applications in physics and biology. The potential physical applications of fullerene-based systems included superconductors, sensors, catalysts, optical and electronic devices, polymer composites, and high-energy fuels.[8–10] Attempts of using fullerene-based systems in different pharmacological fields had greatly increased together with the studies on its physical and chemical properties. The highly hydrophobic property of fullerene-based system challenged to its use in biological applications. The main potential advantage upon fictionalization of fullerene (by attaching polar functional groups onto the fullerene-based systems) is the substantial increase in their water-solubility. Also, it will increase its bioactivity via maximizing low toxicity and advantageous adsorption, distribution, metabolism and elimination properties. The water-soluble fullerene-based derivatives are particularly important for biological applications, such as HIV-protease inhibition, photo driven DNA cleavage, radical scavenging, Antimicrobial activity etc.[11–20] Fulleropyrrolidines are among the most studied fullerene derivatives, which have been used for numerous biological applications.[21] There are many polar and hydrophilic groups, which are have introduced on the fulleropyrrolidine skeleton via substitution to the nitrogen or carbon atoms of pyrrodine moiety to improve its dissolvability as well as its biocompatibility profile and increase the ability to block HIV protease.[22–25] Nitrogen-containing compounds are used as structural components of pharmaceuticals and agrochemicals due to their high biological activities.[26]

The present computational work is dedicated to the analysis of fulleropyrrolidine carbodithioic acid. HF, B3LYP and MP2 were used to obtain geometrical, physical and electronic properties. Vibrational frequencies are

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calculated for the compound with C_{60} at B3LYP/STO-3G level. Vibrational frequencies are further calculated at higher level of theories for the compound without C_{60}.

2. COMPUTATIONAL DETAILS

All calculations are carried out with the Gaussian 03 program system.[27] The geometry of the studied compound with C_{60} (Fig. 1) is optimized by performing the density functional theory (DFT) at the hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange correlation functional[28–30] with STO-3G basis set. Then, the IR calculations are performed at the same level of theory. Because of the computational limitations, we perform optimizations at higher level on the studied compound without C_{60} (Fig. 2). These higher level optimizations are HF/3-21G*, HF/3-21G**, HF/6-31G**, B3LYP/3-21G*, B3LYP/3-21G**, B3LYP/6-31G** and MP2/6-31G**. The IR spectra are calculated for the whole compound with C_{60} at B3LYP/STO-3G and for the compound without C_{60} at different theoretical methods (HF/3-21G*, HF/3-21G**, B3LYP/3-21G*, B3LYP/3-21G** and B3LYP/6-31G**).

3. RESULTS AND DISCUSSION

3.1. The Model Molecule

To build the model molecule a number of modifications are introduced to fullerene. The first modification is fusion of pyrrolidine ring to C_{60} in order to increase both the solubility of C_{60} and the biological activity of the suggested compound. The second modification is the addition of phenyl ring and two sulfur atoms as chalcogene atoms. These modifications form a structure termed fulleropyrrolidine carbodithioic acid. Figure 1 represents the optimize geometry of fulleropyrrolidine carbodithioic acid at B3LYP/STO-3G level. Because of computational limitations, we re-optimized the suggested compound at higher method levels after omitting C_{60}. These levels are HF/3-21G*, HF/3-21G**, HF/6-31G**, B3LYP/3-21G*, B3LYP/3-21G**, B3LYP/6-31G** and MP2/6-31G**. Figure 2 shows the geometrical structure for the studied compound without C_{60}.

3.2. Electronic Properties

Some calculated energies and total dipole moment for compound with and without C_{60} are calculated at different methods and listed in Table I. These energies are the optimization energy and ΔE (the frontier molecular orbital energy gap as LUMO–HOMO energy difference). The optimization energy and ΔE of whole compound with C_{60} is -3482.8 au and 1.58 eV respectively. Table I shows also the optimization energies of molecule without C_{60} at HF/3-21G*, HF/3-21G**, HF/6-31G**, B3LYP/3-21G*, B3LYP/3-21G** B3LYP/6-31G** and MP2/6-31G**. These optimization energies vary from -1317.5 au at B3LYP/6-31G** to -1304.9 au at HF/3-21G*. There are slight changes in optimization energies, although the methods and basis sets calculations are changed. These results indicate that the C_{60} increase the stability of compound and produce lowest energy than that compound without C_{60}. From Table I, the ΔE values of compounds without C_{60} at HF/3-21G* and MP2/6-31G** are similar and equal to 11.0 eV. While the ΔE value at B3LYP with different basis sets (3-21G*, 3-21G** and 6-31G**) are 5.0 eV. These results of ΔE values due to the HF and MP2 methods are related to each other. MP2 is the first MP level to go beyond the HF treatment by adding higher excitations to Hartree-Fock theory as a non-iterative correction.[31] The MP2 energy is the HF energy plus a correction term (perturbation adjustment) that represents a lowering of energy brought about by allowing the electrons to avoid one another better than in the HF treatment:

$$E_{\mathrm{MP2}} = E_{\mathrm{HF}}^{\mathrm{total}} + E^{(2)}$$

The HF term includes inter-nuclear repulsions, and the perturbation correction $E^{(2)}$ is a purely electronic term. $E^{(2)}$ is a sum of terms each of which models the promotion of pairs of electrons from occupied to unoccupied molecular orbitals.[32] On the other hand, the B3LYP is

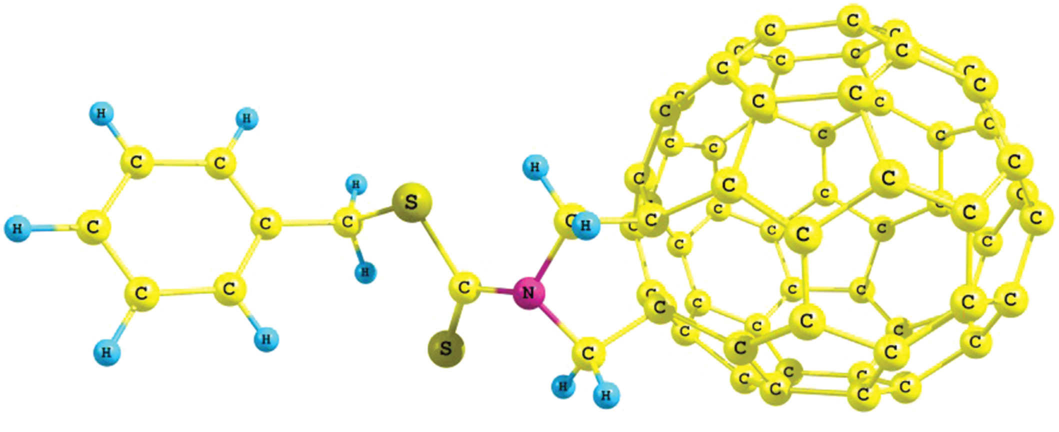


Fig. 1. The optimized structure of fulleropyrrolidine carbodithioic acid which calculated at B3LYP/STO-3G level of theory.

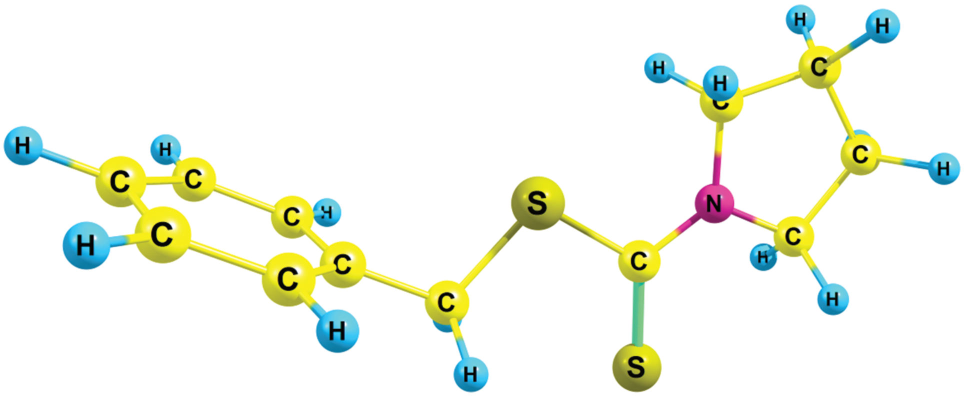
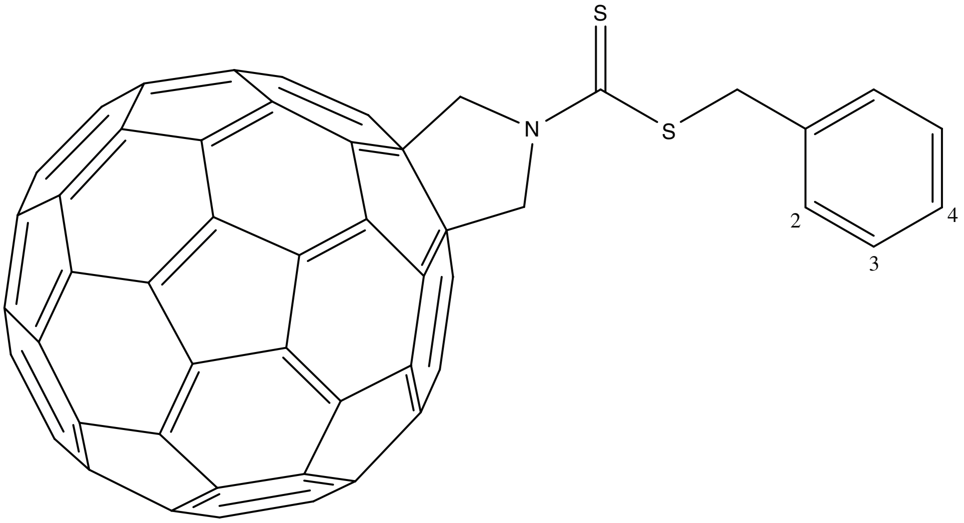


Fig. 2. The structure for fulleropyrrolidine carbodithioic without C_{60}, which is calculated with different level of theories.



Scheme 1. Fulleropyrrolidine-1-carbodithioic acid 2; 3 and 4-substituted-benzyl esters with position ortho, meta and para respectively.

one model of Density Functional Theory (DFT) which is based upon a strategy of modeling electron correlation via general functionalist of the electron density.[22, 32] Table I also represented total dipole moment of compound with and without C_{60} at several theoretical methods. The total dipole moment of whole compound with C_{60} is 1.25 Debye. While the total dipole moment values of compounds without C_{60} are varies from 3.9 Debye (for B3LYP/6-31G**) to 4.3 Debye (for HF/6-31G**). Although the dipole moment is calculated at different methods and basis sets, the change in calculated dipole moment is not large. Due to the hydrophobic and insolubility properties of C_{60}, the dipole moment of whole compound with C_{60} less than that without C_{60}.

3.3. Calculated Infrared Spectra

Table II represents the calculated unscaled infrared spectra of fulleropyrrolidine carbodithioic acid compounds at B3LYP/STO-3G method. The spectrum is assigned by the software itself by performing animation of each normal mode. The characteristic four vibrational modes of C_{60} are located at 1687 cm^{-1}, 1501 cm^{-1}, 805 cm^{-1} and 544 cm^{-1}. The phenyl ring mode is located at 775 cm^{-1}. The band at 3465 cm^{-1} is assigned as the C—H stretching of phenyl ring. The vibrational modes of out and in plane C—H bending are calculated at 1747 cm^{-1} and 1242 cm^{-1} respectively. The pyrrolidine ring has two characteristic

Table I. Some of the calculated energy values in (au), band gap energy ΔE in (eV) and total dipole moment of the studied fulleropyrrolidine carbodithioic acid (with and without C_{60}).

Total dipole moment (Debye)	ΔE (eV)	Optimization energy (au)	Method
The compound with C_{60}			
1.245	1.5843	−3482.8086	HF/STO-3G
The compound without C_{60}			
4.066	11.7799	−1304.8834	HF/3-21G*
4.041	11.7701	−1304.9536	HF/3-21G**
4.303	11.7184	−1312.6497	HF/6-31G**
3.964	4.9977	−1310.9011	B3LYP/3-21G*
3.929	4.9925	−1310.9590	B3LYP/3-21G**
3.863	4.9748	−1317.4690	B3LYP/6-31G**
4.031	11.6819	−1312.6470	MP2/6-31G**

Table II. Calculated unscaled infrared spectra for fulleropyrrolidine carbodithioic acid at B3LYP/STO-3G level of theory.

Band position	Assignment
3465	CH stretch of phenyl ring
3415	CH_2 of pyrrolidine
3403	CH_2
1747	Out of plane CH bend
1687	C—C of C_{60}
1501	C=C of C_{60}
1451	CN of pyrrolidine
1256	C—C atom in CH_2 of pyrrolidine with C atom in C_{60}
1242	In plane CH bend
1458	C=S
805	C—C of C_{60}
775	Phenyl ring mode
544	C—C of C_{60}

vibrational modes; one for CH_2 at 3415 cm^{-1} and the other is assigned for CN at 1451 cm^{-1}. The band located at 1256 cm^{-1} is corresponding to the C–C band, which is coupled between pyrrolidine and C_{60}. The band at 3403 cm^{-1} is assigned for CH_2, finally the characteristic band of C=S is located at 1458 cm^{-1}.

To minimize the computational time higher level of theories are carried out for the present compound without C_{60}. The calculated unscaled infrared spectra for the compound without C_{60} are listed in Table III. HF level of theory is applied with 3-21G* and 6-31G**. B3LYP is further utilized with the respective basis sets 3-21G*, 3-21G** and 6-31G**.

Results of the assigned bands in Table III are shifted clearly toward lower wave numbers as seen for CH bands and toward higher wave numbers as indicated by other bands. This could not be attributed only to the disappearance of C_{60}; this is perhaps due to the poor spectroscopic results of the minimal basis set STO-3G. It is stated earlier that the interaction of a given compound is derived by the type of coordination not attributed to the chain long of its atoms and/or hydrocarbon chains.[33] If we take this into consideration the present structure could be modified with certain substitution in the ester in some places, then the structure could be acted with certain performance in the biological system. The interaction could be happened through these substituted functional groups. Accordingly the interaction of these groups leads the structure toward certain biological application. This could be in agreement with previous findings that interaction depends on coordination type not on the long of the chain. Of course there will be some kinds of shift according to the absence of C_{60} from the structure, but it will not be as high as found in this case which ensure that the shift could be mainly attributed to the effect of basis set more than the absence of C_{60}.

Table III. Calculated unscaled infrared spectra the compound without C_{60} at different theoretical methods (HF/3-21G*, HF/6-31G**, B3LYP/3-21G**, B3LYP/3-21G** and B3LYP/6-31G**).

Band position					
HF		B3LYP			
3-21G*	6-31G**	3-21G*	3-21G**	6-31G**	Assignment
3362	3361	3208	3283	3198	CH stretch of phenyl ring
3276	3218	3030	3080	3010	CH_2 of pyrrolidine
1776	3194	3187	3138	3099	CH_2
1848	1810	1635	1627	1662	Out of plane CH bend
1520	1564	1418	1416	1451	CN of pyrrolidine
1353	1349	1241	1222	1227	C–C
1187	1102	1110	1101	1102	In plane CH bend
1132	1128	1028	1023	1028	C–S
492	497	460	460	496	Phenyl ring mode

4. CONCLUSION AND GENERAL REMARKS

The present study indicates that the investigated spectroscopic analyses of fulleropyrrolidine carbodithioic acid could be achieved by HF and B3LYP with different basis set. A shift is noticed in the calculated bands as the structure is calculated without fullerene owing to the effect of basis set. The present structure could be subjected to substitution to form fulleropyrrolidine-1-carbodithioic acid 2; 3 and 4-substituted-benzyl esters (in position ortho, meta and para respectively) as indicated in Scheme 1. These substitutions could be dedicated for many biological applications especially when the electronic as well as biological properties are changed according to the substituted functional groups. Molecular modeling is necessary for the description of the organization forms of matter. The present study indicate also that molecular modeling at different level of theories help in many areas of science especially for investigating molecules of biological applications. This is in good agreement with previous findings.[34–38]

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