*J. Mater. Environ. Sci. 4 (6) (2013) 867-872*
*ISSN : 2028-2508*
*CODEN: JMESCN*



# Theoretical investigation of substitution effects on the structural and electronic properties of 1-(1-metyl-3-substituted-[1,2,4]selenadiazinyl) pyrrolidinofullerenes

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*Received 3 Feb 2013, Revised 4 July 2013, Accepted 4 July 2013*
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## Abstract
In this work, Quantum mechanical calculations were carried out to study the structural and electronic properties of 1-(1-metyl-3-substituted-[1,2,4]selenadiazinyl) pyrrolidinofullerenes using the HYPERCHEM 7.52 program. Various substituents at the para position of phenyl ring were selected to understand the effect of such structural change on the electronic and structural properties of the molecules. The substituents include: OMe , SMe, N(Me)2, NH2, Me, COMe, F, Cl, and CN. All molecules optimized first using the molecular mechanics force field, and then further geometry optimization was carried out at the PM3 level of semi-empirical molecular orbital theory. The optimized geometries, some of calculated energies, spatial distribution and positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the difference between the HOMO and LUMO orbitals (LUMO–HOMO), known as energy band gap (ΔE), bond lengths, the charges of atoms and electrostatic potential finally were calculated.

*Keywords: Selenium; substitution effects; Fulleropyrrolidine; Hyperchem*

## Introduction
In recent years, there has been a continued interest in fullerene-based systems. These systems are expected to exhibit new interesting physical and chemical properties [1–4]. Many of the important physical, biological and pharmacological applications for such systems have already been demonstrated. The size of C60 molecule is similar to many biologically active molecules, including drugs and steroid hormones [5], therefore it may be efficiently used as a template for creating a variety of biologically active systems. C60 and related substances have shown biological activity, such as HIV-protease inhibition [6,7], DNA photocleavage [8], antibacterial agents [9] and radical scavengers [10].Selenium has been recognized as an essential component of the active site for several enzymes since it is present in the selenocyteine and selenomethionine amino acid derivations. Four glutathione peroxidases (among them cytosolic glutathione peroxidase which is the first established selenoenzyme) protect cells against peroxidative damage by reducing hydrogen peroxide, free fatty acid hydroperoxides, and phospholipids hydroperoxides [11-15] and is related to these species being discussed. Studies even up to seventeen years old depict that the heterocyclic compounds of selenium such as selenirenes, selenophenes, selenadiazoles, selenatriazoles, benzisoselanazolones can have various biological effects. Among such characteristics they are active immunostimulants, inhibitors of enzymes, antioxidants, anti-inflammatory, antitumor, antiviral and antimicrobial agents[16]. Fulleropyrrolidines are among the most studied fullerene derivatives which have been used for numerous biological applications [17,18].
Various organoselenium compounds having a direct Se–N bond have been shown to mimic the active site of GPx. Among such systems is the most promising drug labeled as the Ebselen molecule class [19]. Therefore the covalent binding of the organoselenium compounds having a direct Se–N bond to a fulleropyrrolidine moiety may give rise to new fullerene-based systems which have new chemical and biological properties.
According to a literature survey, it was noted that there is not any report dealing with fulleropyrrolidine-based systems containing substituted [1,2,4] selenadiazinyl group. Therefore, the aim of this work is attracting the

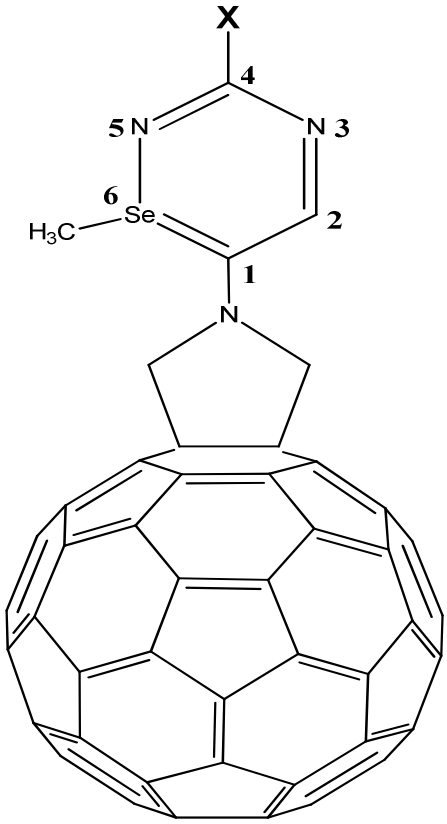
attention to these types of important fullerene derivatives. Various substituents at the 3-position of [1,2,4] selenadiazinyl ring were selected to understand the effect of such structural change on the electronic and structural properties of the molecules. The substituents include: OMe, , SMe, N(Me)2, $NH_2$, Me, COMe, F, Cl, and CN. All molecules optimized first using the molecular mechanics force field, and then further geometry optimization was carried out at the PM3 level of semi-empirical molecular orbital theory.

## 2. Method of calculation

The semi-empirical methods are done on Hyperchem program version 7.5 [20] running on a Windows seven workstation with a Pentium IV PC. The initial geometry ptimization of the studied molecules were performed with the molecular mechanics (MM+) force field [21,22], where the lowest energy conformations are obtained. Further, Geometry optimization was done by performing the semi-empirical molecular orbital theory at the level parametric method (PM3) [23] within restricted Hartree–Fock (RHF) level [24]. The Polak–Ribier algorithm was used for the optimization [25]. The convergence is set to 0.01 kcal/mol.

## 3. Results and discussion

The general chemical structure of the studied molecules is shown in Fig. 1. The optimized geometries are shown in Fig.2. The geometries of the molecules were optimized first by using the molecular mechanics (MM+) force field to obtain the lowest energy structures, then the resulting structures have been optimized by performing the semi-empirical molecule are orbital theory at the level of PM3 of theory.




$X = H , CH_3, OCH_3 , SH_3 , NH_2 , N(Me)_2 , F , Cl , COMe , CN$

**Fig. 1.** The general chemical structure of the 1-(1-metyl-3-substituted-[1,2,4]selenadiazinyl) pyrrolidinofullerenes

Some of selected structural parameters (charges and bond lengths) of the optimized geometries are shown in Table 1.As shown in table 1, there is no intelligible trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar. There is an interaction may be occur between selenium and nitrogen atoms. This interaction may be occurring via the pi-pi interaction. Theoretically the values of Se-N bonds vary from 1.831 to 1.853 nm. These values are agreement with the literature.

**Table (1**) Selected structural parameters (charges and bond lengths) of the studied molecules

| X | H | $CH_3$ | $NH_2$ | $N(CH_3)_2$ | $OCH_3$ | $SCH_3$ | F | Cl | CN | $COCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Bond distance (Å ) | | | | | | | | | | |
| C1-C2 | 1.416 | 1.419 | 1.366 | 1.368 | 1.361 | 1.361 | 1.422 | 1.423 | 1.428 | 1.424 |
| C2-N3 | 1.317 | 1.312 | 1.357 | 1.355 | 1.367 | 1.367 | 1.313 | 1.312 | 1.308 | 1.311 |
| N3-C4 | 1.395 | 1.409 | 1.373 | 1.374 | 1.361 | 1.361 | 1.403 | 1.403 | 1.412 | 1.407 |
| C4-N5 | 1.296 | 1.302 | 1.352 | 1.351 | 1.345 | 1.345 | 1.300 | 1.296 | 1.298 | 1.296 |
| N5-Se | 1.853 | 1.850 | 1.832 | 1.831 | 1.834 | 1.834 | 1.853 | 1.852 | 1.852 | 1.853 |
| Se-C1 | 1.914 | 1.912 | 1.890 | 1.885 | 1.880 | 1.880 | 1.920 | 1.917 | 1.918 | 1.919 |
| Bond angles (° ) | | | | | | | | | | |
| C1-Se-N5 | 105.7 | 105.9 | 104.2 | 104.3 | 103.8 | 103.8 | 106.8 | 106.3 | 106.8 | 106.0 |
| N5-C4-N3 | 127.3 | 125.6 | 129.8 | 128.0 | 131.5 | 131.5 | 130.8 | 127.7 | 126.9 | 126.4 |
| C2-C1-Se | 111.0 | 110.6 | 116.6 | 115.8 | 117.5 | 117.5 | 111.3 | 110.6 | 109.8 | 109.7 |
| Electronic charges | | | | | | | | | | |
| N | 0.264 | 0.270 | 0.120 | 0.123 | 0.066 | 0.068 | 0.285 | 0.284 | 0.311 | 0.296 |
| N3 | -0.165 | -0.153 | -0.345 | -0.333 | -0.328 | -0.291 | -0.132 | -0.125 | -0.098 | -0.119 |
| C4 | 0.016 | 0.035 | 0.096 | 0.130 | 0.247 | 0.037 | 0.143 | -0.039 | 0.122 | -0.048 |
| N5 | -0.268 | -0.270 | -0.396 | -0.393 | -0.356 | -0.325 | -0.283 | -0.255 | -0.233 | -0.247 |
| Se | 0.313 | 0.313 | 0.498 | 0.499 | 0.547 | 0.537 | 0.326 | 0.316 | 0.310 | 0.298 |

The nitrogen atom of fulleropyrrolidine indicates positive charges. Their magnitudes varying from 0.066 to 0.311. The values of charges had shown a slight effect by the change in the type of the chemical group in the [1,2,4] selenadiazinyl ring. The two nitrogen atoms of [1,2,4] selenadiazinyl ring indicate negative charges. The negative charges of N3 varying from -0.098 to -0.333, while for N5 the magnitudes varying from -0.39 to -0.396. The calculated charges of selenium atom indicate excess charges varying from 0.298 to 0.547.

As shown in Fig.2, the optimized structures indicate that the [1,2,4] selenadiazinyl rings that bound to fulleropyrrolidine are not planar in both of un-substituted and substituted molecules with electron-withdrawing groups, where there is bent in the position of selenium atom. This bent in the ring may be decrease the aromatic character of the ring. In contrast the substituted molecules with donating groups yield planar [1,2,4] selenadiazinyl rings this may be due to electron donation of these groups will consolidate the conjunctions of pi-pi interaction of rings. Based on these results the donating substitutes may be making these molecules more stable.

Table 2 presents some of calculated energies and dipole moment values of the optimized geometries. For these calculations, we obtained the smallest value of calculated binding energy for Cl substituent. The $N(Me)_2$ substituent has the largest calculated binding energy. When we compute for the relative energy with respect to the un-substituted molecule, we obtained the values 283.3, 174.6, 723, 379.9, 343.7, 12.3, -15.7, 193.4 and 546.6 kcal $mol^{-1}$for the substituents CH3 , NH2 , N(CH3)2 , OCH3 , SCH3, F, Cl, CN and COCH3 respectively. On the other hand, the heats of formation of all molecules are endothermic and there values are closer to the experimental and theoretical values of fullerenes [26]. The calculated dipole moment values of all molecules (μ), Table 3, indicate that they are polar, where the covalent binding of fulleropyrrolidine to the [1,2,4] selenadiazinyl rings allows for the increasing of the polarity of these complexes. This means that these complexes may be more soluble in the polar and H-bonding solvents such as acetone, tetra hedrofuran or methanol.

**Table(2)** MO energy of the HOMO, LUMO levels, energy band gap ΔE (in eV) dipole moment , heat of formation and binding energy

| Value | H | $CH_3$ | $NH_2$ | $N(CH3)_2$ | $OCH_3$ | $SCH_3$ | F | Cl | CN | $COCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **HOMO** | -7.694 | -7.631 | -8.445 | -8.252 | -8.270 | -8.252 | -7.952 | -7.810 | -8.038 | -7.817 |
| **LUMO** | -3.294 | -3.285 | -3.087 | -3.096 | -3.087 | -3.113 | -3.376 | -3.344 | -3.432 | -3.332 |
| **ΔE** | 4.400 | 4.346 | 5.358 | 5.156 | 5.183 | 5.139 | 4.576 | 4.466 | 4.606 | 4.485 |
| **μ** | 4.610 | 4.284 | 2.333 | 2.296 | 2.053 | 2.293 | 7.102 | 5.939 | 9.051 | 5.191 |
| **ΔH** | 839.11 | 830.97 | 829.62 | 831.4 | 793.91 | 836.94 | 793.58 | 831.72 | 877.52 | 798.01 |
| **Binding Energy** | -11301.8 | -11585.1 | -11476.4 | -12024.8 | -11681.7 | -11645.5 | -11314.1 | -11286.1 | -11495.2 | -11848.4 |

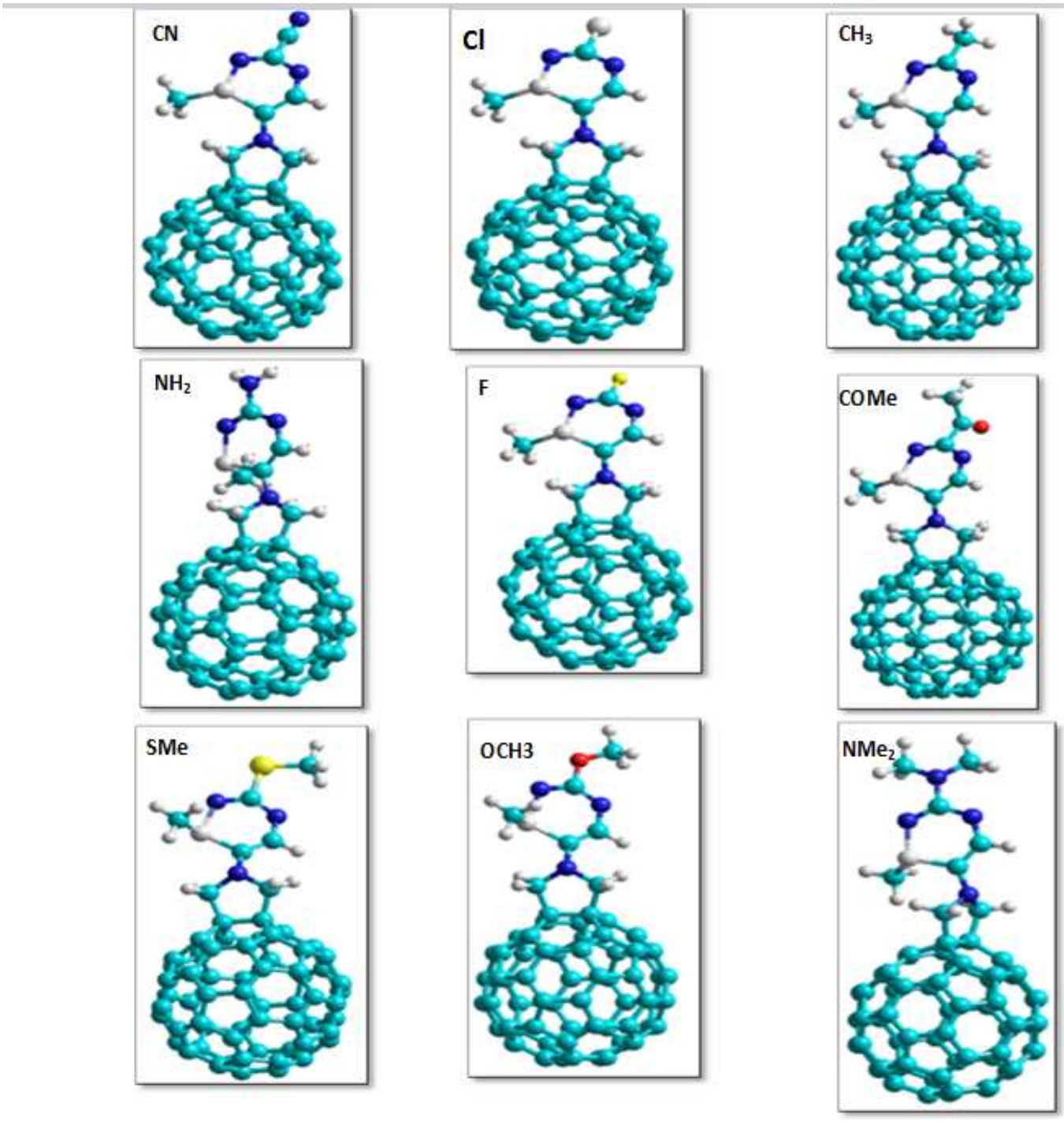



**Fig.2.** The optimized geometries of the 1-(1-metyl-3-substituted-[1,2,4]selenadiazinyl) pyrrolidinofullerenes

The molecular orbitals energy: the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) are present in table 2. The values of the difference between the HOMO and LUMO orbitals (LUMO-HOMO), known as energy band gap (ΔE), are also given in Table 2. The band gaps of unsubstituted and the methyl substituent are similar. The other values are greater that the un-substituted molecule. The spatial distributions of HOMO and LUMO molecules are shown in Fig. 3. In general, LUMO orbitals for all molecules are localized on the fulleropyrrolidine side, while the HOMO orbitals are localized on the substituted [1,2,4] selenadiazinyl group.

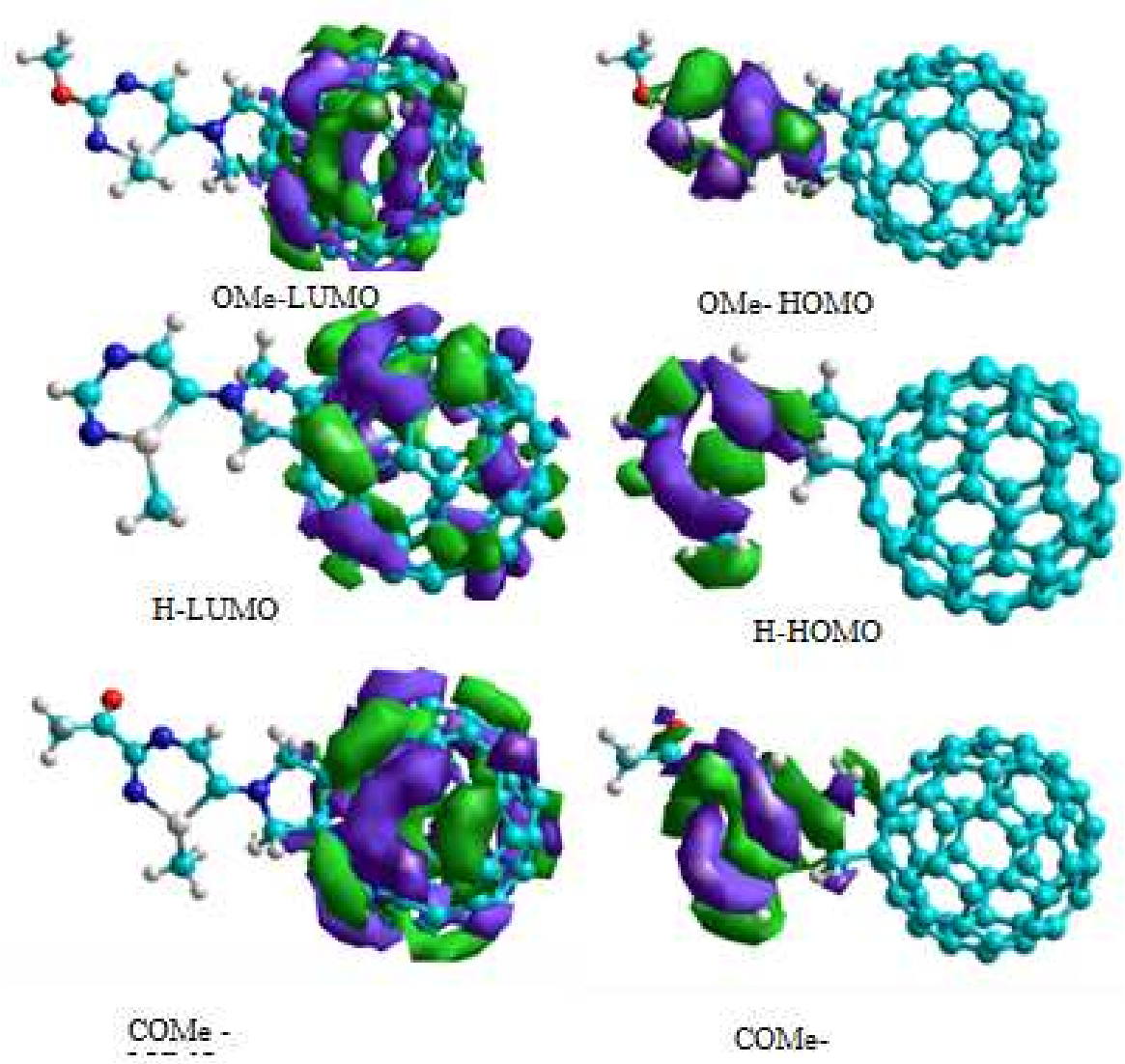



**Fig. 3.** Molecular orbital spatial distribution for the HOMO and LUMO of OMe, H, COMe molecules

## Conclusion

Quantum mechanical calculations were carried out to study the structural and electronic properties of 1-(1-metyl-3-substituted-[1,2,4]selenadiazinyl) pyrrolidinofullerenes using the HYPERCHEM 7.52 program and the results of investigated indicate that the optimized structures of the [1,2,4] selenadiazinyl rings are not planar in and it's bending depend on the type of substituents group. Also, the study indicates that the studied molecules are polar and may be soluble in H-bonding solvents. Finally, shown that the LUMO orbitals for all molecules are localized on the fulleropyrrolidine side, while the HOMO orbitals are localized on the substituted [1,2,4] selenadiazinyl group.

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(2013) ; www.jmaterenvironsci.com