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# Theoretical investigation of the electronic structure of 1-(3,4; 3,5 and 3,6-bis-selenocyanato-phenyl) pyrrolidinofullerenes

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## Abstract

The electronic structures and geometries of 1-(3,4; 3,5 and 3,6-bis-Selenocyanato-phenyl) pyrrolidinofullerenes were investigated theoretically using Density Functional theory at the B3LYP/3-21G* and B3LYP/6-31G* levels of theory. On all levels of theory the *ortho* isomer is predicted to be the most stable. The obtained optimized geometries, electronic properties and energetics of structural variables are discussed.

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## 1. 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 $C_{60}$ 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. $C_{60}$ 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 and some of its organic derivatives have been shown to also exhibit biological activity. Many of organoselenium compounds have shown biological activity in numerous fields such as in the development of antibacterial, antiviral, antifungal, antiparasitic, antiinflammatory and antihistamine agents [11]. Organoselenium compounds which have selenocyanate groups show promising results in a variety of chemopreventative studies [12]. Some compound of this class studied earlier were Se-methylselenocysteine, *p*-methoxybenzeneselenol, benzylselenocyanate and 4-phenylenebis-(methylene)selenocyanate. These compounds have been used mostly as chemopreventive agents for human cancer and usually give good results against breast cancer [13–15].

$C_{60}$, as all fullerenes, is highly hydrophobic and insoluble, which causes significant problems in fullerene applications in biology and medical. Thus, several synthetic methodologies have been developed to functionalize the fullerene with polar functional groups to increase its dissolvability to water and polar solvents [16–18]. One of the most important fullerene functionalization is the formation of *N*-alkyl-fulleropyrrolidines by 1,3-dipolar cycloaddition of azomethine ylides to $C_{60}$ [19]. On the other hand, the selenocyanate group is also a very polar group.

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Therefore the covalent binding of a phenyl ring containing selenocyante group to a fulleropyrrolidine moiety may gave rise to new fullerene-based systems which have new chemical and biological properties.

In this work we have investigated theoretically 1-(3,4; 3,5 and 3,6-bis-selenocyanato-phenyl)pyrrolidinofullerenes for the first time by performing Density Functional Theory (DFT) calculations. These correspond to *ortho* (1-(3,4-bis-selenocyanato-phenyl) pyrrolidinofullerenes), *meta* (1-(3,5-bis-selenocyanato-phenyl)pyrrolidinofullerenes), and *para* (1-(3,6-bis-selenocyanato-phenyl)pyrrolidinofullerenes) isomers which are shown in Fig. 1.

## 2. Computational details

All theoretical calculations in this work were performed using the computational methods implemented in the GAUSSIAN03 package [20]. The geometries of the compounds were optimized at the B3LYP/3-21G* and B3LYP/6-31G* levels of theory, however, frequencies were only computed using the B3LYP/3-21G* method [21,22]. Due to computational limitations we were unable to perform a B3LYP/6-31G* frequency calculation. In addition, NMR constants were evaluated using the IGAIM method using the geometries obtained at the B3LYP/6-31G* level of theory [23]. Moreover, the ONIOM method [24] with the fullerene described using the UFF force-field [25] was used to compare geometries, energies and frequencies to the full DFT optimizations. In our recent investigations on similar Se containing systems [26] we have found that the DFT-B3LYP method is able to accurately predict experimental parameters [27].

## 3. Results and discussion

The optimized B3LYP/6-31G* structures for the *ortho*, *meta* and *para* isomers are presented in Fig. 1. In the figure, the yellow spheres are C atoms, blue spheres are H atoms, red spheres are N atoms, and orange spheres are Se atoms. In addition B3LYP/3-21G* spectra for the three molecules are also presented.

Fig. 1 also shows the bond lengths and bond angles for each of the molecules. The general geometries of all three isomers are very similar (in all three computational approaches used), the major difference being the geometrical structure of the *ortho* structure. In this structure we see that the Se–Se distance (orange spheres in the figure) is ~3.2 Å, with a bond order between them of approximately 0.004. Interestingly, this is very similar to the Se–O bond order in *ortho* 2-Se-(2-methyl-2-propenyl)-1-benzoic acid [26] where the distance was 3.21 Å with a bond order of 0.0005. In the *para* and *meta* isomers the Se–Se distances are 5.8 and 6.6 Å, respectively. These bond distances are quite significant and yield bond orders essentially equal to 0.0. Therefore, we do not expect any stabilization of these structures resulting from Se–Se interactions. Generally speaking, the bond order is a relative value that is computed based on Natural Bond Orbital (NBO) Analysis [28,29] that computes the interactions between various atoms in the molecule. These values are relative, and are meant to be analyzed quantitatively. Values of 0.0 and those below 0.001 signify that there is minimal interactions between the atoms of interest.

The calculated spectra suggest that the *para* isomer should have more intense modes, particularly in the 500–900 $\text{cm}^{-1}$ and 1200–1500 $\text{cm}^{-1}$ range. The modes in the first range correspond primarily to the vibrations of the five-membered ring attached to the fullerene. The latter vibrations correspond to internal motions in the six-membered phenyl ring attached to the pyrrolidinofullerene group. The most intense peaks in all the systems correspond to the CH rock mode of the six-membered phenyl ring, which can be seen at 1615 $\text{cm}^{-1}$. The basic vibrational modes are presented and assigned in Table 1. It is also interesting to note that the ONIOM method, while much less expensive from the computational point of view, gives very similar vibrational spectra with the maximum discrepancy of 35 $\text{cm}^{-1}$.

In addition to calculation of the vibrational modes for this molecule, we have also calculated IGAIM NMR shifts. While there are many shifts that can be discussed we will focus on the Se shifts since these are the ones that can be used to identify the molecules. For the *ortho* structure we should get two $^{77}$Se shifts at 1494 ppm, and 1582 ppm, that correspond to the first and second Se–CN groups. The higher second value is probably due to the interaction of the first Se–CN group with the ring since it has the CN group pointing away from the plane which causes a change in the shift due to its interactions with the carbon atoms of the phenyl ring. For the *meta* structure one should observe two equivalent shifts at 1507 ppm. As for the final *para* structure we should observe at 1491 ppm and1573 ppm, the latter being higher due to its closer proximity to the N atom of the five-membered ring (Se–N distance of 3.18 Å). It is interesting to note that while in the *ortho* isomer the Se–Se interaction causes the $^{77}$Se shifts to lower, the Se–N interaction in the *para* structure is stronger as can be seen by the slightly lower shift (by ~3 ppm). This supports our initial assertion of strong Se interactions with electronegative atoms [26].

Table 2 has the HOMO/LUMO gaps, total energies, relative energies and corrected enthalpy differences. Table 3 shows the thermodynamic properties for the molecules in Fig. 1: entropy, heat capacity at constant pressure and enthalpy content at three different temperatures calculated using B3LYP/3-21G* frequencies. The fits were performed according to the equations implemented by the National Institute of Standards and Technology (NIST) [27]. For these calculations, the correct thermal energies shown in Table 2 ($E^{\text{corr}}$) are computed using the basic thermodynamic relationship, where the free energy changes are described as: $\Delta H - TS$, where $\Delta H$ is the enthalpy change, $T$ is the temperature, and $S$ is the entropy.

The results suggest that the HOMO/LUMO gap for the *meta* structure is the highest, while *para* structure has the