

# Investigation of ethene-bisfullerenes and their derivatives as photovoltaic system $[C_{28}X_1=X_2C_{28}]$ : Semiempirical study

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## ABSTRACT

A computational study of  $C_{28}X_1=X_2C_{28}$  complexes using semiempirical methods (AM1 and PM3) was presented. The difference between the most stable and the least stable was about 50 Kcal/mol for PM3 and 30 Kcal/mol for AM1. The study of the frontier orbitals in the ground state revealed that the LUMO energy levels of the  $C_{28}X_1=X_2C_{28}$  complexes for  $X_2=C$  compare reasonably well with that on the  $C_{28}$  fullerene cage (acceptor moiety). The HOMO energy levels of these complexes ( $X_1=Si, Ge; X_2=C$ ) were quite similar. The LUMO and LUMO+1 localized on the  $C_{28}$  cage subunit on the  $X_2$  ( $X_2=C$ ) behave as acceptor of electron, while HOMO and LUMO+3 which are localized on the  $C_{28}$  cage on the  $X_1$  side ( $X_1=Si$  and  $Ge$ ) behave as electron donor.

**Key words:** Ethene-bis-fullerenes, photovoltaic system, complexes.

## INTRODUCTION

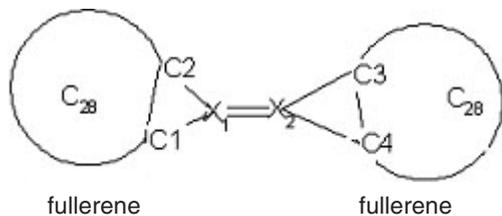
The study of stabilizing multiple bonds involving heavier main group elements was initially besieged by several road-blocks and controversies, amongst is the double bond rule which states that those elements with a principal quantum number equal to or greater than 3 are not capable of forming multiple bonds because of considerable Pauli repulsion between the inner electrons<sup>1</sup>. However, with the collapse of this rule in 1981 following the synthesis and isolation of stable compounds containing Si=Si and Si=C<sup>2,3</sup> and other similar compounds with elements such as Ge, Sb, Se, As, Si, P, Pb and Te have been elucidated by simple crystal X-ray diffraction<sup>4</sup>.

A quarter of a century ago, possibility of an organic molecule that would be capable of realizing electronic devices was theoretically demonstrated<sup>5</sup>. Since then, a remarkable series of

experimental and theoretical investigations have shown the feasibility of many devices, such as a molecular rectifier, a resonant tunneling diode, a connection between a molecule and an electrode and an organic solar cell<sup>6,7</sup>. Electron transfer phenomena in organic semiconductors have been the backbone in designing donor-acceptor systems. Various supramolecular systems based on donor-acceptor pairs with fullerenes as electron acceptors have been proposed. Such systems include polymer- $C_{60}$ <sup>8</sup>, phthalocyanine- $C_{60}$ <sup>9</sup>, free-base porphyrins- $C_{60}$ , zinc porphyrins- $C_{60}$ <sup>10</sup>, Chlorin- $C_{60}$ <sup>11</sup>, Bis-porphyrin- $C_{60}$ <sup>12</sup>, Bis-zinc porphyrins (D)-pyridine<sup>13</sup> and TTF- $C_{60}$  and TTF-S- $C_{60}$ <sup>14</sup>.

Fullerenes are good  $\pi$ -electron acceptor without changes the electronic properties of the organic molecules which they are bonded<sup>11</sup>. The purpose of this work is to investigate the stable geometric and electronic structures of the fullerenes with main group elements involving double bonds

inform of the modeled  $C_{28}X_1=X_2C_{28}$  (where  $X_1, X_2 = C, Si$  and  $Ge$ ) complexes.



**Fig. 1: Schematic diagram of ethene-bisfullerenes (for  $X_1, X_2 = C, Si$  or  $Ge$ )**

### Computational method and Modeling

The optimized geometries and energetics (in terms of heat of formation of the modeled complexes) of all the structures were obtained with semiempirical methods at AM1 and PM3 levels<sup>15</sup>. All calculations were performed using Spartan 04 essential program<sup>16</sup>. After the optimization, we investigated the localization of the frontier orbitals. The spatial distribution of the frontier orbitals (HOMO and LUMO) provide a strategy by which the electronic properties of the complexes could be understood.

## RESULTS AND DISCUSSION

### Geometry and Stability

Full geometry optimization of  $C_{28}X_1=X_2C_{28}$  complexes by AM1 and PM3 levels yielded three different conformations as shown in Figure 2. The complexes gave a chair conformation for  $X_1, X_2=Si$  and  $Ge$ , Cisoid conformation for  $X_1=Si$  and  $X_2=Ge$ , while in others the  $X_1=X_2$  bond was more or less distorted. The  $X_1=X_2$  bond lengths for  $C_{28}X_1=X_2C_{28}$  complexes (Figure 1) are 2.570Å ( $X_1, X_2=Ge$ ) to 1.327Å ( $X_1, X_2=C$ ) with PM3 and 2.028Å ( $X_1, X_2=Ge$ ) to 1.327Å ( $X_1, X_2=C$ ) with AM1. The values of bond lengths calculated with AM1 for  $X_1=Si; X_2=C$  and  $X_1=Ge; X_2=Si$  are closer to the experimental values determined by single crystal X-ray diffraction method for  $R_2X_1=X_2R_2$  systems (4). Generally, bond lengths for  $X_1=X_2$  in  $C_{28}X_1=X_2C_{28}$  complexes are longer when  $X_1=X_2$  than that of  $X_1 \neq X_2$ . The bond angles calculated with PM3 for  $X_2X_1C_1$  are 116.33° - 156.48° and 110.95° - 158.53° for  $X_1X_2C_4$ . The  $C_1X_1C_2$  and  $C_3X_2C_4$  are 99.74° ( $X_1, X_2=C$ ) to 44.61° (for  $X_1=Si$  and  $X_2=Ge$ ) as shown in Table 2, indicating that distortions are not on the fullerenes cage.

**Table 1: Heats formation,  $H_f$  (Kcal/mol), energy band gaps,  $\Delta$  (eV) and mulliken charges calculated at PM3 and AM1(in bracket) levels**

$X_1=X_2$	$H_f$	$\Delta$	Mulliken charges		Dipole moments
			$X_1$	$X_2$	
C=C	1593.69 *(1849.74)	5.26 (5.30)	0.041 (0.044)	0.041 (0.044)	0.09
Si=Si	1590.71 (1861.69)	5.01 (5.18)	0.399 (0.553)	0.404 (0.554)	0.65
Ge=Ge	1628.37 (1835.62)	5.08 (5.19)	0.814 (1.932)	0.819 (1.208)	1.11
Si=C	1595.77 (1835.99)	4.96 (5.10)	0.722 (1.377)	-0.266 (-0.554)	1.51
Ge=C	1624.95 (1865.51)	4.97 (4.89)	0.142 (0.869)	0.085 (-0.273)	1.93
Si=Ge	1588.40 (1849.76)	5.05 (4.98)	0.612 (1.593)	-0.089 (-0.852)	1.29

The heats of formation from PM3 calculations for  $C_{28}X_1=X_2C_{28}$  complexes almost double that of  $C_{28}$  fullerene (Table 2). The most stable complex is that of Si=Ge (for  $X_1=Si$  and  $X_2=Ge$ ) with 1588.40 Kcal/mol and the least stable is that of Ge=Ge (for  $X_1, X_2=Ge$ ) with 1628.37Kcal/mol. The difference between the most stable and the least stable is about 50Kcal/mol for PM3 and 30Kcal/mol for AM1, this indicates that these complexes would be relatively stable when they are eventually synthesized. However, the order of stability predictions of both PM3 and AM1 are not in agreement. For instance, the most complex by AM1 prediction is the least stable by PM3 calculations (Table 1).

### Electronic Structures

The electronic structures of these complexes are discussed as difference in HOMO and LUMO energy ( $\text{\AA}$ ) as shown in Table 2. These complexes presented lower energy band gaps as

compared to  $C_{28}$  (5.34eV) and  $C=C$  ( $X_1, X_2=C$ ; 5.26eV) as calculated by PM3. The  $\text{\AA}$  calculated for  $C_{28}X_1=X_2C_{28}$  complexes when  $X_1=X_2$  are higher than when  $X_1 \neq X_2$ . The order of band gaps does not coincide with the order of stability as predicted by both AM1 and PM3. For instance, Si=C ( $X_1=Si$ ;  $X_2=C$ ) and Ge=C ( $X_1=Ge$ ;  $X_2=C$ ) are second most stable and least respectively have energy band gap of  $\sim 4.96\text{eV}$  which negate general belief that the higher the stability the higher the band gap (17-20). The Mulliken charges on  $X_1$  and  $X_2$  for the complexes when  $X_1=X_2$  are all positive, and for  $X_1 \neq X_2$  are positive on  $X_1$  and negative on  $X_2$  (Table 2). This indicates that  $C_{28}X_1=X_2C_{28}$  complexes when  $X_1 \neq X_2$  lead to the formation of polar covalent bonds.

### Frontier Molecular Orbitals

Molecular orbital analysis are performed using PM3 method in order to gain insight into the intermolecular interactions through  $X_1=X_2$  double bond of the complexes as presented (Figure 3). It

**Table 2: Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) calculated at PM3 and AM1 (in parenthesis) levels**

	C=C	Si=Si	Ge=Ge	Si=C	Ge=C	Si=Ge
X1=X2	1.327 (1.327)	1.822 (2.019)	2.570 (2.028)	1.590 (1.583)	1.706 (1.750)	1.937 (2.053)
X1-C1	1.463 (1.462)	1.804 (1.794)	2.015 (1.930)	1.799 (1.776)	1.981 (1.969)	1.793 (1.761)
X1-C2	1.463 (1.461)	1.806 (1.798)	1.463 (1.936)	1.800 (1.782)	1.974 (1.969)	1.796 (1.769)
C1-C2	2.237 (2.234)	1.596 (1.622)	1.576 (1.609)	1.610 (1.645)	1.527 (1.587)	1.598 (1.650)
$X_2$ -C3	1.463 (1.462)	1.803 (1.794)	2.013 (2.017)	1.458 (1.455)	1.467 (1.452)	2.007 (2.016)
$X_2$ -C4	1.463 (1.461)	1.804 (1.798)	2.019 (2.008)	1.457 (1.452)	1.469 (1.451)	1.997 (2.010)
C3-C4	2.237 (2.234)	1.598 (1.622)	1.576 (1.524)	2.216 (2.222)	1.610 (2.225)	1.520 (1.529)
$X_2X_1C1$	130.29 (130.30)	150.28 (153.13)	129.94 (155.58)	153.82 (152.98)	156.48 (156.26)	151.64 (153.39)
$X_1X_2C4$	129.97 (130.01)	150.03 (153.32)	133.70 (157.76)	130.53 (130.20)	146.53 (129.72)	153.36 (158.90)
C1 $X_1$ C3	99.74 (99.98)	52.51 (53.69)	45.94 (49.20)	53.14 (55.08)	45.44 (47.52)	52.89 (55.74)
C2 $X_2$ C4	99.74 (96.68)	52.57 (53.69)	46.01 (44.49)	98.42 (99.68)	66.49 (100.06)	44.61 (44.66)

is interesting to note that the LUMO energy levels of the  $C_{28}X_1=X_2C_{28}$  complexes for  $X_2=C$  compare favourably well with that on the  $C_{28}$  fullerene cage (acceptor moiety) (8-15). The HOMO energy levels of these complexes ( $X_1=Si, Ge; X_2=C$ ) are quite similar.

Figure 4 shows the spatial orientation diagram for the molecular orbital spatial distribution

for the HOMO and LUMO energy levels. Furthermore, LUMO+1, LUMO+2 and LUMO+3 energy levels of  $C_{28}X_1=X_2C_{28}$  complexes for  $X_1=Si, Ge; X_2=C$  are studied. It was observed that LUMO and LUMO+1 localized on the  $C_{28}$  cage subunit on the  $X_2$  side ( $X_2=C$ ) behave as acceptor of electron, while HOMO and LUMO+3 localized on the  $C_{28}$  cage on the  $X_1$  side ( $X_1=Si$  and  $Ge$ ) behave as electron donor. The same tendency for localization of the

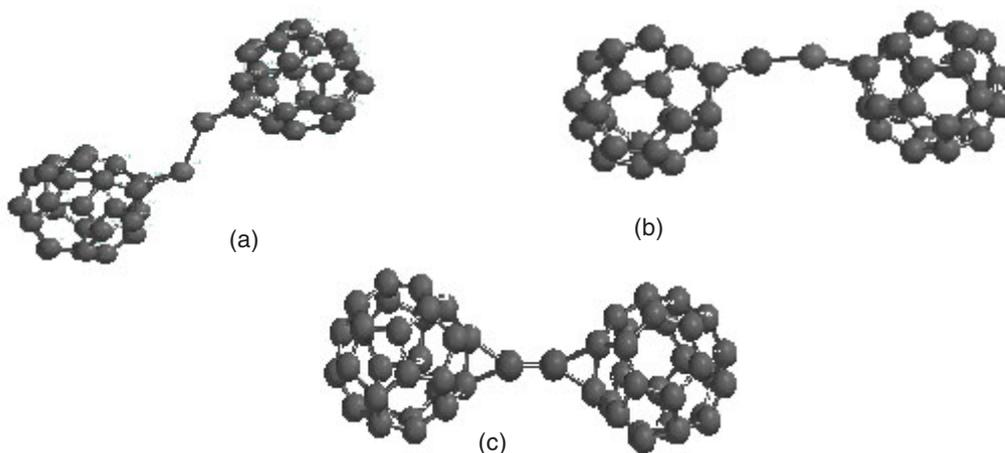


Fig. 2. Isomers observed by PM3 optimization: a) trans isomer for  $Ge=Ge$ , b) cisoid isomers for  $Si=Ge$  and c) undistorted geometry for  $Si=Si, C=C, Si=C$  and  $Ge=C$

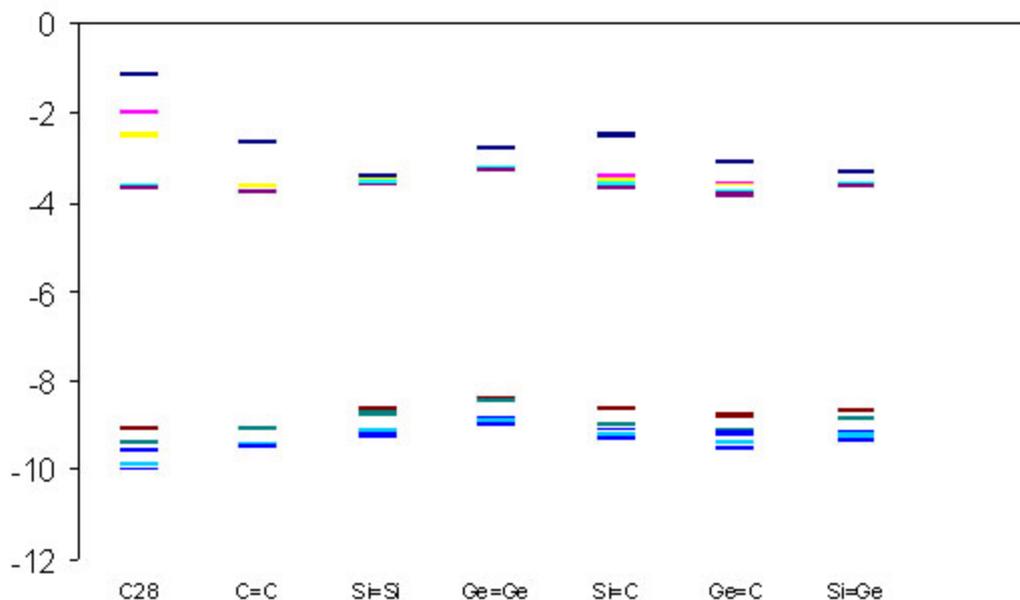
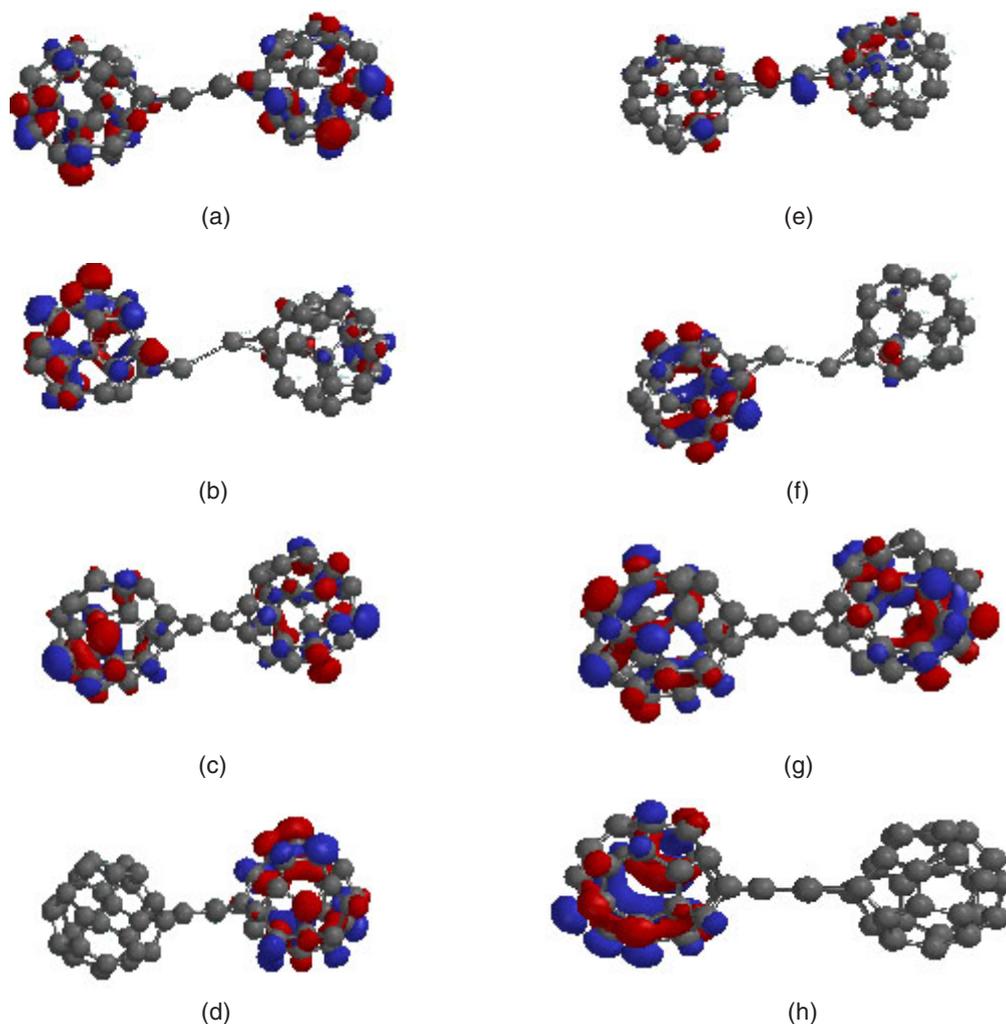


Fig. 3: Schematic molecular orbital diagram of the five highest occupied and five lowest unoccupied orbital levels for the  $C_{28}X_1=X_2C_{28}$  complexes



**Fig. 4: Molecular orbitals spatial orientation for the HOMO and the LUMO for  $C_{28}X_1=X_2C_{28}$  complexes; a) HOMO for  $X_1, X_2=Si$ , b) HOMO for  $X_1=Ge, Si; X_2= Si, Ge$  and  $C$ , c) HOMO for  $X_1, X_2=C$ , d) HOMO for  $X_1= Si, Ge; X_2=C$ , e) LUMO for  $X_1, X_2=Si$ , f) LUMO for  $X_1=Ge, Si; X_2= Si, Ge$  and  $C$ , g) LUMO for  $X_1, X_2=C$ , h) LUMO for  $X_1= Si, Ge; X_2=C$**

frontier orbitals has been reported for donor-fullerene (acceptor) supramolecular systems (10-12). Therefore these systems involving two fullerenes with careful selection of  $X_1$  and  $X_2$  can behave as donor-acceptor systems which could serve as new materials for photovoltaic devices.

#### CONCLUSION

Semi empirical methods (AM1 and PM3) were used to model fullerene  $X_1=X_2$  fullerenes

complexes. The energy band gaps were lower than that of  $C_{28}$  fullerene cage. The electron transport in these systems was proposed based on the spatial distribution of the frontier orbitals (HOMO and LUMO). It was seen that the HOMOs are localized on the fullerene on the  $X_1$  ( $X_1=Si$  and  $Ge$ ), the LUMOs are localized on the fullerene on the  $X_2$  ( $X_2=C$ ). If  $X_1$  and  $X_2$  are carefully selected from the main group elements, fullerenes can be used as donor-acceptor systems.

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