



Switching behavior of an actuator containing germanium, silicon-decorated and normal C₂₀ fullerene

Seyyed Amir Siadati,^{a,b,*} Solmaz Rezaadeh^c

^a Department of Chemistry, Tofiqh Daru Research and Engineering Pharmaceutical Company, Tehran, Iran

^b Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

^c Department of Chemistry, Payambar-e-Azam Educational Complex, Islamic Azad University, Tehran, Iran

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ABSTRACT

NANO MACHINES which are of the capital aims of many advanced research projects are complexes of different devices and actuators that each of them plays a pre-defined role in the overall unit. Nano sensors, nano batteries, nano engines, and nano switches, which contain the most interesting devices for researchers in the related field, are being under consideration for the advance research projects of nano technology. Therefore, in the present project, we have made attempts to reveal the switching behavior of the benzene-C₂₀ fullerene system *via* a 1,5-sigmatropic shift of the germanium, and silicon-decorated C₂₀ fullerene carbon atoms on the benzene ring.

The results showed that in the case of the silicon-decorated C₂₀ fullerene, changing the system from state A to state B *via* changing the temperature (24.7 kcal mol⁻¹) is much easier than that of germanium-decorated (27.5 kcal mol⁻¹) or normal C₂₀ fullerene (37.8 kcal mol⁻¹). It seems that further studies on this phenomenon, might be beneficial for designing the thermal sensor systems, and energy storage devices.

1. Introduction

The alkyl and hydride shifts are types of the sigmatropic shifts which have been discovered and used in synthesizing of many natural products during daces [1,2]. The sigmatropic is also a branch of pericyclic reactions which are of the most interested organic reactions [3]. In fact, the sigmatropic is a reaction which results in breaking a one σ -bond and forming another in an uncatalyzed or recently catalyst assisted intramolecular process [4]. A wide range of different types sigmatropic reactions were found and then used for further application, which carbon shifts and hydride shifts are of those sigmatropics [1]. These intramolecular reactions may proceed under thermal or light irradiation conditions and they are allowed or forbidden for passing of the certain reaction channels [5,6]. Being allowed or forbidden in passing the certain reaction channels could be determined by symmetry of the frontier molecular orbitals [7]. These predications follow the *Woodward-*

Hoffmann rules about the pericyclic reactions [8], and also the hypothesis of the *Mobius topology* [9].

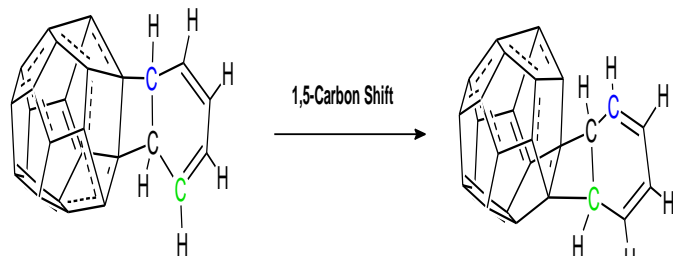
A [1,5] shift involves the migration of apart of a molecule (especially hydride or alkyl group) from atom 1 to the atom 5, of a π system. Hydrogen has been shown to shift in both cyclic and open chain π network, while; it seems the [1,5] alkyl shifts in an open-chain system is not favorable [10]. However, many reports revealed about rate preferences for [1,5] alkyl shifts in cyclic systems [11].

The [1,5] alkyl shift in absence of the light irradiation must occur in an antarafacial migration (which are impossible for transformations) or the carbon center takes under inversion. But when the light is irradiated to the system and the π electrons of the system become excited, the pattern of the HOMO orbital transforms to LUMO and thus, the [1,5] alkyl shift would be possible [12].

In this work, we have investigated the possibility of [1,5] sigmatropic shift of C₂₀ fullerene carbon atoms on the benzene ring, both, in absence and in presence of light

* Corresponding author. chemistry_2021@yahoo.com

irradiation (Scheme 1). The results showed that this sigmatropic process is favorable under light irradiation with triplet excited state. Moreover, the results of the FMO calculations and the DOS plots reveal about the possibility of using this system for designing a nano-sized sensor [13-15].



Scheme 1. The 1,5-sigmatropic shift of C₂₀ fullerene carbon atoms on the benzene ring

In this work, we have examined the switching behavior of the benzene-C₂₀ fullerene system *via* a 1,5-sigmatropic shift of the germanium, and silicon-decorated C₂₀ fullerene carbon atoms on the benzene ring. The results of the work showed that in the case of the silicon-decorated C₂₀ fullerene, changing the system from state A to state B, by changing the temperature (24.7 kcal mol⁻¹) is much easier than that of germanium-decorated (27.5 kcal mol⁻¹) or normal C₂₀ fullerene (37.8 kcal mol⁻¹). Following this phenomenon, may be useful for consideration this system for semiconductor sensor system, and also energy storage applications.

2. Computational

All possible species containing hypothesized intermediates, reactants, TSs, and products were optimized and then the harmonic vibrational frequencies of all stationary points along the reaction pathway were calculated by Gaussian 03 chemical quantum package [16]. The Density Functional Theory (DFT) method in Beck's three-parameter hybrid exchange functioning with the correlation functional of Lee, Yang, Parr (B3LYP) [17,18] by using the 6-311g(d,p) basis set [19] was applied for optimization of the geometries and making the subsequent calculations. The transition state structures (TSs) were localized using the synchronous transit-guided quasi-Newton (STQN) procedure [20,21] and the frequencies of each structure were extracted to calculate the thermodynamic and kinetic parameters in each case. In addition, the intrinsic reaction coordinates (IRC) calculations verified the transition states structure [22,23]. To calculate the electrical charge of each atom in reactants as well as the transition states and the products, natural bond orbital (NBO) analysis was used [24,25]. The rate constant of the reaction as listed in Table 1, was calculated by relation 1.

$$k = \left(\frac{k_B T}{h}\right) \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad (1)$$

Where k_B is the Boltzmann constant, h is plank's constant, k is the rate constant of the reaction, T is the Kelvin temperature and R is the universal gas constant. The related partial bond order was then determined using Pauling relation (relation 2) [26]; and the synchronicity relation [27,28] was used to define the synchronicity value [29,30] of the selected pathways (see relation 3).

$$n_x = n_0 \exp\left(\frac{r_0 - r_x}{c}\right) \quad (2)$$

Where, the bond order n_x of a bond length r_x is a function of a standard bond of length r_0 , whose bond order is defined as n_0 .

$$S_y = 1 - \frac{\sum_{i=1}^n \frac{|\partial B_i - \partial B_{av}|}{\partial B_{av}}}{2n-2} \quad (3)$$

Where, ∂B_i is the relative variation of bond order index, B_i at the transition state, and the Global Electron Density Transfer (GEDT) was determined by using the following formula [31-33];

$$\text{GEDT} = -\sum q_A \quad (4)$$

Where; q_A is the net Mulliken charge as well as the sum covered the entire atoms of dipolar species.

3. Results

As shown in Figure 1, first, we designed and calculated the reactant and the transition state of the [1,5]-sigmatropic shift of C₂₀ fullerene carbon atoms on the benzene ring in an ambient conditions and in absence of the light, and then extracted the frequencies of the optimized structures to reach to the thermodynamic and kinetic parameters for the reaction. In continue, we have optimized the reactant, and the transition state with a spin multiplicity of 3, and recalculated the other required tasks to determine the thermodynamic and kinetic data in the triplet excited state).

After that, we planned and calculated the same reaction pathway for the cyclobutadiene /C₂₀ system to investigate the possibility of the same reaction for this molecular system, but in spite of our efforts, we could not locate a trustable transition state for the cyclobutadiene /C₂₀ system. The key thermodynamic and kinetic parameters for the reaction channels were given in Table 1.

The Gibbs free energy differences between reactant and the transition state of the Benzene/C₂₀ system in absence and under light irradiation, were about 37.8 kcal mol⁻¹, and 19.1 kcal mol⁻¹, respectively, which showed the process is very slow or even impossible in absence of light irradiation, while; it is favorable in the light triplet excited state. Subsequently, the rate constant for the Benzene/C₂₀ system in the light triplet excited state was 6.18(10⁻²) s⁻¹, showing that the process was possible. Thus, further attentions were only directed to the Benzene/C₂₀ system in the light triplet excited state.

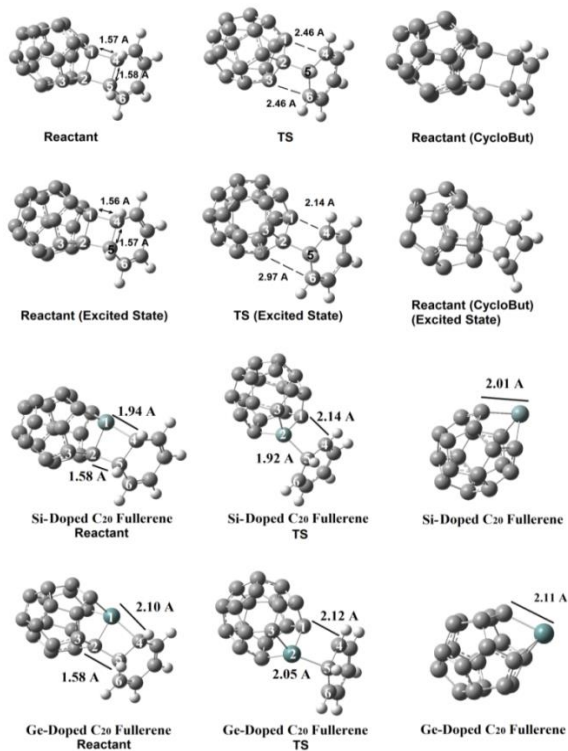


Figure 1. The structures of the key detected and localized species optimized at B3LYP/6-311G(d,p) level.

Table 1. The key thermodynamic and kinetic parameters for the considered reaction channels. ($T=298.15\text{K}$; $\Delta G^{0,\#}$ and $\Delta H^{0,\#}$ are in kcal mol^{-1} , and $\Delta S^{0,\#}$ is in $\text{kcal mol}^{-1} \text{K}^{-1}$)

Reaction	$\Delta G^{0,\#}$	$k(\text{s}^{-1})$	$\Delta H^{0,\#}$	$\Delta S^{0,\#}$
Benzene/ C_{20}	19.1	$6.18(10^{-2})$	19.2	$0.292(10^{-3})$
Benzene/ C_{20}	37.8	$1.21(10^{-15})$	36.3	$1.76(10^{-3})$
Benzene/ C_{19}Si	24.7	$4.85(10^{-6})$	26.0	$4.29(10^{-3})$
Benzene/ C_{19}Ge	27.5	$1.21(10^{-8})$	28.3	$2.51(10^{-3})$

The main difference between the two transition state (TS) of the normal condition, and TS for the excited state which could be seen at the first glance, is the highly symmetry of the TS of the normal state. As given in Table 2, the distances of C(1)-C(4), and C(3)-C(6), are 2.14 \AA and 2.97 \AA , respectively, for TS of the excited state, while; the distances of C(1)-C(4), and C(3)-C(6), are 2.46 , and 2.46 angstroms (for the TS of the normal state), which are close to each other. The relative asymmetry of the TS of the excited state compared to the TS of the normal state may be one of the reasons led to lower $\Delta G^{0,\#}$ for the excited state reaction channel. The relative partial bond orders for the selected bonds were calculated using the Pauling relation [26]; and the 0.144 , 0.244 , 0.875 values were obtained for C(1)-C(4), C(3)-C(6), and C(4)-C(5) bonds of the excited state TS, respectively. Subsequently, the partial bond orders for the selected reaction channel were 14.4% , 24.4% , and 12.5% for C(1)-C(4), C(3)-C(6), and C(4)-C(5) bonds, respectively.

Table 2. The key geometrical parameters for 1,5-sigmatropic shift of C_{20} fullerene carbon atoms on the benzene ring. Distances are in angstrom (\AA).

	C(1)-C(4)	C(3)-C(6)	C(4)-C(5)	C(5)-C(6)
Reactant	1.57	-	1.58	1.50
TS	2.46	2.46	1.52	1.52
Reactant (excited state)	1.56	-	1.57	1.50
TS (excited state)	2.14	2.97	1.53	1.50

Using the synchronicity relation [29,30], the -0.372 , 1.98 , and 0.571 values were determined for $\partial B_{\text{C}(1)-\text{C}(4)}$, $\partial B_{\text{C}(3)-\text{C}(6)}$, and $\partial B_{\text{C}(4)-\text{C}(5)}$, respectively. Therefore, the average ∂B for the reaction route becomes 0.726 , while the value of the synchronicity would be 0.999 showing that the process is nearly synchronous in some extent. The Global Electron Density Transfer calculation was used to determine the $GEDT$ value for the selected channel ($0.251e$), which showed the relatively polar character of the triplet excited transition state (Benzene/ C_{20} system).

Table 3. The natural bond orbital NBO calculations for the key atoms of the selected reaction channel (Benzene/ C_{20} system).

	C (1)	C (3)	C (4)	C (6)
Reactant (excited state)	-0.021	-0.024	-0.121	-0.079
TS (excited state)	0.001	0.015	-0.110	-0.113
$\Delta(\text{charge})$	-0.022	-0.039	-0.011	0.034

Table 3 shows the charge distribution in the reactant, and TS of the selected channel, and the charge difference between TS and reactant (Δcharge) by using the Natural Bond Order calculations. The results show that a small negative charge increased on C₁, C₃, and C₄ atoms at the TS. Increase in the negative charge on C₃, and decrease of that charge on C₆ may show the formation of C₃-C₆ bond; while; increase in the negative charge on C₁, and C₄ may be due to the breaking of C₁-C₄.

The results of the density of state DOS plots and the frontier molecular orbital FMO calculations show that by switching the system from state A to state B, the electrical conductivity of the system changes due to the change of HOMO-LUMO energy gap E_g from -1.99 eV to -1.91 . This phenomenon may be useful for consideration of this system for semiconductor sensor system, and also energy storage applications (Figure 2).

The results show, after increasing the temperature and receiving energy by the system ($37.8 \text{ kcal mol}^{-1}$ for normal fullerene; $27.5 \text{ kcal mol}^{-1}$ for germanium doped fullerene; and $24.7 \text{ kcal mol}^{-1}$ for silicon doped fullerene), the state of the system changes from form A to form B; and subsequently the HOMO-LUMO gap (E_g) changes from -1.99 eV to -1.91 eV for normal fullerene; -2.29 eV to -1.89 eV for silicon doped fullerene; and -2.31 eV to

1.69 eV for germanium doped fullerene, respectively. Also, by changing the E_g , the electrical conductivity of the system changes and it causes to create a signal for further applications. Thus, by increasing the temperature, the system receives energy and turns from state A to B; and subsequently, the E_g and the electrical conductivity changes; and this property of the system might be applicable for thermal sensor applications. However, it should be noted that due to the high energy barrier of changing the state from A to B in the normal C_{20} fullerene system (37.8 kcal mol⁻¹), using this fullerene/benzene sensor is not suitable; while, due to the relatively lower energy barrier for changing the state A to B in the germanium (27.5 kcal mol⁻¹) or the silicon doped systems (24.7 kcal mol⁻¹), use of these two systems seem to be logical.

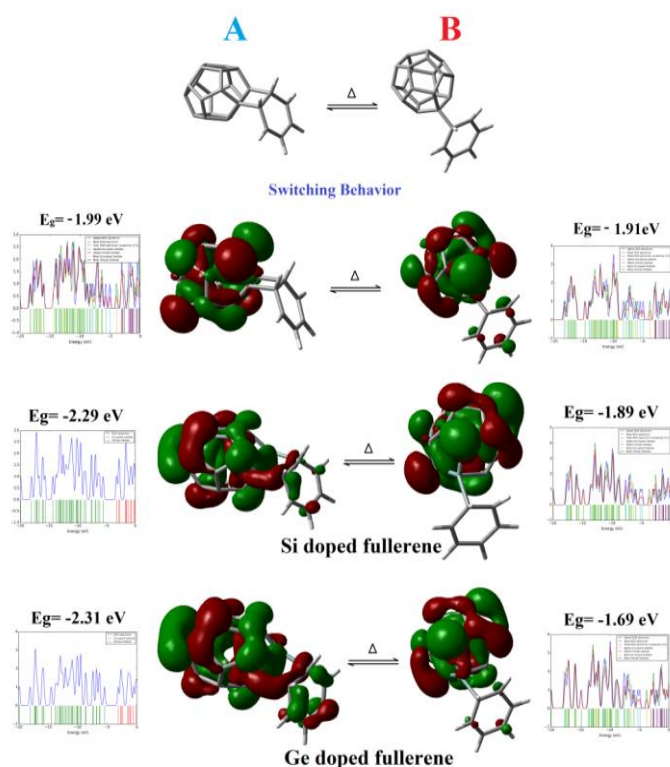


Figure 2. The density of state DOS plots, and the highest occupied molecular orbital HOMO forms for the system during its switching behavior

4. Conclusion

Changes of the temperature lead to change on this benzene/fullerene system from state A to B or vice versa; subsequently, it leads to change on the electrical conductivity of the system and causes to create a signal. The calculations indicate that increasing the temperature and receiving energy by this actuator (37.8 kcal mol⁻¹ for normal fullerene; 27.5 kcal mol⁻¹ for germanium doped fullerene; and 24.7 kcal mol⁻¹ for silicon doped fullerene), lead the system to change from state A to B; and thus the E_g changes from -1.99 eV to -1.91 eV for normal fullerene; -2.29 eV to -1.89 eV for silicon doped fullerene; and -2.31 eV to -1.69 eV for germanium doped fullerene, respectively. However, it should be noted that

the normal benzene/ C_{20} fullerene system might not be suitable for this type of thermal sensor application due to the high energy barrier of changing state A to B (37.8 kcal mol⁻¹); while, use of the germanium (27.5 kcal mol⁻¹) or the silicon-doped systems (24.7 kcal mol⁻¹) seem to be logical, due to the relatively lower energy barrier for changing the state A to B. Finally, it seems that further studies on this phenomenon, might handle designing the thermal sensor systems, and energy storage devices.

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