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Theoretical Study on the Rearrangement between the Isomers of $C_{60}X$ ($X = O$ and S)

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The rearrangements between the closed [6,6] and open [5,6] isomers of $C_{60}O$, as well as the closed [6,6], closed [5,6], and open [5,6] isomers of $C_{60}S$ have been studied using semiempirical AM1 and MNDO methods. The results show that the interconversion of the two isomers of $C_{60}O$ follows a two-step pathway involving an intermediate and two transition states. The calculated activation barriers for the migration of oxygen from [6,6]-bond to [5,6]-bond through an intermediate are 189.1 and 54.6 kJ mol^{-1}, respectively. In the opposite way, the calculated activation barriers for the migration of oxygen from [5,6]-bond to [6,6]-bond through an intermediate are 293.2 and 2.7 kJ mol^{-1}, respectively. The interconversion of the closed [6,6] and the open [5,6] isomers of $C_{60}S$ also follows a stepwise pathway via a local energy minimum corresponding to the closed [5,6] isomer. The calculated activation barriers for the migration of sulfur from [6,6]-bond to [5,6]-bond (in open [5,6] isomer) through the closed [5,6] isomer are 233.2 and 1.2 kJ mol^{-1}, respectively. In the opposite way, the calculated activation barriers for the migration of sulfur from [5,6]-bond (in open [5,6] isomer) to [6,6]-bond via the closed [5,6] isomer are 82.0 and 150.5 kJ mol^{-1}, respectively. The large barriers suggested that it should be possible to isolate the closed [6,6] and open [5,6] isomers of $C_{60}O$ at room temperature. This is consistent with experimental results. In addition, it can be inferred from our results that rearrangement between the two isomers of $C_{60}O$ can take place under heating or lighting conditions. Meanwhile, it can be deduced from our results that it should be possible to isolate both the closed [6,6] and the open [5,6] isomers of $C_{60}S$ at room temperature and to convert one into the other when certain energy is offered. It seems that the closed [5,6] isomer of $C_{60}S$ may not be observed experimentally at room temperature.

Introduction

The fullerene oxide, $C_{60}O$, is the simplest fullerene derivative and the key fullerene oxidation product[1−16] that plays an important role in the synthesis of various organic,[6,9−10] organometallic,[10−12] and polymeric[13] fullerene derivatives. Many methods have been used to produce $C_{60}O$, including photooxygenation,[1,2] electrochemical oxidation,[3] ozonization,[4−7] and epoxidation.[14−16] In 1992, detailed experimental work reported by Creegan et al.[2] on the synthesis and characterization of $C_{60}O$ suggested an epoxide structure with C_{2v} symmetry (the closed [6,6] pattern). In the same year, Elemes et al.[14] reported epoxidation of C_{60} with dimethyldioxirane to generate the epoxide $C_{60}O$. On the basis of the presence of two kinds of bonds in C_{60}, results of theoretical investigations[17−22] suggested two stable isomers of $C_{60}O$, namely, the closed [6,6] (epoxide) and the open [5,6] (ether) isomers, while the open [6,6] and closed [5,6] structures were not located in local energy minima. In 1997, Hao et al.[23] provided an observation of two isomers of $C_{60}O$ (the closed [6,6] and the open [5,6] isomers) in the products of the ozonization of C_{60}. Recently the synthesis of the open [5,6] isomer of $C_{60}O$ reported by Weisman et al.[24,25] has confirmed the long-standing computational predictions that the epoxide and ether isomers of $C_{60}O$ are both isolable. Comparably, only the closed [6,6]- and open [5,6]-methano- and -iminofullerenes have been found so far, and the so-called open [6,6] and closed [5,6] isomers have never been observed.[26−28] Computational studies[18,27,29,31] show that open [6,6] and closed [5,6]-methano- and -iminofullerenes are less stable than closed [6,6] and open [5,6] isomers, because open [6,6] and closed [5,6] isomers require the introduction of three and two unfavorable double bonds, respectively, in five-membered rings; while the electronic basis for the experimentally preferred formation of the closed [6,6]- and open [5,6]-methano- and -iminofullerenes is the preservation of the bonding pattern within C_{60} by these two structures and the relative stability of these two isomers reflects the degree to which their electronic structure matches that of C_{60}.[29−31] It is worthwhile to note that the decay products[25] of open [5,6] isomer of $C_{60}O$ include the closed [6,6] isomer of $C_{60}O$. This incited us to investigate the rearrangement between the closed [6,6] and open [5,6] isomers of $C_{60}O$. Diederich et al.[28,29] suggested that thermal interconversion of the open [5,6]- and closed [6,6]-methanofullerenes can occur following a stepwise pathway through a shallow local minimum corresponding to the closed [5,6] isomer; however, the $C_{60}CH_2$ methanofullerene is an exceptional case for this interconversion mechanism owing to the absence of its closed [5,6] isomer. Recently, Hall et al.[26] have reported that the open [5,6] fulleroids with radical stabilizing groups on the methano bridge can rearrange both by a zero-order photochemical process and by a higher energy unimolecular pathway involving disrotatory closure to the closed [5,6] fullerene, which subsequently rearrange to the closed [6,6] fullerene via a biradical-like intermediate. With respect to $C_{60}O$, Raghavachari[18] suggested that an intermediate should be involved in the process of the rearrangement between the two isomers of $C_{60}O$ on the bases of their MNDO calculations. However, to our knowledge the detailed mechanism has not been reported so far.

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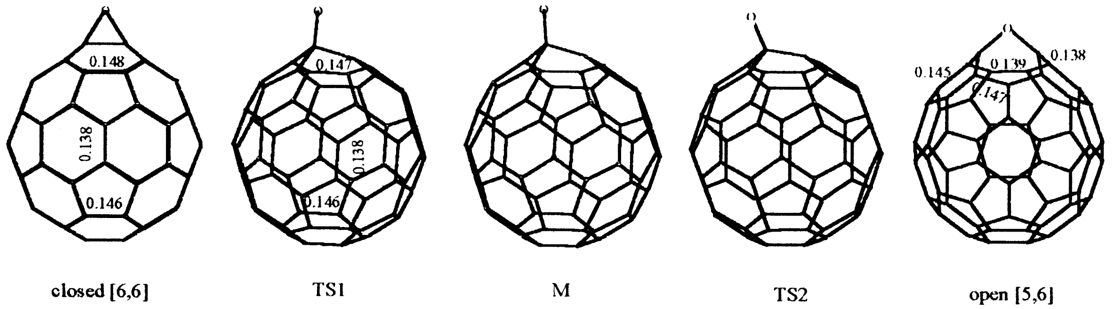

Figure 1. AM1 optimized geometries of all the species in the pathway for the arrangement between the two isomers of $C_{60}O$. TS1 is the transition state connecting the closed [6,6] isomer to the intermediate (M); TS2 is the transition state connecting **M** to the open [5,6] isomer.

Several sulfur containing fullerene derivatives have been observed,[32−35] mostly with high sulfur content. As an analogue of the relatively well studied $C_{60}O$ the simplest derivative of sulfur containing fullerene $C_{60}S$ has not been synthesized. It is believed to have potential applications. The calculations performed by Slanina and Lee[36] showed that $C_{60}S$ has three stable isomers, namely closed [6,6], closed [5,6], and open [5,6] isomers. To date no report on the mechanisms of the rearrangements between the three isomers of $C_{60}S$ has been found.

In the present work, we have performed semiempirical (AM1 and MNDO) calculations on the rearrangement between the closed [6,6] and open [5,6] isomers of $C_{60}O$, as well as the three isomers of $C_{60}S$. The detailed mechanisms of the arrangement between the isomers of $C_{60}O$ and $C_{60}S$ have been suggested.

Computational Details

The size of the system studied prevents the use of ab initio molecular quantum mechanical methods. Therefore, we have performed all calculations presented here with the AM1 and MNDO semiempirical method as implemented in the *Gaussian94* program.[37] To confirm that each of the species is a local minimum or a first-order saddle point on the potential energy surface, calculations of the vibrational frequencies were performed by the same method. IRC[38] (intrinsic reaction coordinate) calculations were further carried out to confirm the reaction mechanisms and to characterize the nature of the transition states. The calculated results confirm that despite of some difference in geometries and relative heat of formation at different levels (AM1 and MNDO), the mechanisms studied here are consistent. Since the AM1 method has been preferred over other semiempirical methods for the study of fullerene derivative such as $C_{60}O$,[21] the mechanisms studied here are presented based on the results calculated at AM1 level.

Results and Discussion

Rearrangement of Closed [6,6] and Open [5,6] Isomers of $C_{60}O$. The experimental[2,14,23,25] and theoretical[17−22] results have shown that $C_{60}O$ has two isomers−the closed [6,6] and open [5,6] species. In this work, we have independently carried out AM1 and MNDO calculations indicating closed [6,6] and open [5,6] isomers of $C_{60}O$ are local energy minima and the so-called open [6,6] and closed [5,6] structures are not found on the energy profile. Meanwhile, our results agree with those of Raghavachari[17,18] that the open [5,6] isomer is more stable than the closed [6,6] isomer of $C_{60}O$. The difference of heat of formation between them is 52.2 kJ mol^{-1} at AM1 level, while calculations at higher level of theory indicates a smaller energy difference between them.[18] Since the C−C bonds being bridged in the two isomers of $C_{60}O$ are adjacent bonds in C_{60}, the rearrangement process involves the migration of the oxygen from one C−C bond to the next. Our calculations found that the rearrangement includes two steps. The first step is the C−O bond broke and the migrating oxygen attached to one carbon atom, and that finally led to an intermediate (M), in which the oxygen is attached to only one carbon with a relatively shorter C−O distance (0.1278 nm) and weakened C−C bonds of roughly equal length (0.1600 nm) at that carbon. This structure implies that the intermediate **M** has some biradical character.[26] Vibrational analysis indicates that this is a local minimum. However, it is significantly less stable than either of the two bridged isomers. It is 186.5 kJ mol^{-1} less stable than the epoxide at the AM1 level. The second step is the migrating oxygen in the intermediate moved toward another carbon atoms and formed a new carbon−oxygen bond, and that led to another isomer of $C_{60}O$.

TABLE 1: AM1 Calculated Bond Distances, Bond Angles, and Dihedral Angles of All the Species Involved in the Rearrangement between the Isomers of $C_{60}O^{a}$

	closed [6,6]	TS1	M	TS2	open [5,6]
r_{1-O}	0.1420	0.2207	0.2362	0.2470	0.2397
r_{C2-O}	0.1420	0.1303	0.1278	0.1338	0.1401
r_{C3-O}	0.2585	0.2487	0.2454	0.2046	0.1401
r_{C4-O}	0.2585	0.2487	0.2454	0.2489	0.2417
r_{C1-C2}	0.1546	0.1530	0.1562	0.1498	0.1382
r_{C2-C3}	0.1491	0.1563	0.1583	0.1550	0.2169
r_{C2-C4}	0.1491	0.1563	0.1583	0.1546	0.1453
$\alpha_{O-C2-C1}$	57.0	102.1	112.2	121.0	118.9
$\alpha_{O-C2-C3}$	125.2	120.1	117.8	89.9	
$\alpha_{C1-O-C2}$	66.0				
$\alpha_{C2-O-C3}$					101.4
$\alpha_{O-C2-C4}$	125.2	120.1	117.8	119.1	115.7
$\varphi_{O-C2-C1-C3}$	116.1	127.0	128.8	102.6	42.0

[a] Bond distance (r) in nm; bond angle (α) and dihedral angle (φ) in degrees.

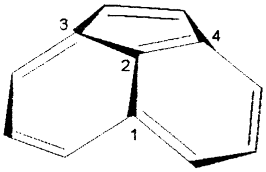

Figure 2. The numbering of the atoms in the reaction site of the $C_{60}O$ sphere.

The AM1 optimized geometries of reactant, transition states, intermediate and product are shown in Figure 1 and their main geometric parameters are collected in Table 1. The numbering of atoms in the reaction site is shown in Figure 2.

The TS1 that connected the closed [6,6] isomer with the intermediate (M) has an imaginary vibrational frequency of 259 *i*cm^{-1}. In the TS1, the C1−O bond (0.2207 nm) is substantially broken and the length of C2−O bond (0.1303 nm) is shortened significantly. The O−C2−C1 angle in the TS1, 102.1°, is quite

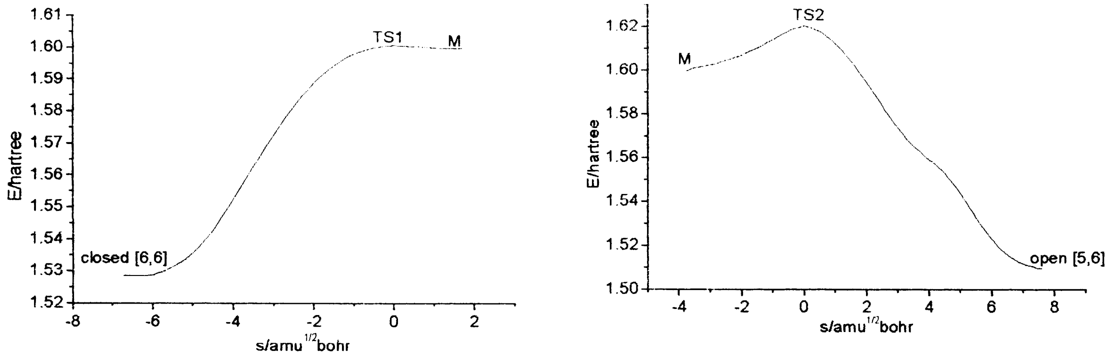

Figure 3. The intrinsic reaction coordinate for the rearrangement between the two isomers of $C_{60}O$.

increased from the initial 57.0° in the closed [6,6] isomer. These geometric changes indicate that the migrating oxygen moved toward carbon atom of C2. In the intermediate (M), the C2−O bond is shortened to 0.1278 nm and the bond angles of O−C2−C3 (117.8°), O−C2−C4 (117.8°), and O−C2−C1 (112.2°) come to a rough equality. It can be seen from these geometric features that the intermediate (M) can be stabilized by the strong bond of C2−O and the equalization of the interactions between the oxygen and the carbon atoms (i.e., C1, C3, C4, etc.) around it. With the moving of the migrating oxygen in the intermediate (M) toward carbon atom C3 we obtained the TS2. The TS2 that connected the intermediate (M) and the open [5,6] isomer has an imaginary vibrational frequency of 583 $i\mathrm{cm}^{-1}$. In the TS2, the bond length of C3−O is shortened significantly from 0.2454 nm in the intermediate (M) to 0.2046 nm, and the O−C2−C3 angle decreased from 117.8° in intermediate to 89.9°. The interaction between the oxygen and carbon atom C3 increased with the geometric changes. Finally, with the migrating oxygen in TS2 moving toward carbon atom C3 the C3−O bond (0.1401 nm) formed and the C2−C3 bond (0.2169 nm) broke completely. This product is the open [5,6] isomer of $C_{60}O$. The breaking of the C2−C3 bond between the five- and the six-membered rings keeps the characters of the three conjugate double bonds (≈0.1380 nm) in the six-membered ring and the characters of the single bonds (≈0.1460 nm) in the five-membered ring. Therefore, the structural and electronic properties of the original C_{60} have been mostly kept intact. It can be seen from bond lengths labeled in Figure 1 that in the process of the rearrangement between the closed [6,6] and open [5,6] isomers of $C_{60}O$ the influence of interactions upon the geometry is limited to the local area where the reaction takes place. The single bonds and double bonds in the C_{60} sphere away from the reaction sites are not much distorted from their original bonds of C_{60}.

Calculations following the intrinsic reaction coordinate (IRC) for TS1 and TS2 have shown a monotonic decrease in energy and resulted in the formation of the suggested products and reactants. No distinct intermediates or second transition structures were found. This result confirmed our calculation is correct. (See Figure 3).

The heats of the formation of the two isomers, transition states, and the intermediate (M) are collected in Table 2. The reaction pathway of rearrangement of [6,6] and [5,6] isomer obtained by the computational results is shown in Figure 4.

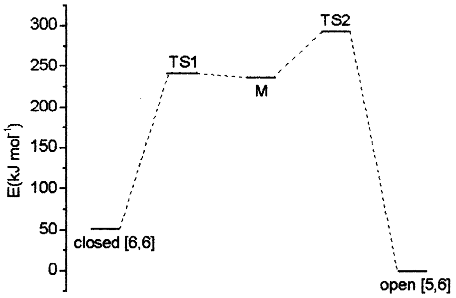

Figure 4. AM1 calculated energy profile for the rearrangement between the isomers of $C_{60}O$.

TABLE 2: AM1 Calculated Heats of Formation ($\Delta H_f°$) and Relative Heat of Formation ($r\Delta H_f°$) of Reactant, Intermediate, Transition States, and Product for the Rearrangement between the Isomers of $C_{60}O$, Together with Activation Energy (E_a) and Reverse Activation Energy E_a(r), Heats of Reaction (ΔH_r), and Reverse Heats of Reaction (ΔH_r(r)) (unit: kJ mol^{-1})

	closed [6,6]	TS1	M	TS2	open [5,6]
$\Delta H_f°$	4013.5	4202.6	4199.9	4254.5	3961.3
$r\Delta H_f°$	52.2	241.3	238.7	293.2	0.0
E_a		189.1		54.6	
E_a(r)		2.7		293.2	
ΔH_r			186.4		−238.7
ΔH_r(r)	−186.4		238.7		

It can be found from Table 2 that the open [5,6] isomer (geometry with C_S symmetry) has the lower heat of formation than that of the closed [6,6] isomer (geometry with C_{2v} symmetry) by 52.2 kJ mol^{-1} at present level of calculation. It is worthwhile to note that the heat of formation of the intermediate (M) is only 2.7 kJ mol^{-1} lower than that of TS1. This fact indicates that the intermediate (M) is considerably unstable. As shown in Figure 4, in the process of the migration of oxygen from [6,6]-bond to [5,6]-bond (assumed to be the forward reaction) it need to overcome the activation barriers of 189.1 and 54.6 kJ mol^{-1} in turn. In the opposite way, in the process of the migration of oxygen from the [5,6]-bond to [6,6]-bond (assumed to be the reverse reaction) the activation barriers are 293.2 and 2.7 kJ mol^{-1} in turn. The first step of forward reaction and the reverse reaction are endothermic by 186.4 and 238.7 kJ mol^{-1}, respectively.

From a kinetic point of view the interconversion between the two isomers is difficult to take place. This suggested that it should be possible to isolate both isomers of $C_{60}O$ at room temperature, which has been confirmed by a recent experimental result.[25] On the other hand, these results imply that rearrangement between the two isomers can take place under heating or lighting conditions.

$C_{60}S$. $C_{60}S$ has four possible isomers theoretically, namely the closed [6,6], open [6,6], closed [5,6], and open [5,6] isomers. However, the results of calculations on $C_{60}S$ performed by Slanina and Lee[36] using semiempirical MNDO method indicated that the open [6,6] isomer is not a local energy minimum. Therefore $C_{60}S$ should have the closed [6,6], closed [5,6], and open [5,6] isomers. The closed [6,6] isomer is most stable and

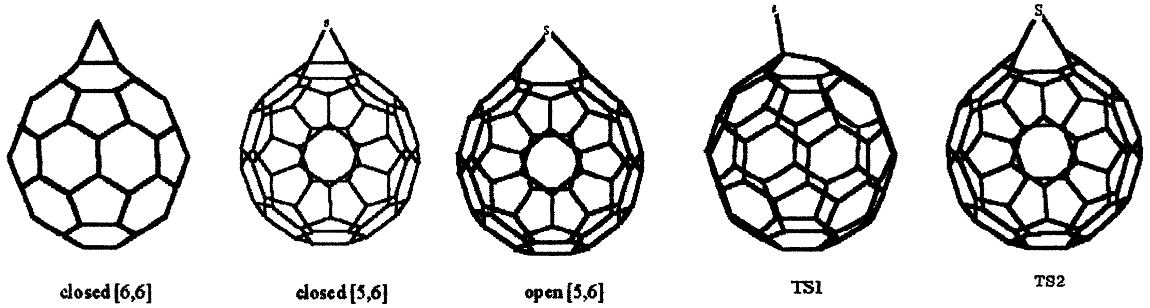

Figure 5. AM1 optimized geometries of all the species in the pathway for the arrangement between the three isomers of $C_{60}S$.

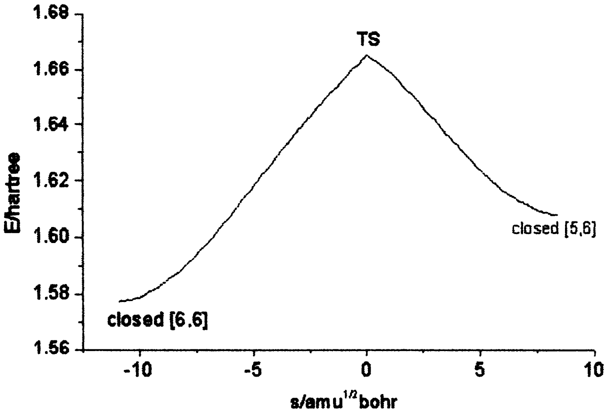

Figure 6. The intrinsic reaction coordinate for the rearrangement between the closed [6,6] and the closed [5,6] isomers of $C_{60}S$.

TABLE 3: AM1 Calculated Heats of Formation of the Three Isomers of $C_{60}S$ and Their Relative Heats of Formation (unit: kJ mol^{-1})

	closed [6,6]	closed [5,6]	open [5,6]
$\Delta H_f°$	4139.1	4221.8	4141.1
$r\Delta H_f°$	0.0	82.7	1.9

the closed [5,6] isomer is most unstable. The result of our present calculations on isomers of $C_{60}S$ at AM1 and MNDO levels is in agreement with that of Slanina nad Lee.[36]

Our calculations on $C_{60}S$ at AM1 level indicate that the closed [6,6] isomer has geometry with C_{2v} symmetry, and the closed [5,6] isomer as well as the open [5,6] one has geometry with C_s symmetry (Figure 5). The heats of formation of the three isomers are listed in Table 3. It can be seen that the closed [6,6] and the open [5,6] isomers are essentially isoenergetic. The closed [5,6] one is 82.7 kJ mol^{-1} higher in heat of formation than that of closed [6,6] isomer.

Similar to the rearrangement between the closed [6,6] and the open [5,6] isomers of $C_{60}O$, our calculations show that the rearrangement of $C_{60}S$ also include two steps. The first step is the C1−S bond broke and the sulfur migrated to carbon atom of C3, and that led to the closed [5,6] isomer. The second step is the C2−C3 bond in closed [5,6] isomer broke and that led to the open [5,6] isomer of $C_{60}S$.

Rearrangement between the Closed [6,6] and the Closed [5,6] Isomers. The optimized geometry of TS1 is shown in Figure 5. TS1 is the transition structure that connects closed [6,6] and closed [5,6] isomers of $C_{60}S$. The numbering of atoms in the reaction site is the same as that of $C_{60}O$ (Figure 2).

There is only one imaginary frequency of 913i cm^{-1} for TS1. IRC calculations verify that TS1 lies on the pathway for the conversion of closed [6,6] and closed [5,6] isomers with no other stationary points between the reactant and product (Figure 6).

The main geometric parameters of the two isomers and the transition state TS1 are listed in Table 4. In the transition structure of TS1, the C1−S bond is quite elongated from 0.1747 nm in the closed [6,6] isomer to 0.2575 nm, the C3−S bond is significantly shortened from 0.2882 nm in the closed [6,6] isomer to 0.2455 nm, the S−C2−C1 angle increased, and the S−C2−C3 angle decreased.

TABLE 4: AM1 Calculated Bond Distances, Bond Angles, and Dihedral Angles of All the Species Involved in the Rearrangement between the Closed [6,6] and the Closed [5,6] Isomers of $C_{60}S$[a]

	closed [6,6]	TS1	closed [5,6]
$r_{\text{C1-S}}$	0.1747	0.2575	0.2826
$r_{\text{C2-S}}$	0.1747	0.1725	0.1748
$r_{\text{C3-S}}$	0.2882	0.2455	0.1748
$r_{\text{C4-S}}$	0.2882	0.2843	0.2810
$r_{\text{C1-C2}}$	0.1550	0.1467	0.1445
$r_{\text{C2-C3}}$	0.1497	0.1526	0.1639
$r_{\text{C2-C4}}$	0.1497	0.1515	0.1493
$\alpha_{\text{S-C2-C1}}$	63.7	107.3	124.3
$\alpha_{\text{S-C2-C3}}$	125.2	97.9	62.0
$\alpha_{\text{C1-S-C2}}$	52.7		
$\alpha_{\text{C2-S-C3}}$			55.9
$\alpha_{\text{S-C2-C4}}$	125.2	122.6	120.1
$\varphi_{\text{S-C2-C1-C3}}$	118.2	106.0	72.2

[a] Bond distance (r) in nm; bond angle (α) and dihedral angle (φ) in degrees.

TABLE 5: AM1 Calculated Bond Distances, Bond Angles, and Dihedral Angles of All the Species Involved in the Rearrangement between the Closed [5,6] and the Open [5,6] Isomers of $C_{60}S$[a]

	closed [5,6]	TS2	open [5,6]
$r_{\text{C1-S}}$	0.2826	0.2802	0.2679
$r_{\text{C2-S}}$	0.1748	0.1733	0.1699
$r_{\text{C3-S}}$	0.1748	0.1733	0.1699
$r_{\text{C4-S}}$	0.2810	0.2791	0.2697
$r_{\text{C1-C2}}$	0.1445	0.1431	0.1380
$r_{\text{C2-C3}}$	0.1639	0.1740	0.2287
$r_{\text{C2-C4}}$	0.1493	0.1484	0.1454
$\alpha_{\text{S-C2-C1}}$	124.3	124.4	120.6
$\alpha_{\text{S-C2-C3}}$	62.0		
$\alpha_{\text{C1-S-C2}}$			
$\alpha_{\text{C2-S-C3}}$	55.9	60.3	84.6
$\alpha_{\text{S-C2-C4}}$	120.1	120.1	117.4
$\varphi_{\text{S-C2-C1-C3}}$	72.2	68.8	−50.6

[a] Bond distance (r) in nm; bond angle (α) and dihedral angle (φ) in degrees.

The calculated energy results are collected in Table 6. The energy profile for the rearrangement is shown in Figure 8. The computed energy barrier for the migration of sulfur atom from the [6,6]-bond to the [5,6]-bond (assumed to be the forward reaction) is 233.2 kJ mol^{-1}, and the energy barrier of reverse reaction (from [5,6] isomer to [6,6] isomer) is 150.5 kJ mol^{-1} (Figure 8). The forward reaction is endothermic by 82.7 kJ mol^{-1}.

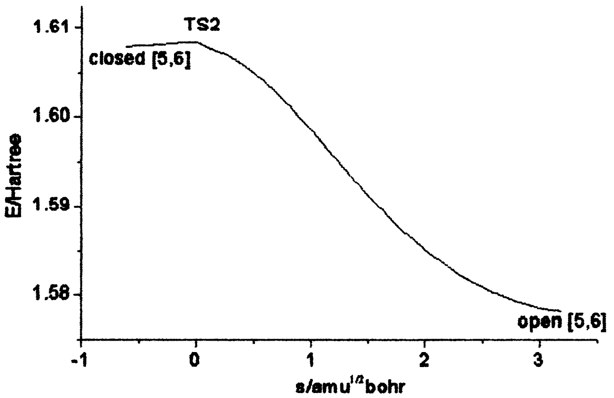

Figure 7. The intrinsic reaction coordinate for the rearrangement between the closed [5,6] and the open [5,6] isomers of $C_{60}S$.

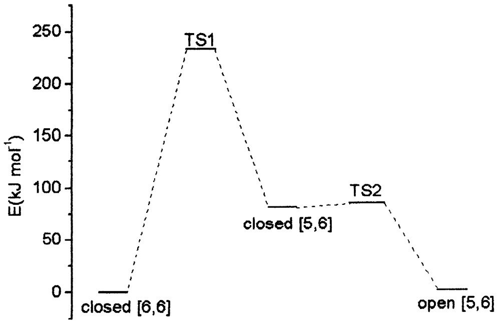

Figure 8. AM1 calculated energy profile for the rearrangement between the closed [6,6] and the open [5,6] isomers of $C_{60}S$.

TABLE 6: AM1 Calculated Heats of Formation ($\Delta H_f°$) and Relative Heat of Formation ($r\Delta H_f°$) of Reactant, Intermediate, Transition States, and Product for the Rearrangement between the Isomers of $C_{60}S$, Together with Activation Energy (E_a) and Reverse Activation Energy E_a(r), Heats of Reaction (ΔH_r) and Reverse Heats of Reaction (ΔH_r(r)) (unit: kJ mol^{-1})

	closed [6,6]	TS1	closed [5,6]	TS2	open [5,6]
$\Delta H_f°$	4139.1	4372.3	4221.8	4223.0	4141.1
E_a		233.2		1.2	
E_a(r)		150.5		82.0	
ΔH_r			82.7		−80.8
ΔH_r(r)	−82.7		80.8		
$r\Delta H_f°$	0.0	233.2	82.7	83.9	1.9

Rearrangement between the Closed [5,6] and the Open [5,6] Isomers. The optimized geometry of TS2 that connects closed [5,6] and open [5,6] isomers of $C_{60}S$ is shown in Figure 5. The numbering of atoms in the reaction site is the same as that of $C_{60}O$ (Figure 2). There is only one imaginary frequency of 448*i*cm^{-1} for TS2. IRC calculations verify that TS2 lies on the pathway for the conversion of closed [5,6] and open [5,6] isomer with no other stationary points between the reactant and product (Figure 7).

The main geometric parameters of the two starting isomers and the transition state TS2 are collected in Table 5. We observed very little change in the geometric parameters of TS2 relative to closed [5,6] isomer. The only remarkable differences are an elongating by 0.0101 nm of the C2−C3 bond and an increase of about 4.5° in the C2−S−C3 angle. These results indicate that the conversion of the closed [5,6] isomer to the open [5,6] isomer is mainly a process of the breaking of C2−C3 bond together with the shortening of the two C−S bonds and the increasing of the bridging bond angle of C2−S−C3.

Table 6 and Figure 8 show that the computed energy barrier for the conversion of the closed [5,6] to the open [5,6] isomer (assumed to be the forward reaction) is only 1.2 kJ mol^{-1} and the process is exothermic by 80.8 kJ mol^{-1}. This implies that the closed [5,6] isomer of $C_{60}S$ is considerable unstable. On the other hand, we predict that at higher temperature this small energy barrier may fade away due to energy increase of the reaction system $C_{60}S$ induced by molecular movement of vibration and rotation, etc. In the opposite way, the activation barriers for the conversion of the open [5,6] to the closed [5,6] isomer (assumed to be the reverse reaction) is computed to be 82.0 kJ mol^{-1} and the reverse reaction is endothermic by 80.8 kJ mol^{-1}.

TABLE 7: Total Energy (Hartree) and Relative Energy (kJ mol^{-1}) of All the Species Involved in the Rearrangement between the Isomers of $C_{60}O$ and $C_{60}S$ Calculated at the ab Initio B3LYP/6-31G//AM1 Level

	$C_{60}O$		$C_{60}S$	
	total energy	relative energy	total energy	relative energy
closed [6,6]	−2360.723 38	25.6	−2683.710 25	0.0
TS1	−2360.671 64	161.4	−2683.668 20	110.4
M/closed [5,6]	−2360.657 20	199.3	−2683.681 33	75.9
TS2	−2360.661 96	186.8	−2683.677 45	86.1
open [5,6]	−2360.733 12	0.0	−2683.709 87	1.0

From the whole discussion it can be seen that there are two barriers for the interconversion between the closed [6,6] and open [5,6] isomers. The calculated energy barriers for the conversion of the closed [6,6] isomer to the open [5,6] isomer (assumed to be the forward reaction) are 233.2 kJ mol^{-1} and 1.2 kJ mol^{-1}. The opposite conversion's barriers from open [5,6] to closed [6,6] isomer are 82.0 and 150.5 kJ mol^{-1}. The large energy barriers suggest that it should be possible to isolate the two isomers of $C_{60}S$. It can also be deduced from the results that rearrangement between the closed [6,6] and the open [5,6] isomers can take place when certain energy is offered. However, it seems impossible for the closed [5,6] isomer of $C_{60}S$ to be observed in experiment at room temperature due to its instability.

From Figures 4 and 8 we can see that the two rearrangement mechanisms of $C_{60}O$ and $C_{60}S$ are similar. It is also interesting to compare the intermediate of rearrangement of $C_{60}S$ and $C_{60}O$. The interconversion between the two isomers of $C_{60}O$ involves an intermediate where the oxygen is attached to only one carbon, however, the intermediate of $C_{60}S$ is the closed [5,6] isomer. Our calculations at AM1 and NMDO levels show that the intermediate **M** is a shallow energy minimum. The energy barrier for the conversion of this intermediate into the more stable close [6,6] isomer of $C_{60}O$ is only 2.7 kJ mol^{-1} at AM1 level. This indicates that the intermediate **M** is very unstable. Moreover, the AM1 method overestimates the stability of fullerenes structures with open bonds.[27,29,39] So the intermediate M, which has some biradical character, should be difficult to isolate or even detect. Although our calculations support a stepwise mechanism, it is not yet possible to draw a definite conclusion on the mechanism that operates in the rearrangement between the two stable isomers of $C_{60}O$. To explore this mechanism further, we performed B3LYP/6-31G//AM1 single-point calculations for this system. The calculated results are listed in Table 7. It can be seen from Table 7 that the intermediate **M** has disappeared using ab initio density functional theory method, which indicates that maybe the interconversion of the two isomers of $C_{60}O$ follows a one-step pathway via a biradical-like transition state which is probably near the intermediate on the energy profile, so the profile for the interconversion between closed [6,6] and open [5,6] isomers for $C_{60}O$ will become unimodal. On the other hand, the absence of the intermediate **M** probably implies the forbiddance of the thermal interconversion of the two isomers, which will be analogous to the case of the $C_{60}CH_2$ methanofullerene.[28,29] B3LYP/6-31G//AM1 single point calculations for $C_{60}S$ reaction system were also performed, the results are also given in Table 7. Different from the intermediate of $C_{60}O$, the [5,6] system for $C_{60}S$ maintains a local energy minimum at B3LYP/6-31G level evaluated at the AM1 geometry, which indicates that the [5,6] closed isomer of $C_{60}S$ has larger stability than the intermediate **M** of $C_{60}O$. This different stability can also be seen obviously by comparing the relative heat of formation in Tables 2 and 6: the intermediate of $C_{60}O$ and the closed [5,6] system of $C_{60}S$ are 238.7 and 80.8 kJ mol^{-1} higher in heats of formation than their [5,6] open isomers, respectively. The difference between the two intermediates should be mainly ascribed to two points: First, the oxygen and sulfur having different atomic size−the atomic size of sulfur is larger than that of oxygen. Second, sulfur has a greater Pauli repulsion than oxygen. This difference is also presented between the closed [5,6] systems for X = NCH_3 and X = PCH_3 with $C_{60}PCH_3$ having larger stability.[31]

Conclusions

From the results obtained in the present investigation we emphasize the following important points:

(1) The mechanism of the rearrangement between the two isomers, namely the closed [6,6] and the open [5,6] isomers of $C_{60}O$, involves two steps with an intermediate where the oxygen is attached to only one carbon. In the way of the rearrangement from closed [6,6] to open [5,6] isomers, the first step is a process with the breaking of C1−O bond, and the second step is a process with the forming of C3−O bond and the breaking of C2−C3 bond. Although our calculations support a stepwise mechanism, it is not yet possible to draw a definite conclusion on the mechanism that operates in the rearrangement between the two stable isomers of $C_{60}O$, because the intermediate, which has biradical character, is very unstable, and it has disappeared using ab initio density functional method. Therefore, maybe the interconversion of the two isomers of $C_{60}O$ follows a one-step pathway via a biradical-like transition state which is probably near the intermediate on the energy profile.

(2) The mechanism of the rearrangement between the closed [6,6] and the open [5,6] isomers of $C_{60}S$ involve two steps with the closed [5,6] isomer as an intermediate. In the way of the rearrangement from closed [6,6] to open [5,6] isomers, the first step is a process with the breaking of C1−S bond and the forming of C3−S bond, and the second step is a process with the breaking of C2−C3 bond.

(3) The large activation barriers indicated that the interconversion between the closed [6,6] and the open [5,6] isomers of $C_{60}X$ (X = O, S) is very difficult to take place at room temperature. This suggests that it should be possible to isolate the closed [6,6] and open [5,6] isomers of $C_{60}X$ (X = O, S). Our results provide good aspects for explaining the fact that both the closed [6,6] and open [5,6] isomers of $C_{60}O$ have been synthesized and isolated experimentally.

(4) Similar mechanism has been suggested for the rearrangement between isomers of $C_{60}O$ and $C_{60}S$. The interesting difference between the intermediate of rearrangement of $C_{60}O$ and $C_{60}S$ may result mainly from their different atomic sizes and from the different Pauli repulsions of oxygen and sulfur.

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