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Cycloaddition of Benzyne to Armchair Single-Walled Carbon Nanotubes: [2 + 2] or [4 + 2]?

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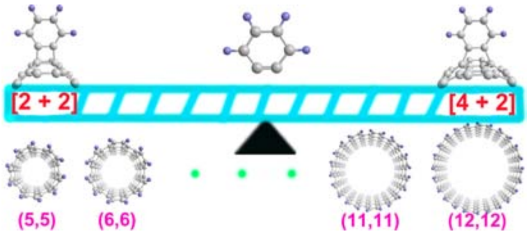
ABSTRACT



The reaction mechanism and regioselectivity of cycloaddition reactions of benzyne to armchair single-walled carbon nanotubes were investigated with quantum chemical methods. The [2 + 2] cycloaddition reaction follows the diradical mechanism, whereas the [4 + 2] cycloaddition reaction adopts the concerted mechanism. More importantly, the [2 + 2] product is always more stable thermodynamically than the [4 + 2] ones, regardless of the diameter, while the [4 + 2] cycloaddition becomes kinetically more favored as the diameter goes up.

Thanks to their novel mechanical, geometrical, and electronic properties, single-walled carbon nanotubes (SWNTs) show a great amount of promising applications in many fields such as electronics, optics, and material science.[1,2] Chemical functionalization of SWNTs not only increases their solubility into inorganic, organic, and biological systems but also provides opportunities for tuning their physical and chemical properties.[3−6] Functionalized SWNTs exhibit modulated properties and have unprecedented applications, implying possibilities for using them to fabricate novel nanodevices. Interestingly, Han and co-workers theoretically suggested that when benzyne is bonding to the sidewall of SWNTs through cycloaddition (CA) reactions, the resulting functionalized SWNTs could be made as molecular paddle wheels and used as nanogears.[7] In 2010, Guitián, Langa and co-workers reported a successful experiment of CAs between benzyne and SWNTs.[8] Very recently, the same group performed an experimental and theoretical study on the CA of arynes to SWNTs.[9] Meanwhile, Tagmatarchis et al. found that carbon nanohorns, which are horn-shaped single-walled tubules with a conical tip,[10] can also afford the CA reaction with benzyne.[11]

The CA of benzyne to the sidewall of SWNT can form two possible products, the [2 + 2] and [4 + 2] cycloadducts,

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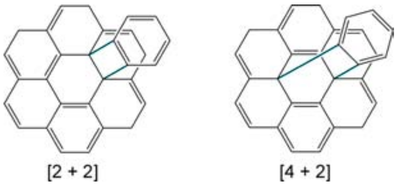
Scheme 1. Two Possible Products of Cycloaddition Reactions of Benzyne and SWNTs: [2 + 2] (left) and [4 + 2] (right)



as shown in Scheme 1. It is long-believed that the tube diameter plays a critical role in determining the CA type; that is, once the SWNT diameter is larger than C_{60} (0.683 nm), the [4 + 2] products would be more stable than the [2 + 2] products.[8,12] Indeed, the previous theoretical studies have revealed that, for zigzag (n,0) (n = 10, 14, and 18) SWNTs, [4 + 2] products are more thermodynamically stable than the [2 + 2] ones.[9,12] However, the cycloaddition of benzyne upon the sidewalls of armchair (n,n) SWNTs has not been systematically studied with theoretical methods up to now. Furthermore, the previous studies only focused on the reaction energies of CAs of benzyne and SWNTs.[9,12] Thus, the reaction mechnaisms of these two kinds of CA reactions remain unclear. Here, we report the reaction mechnaisms of both [2 + 2] and [4 + 2] CAs and the influence of the SWNT diameter on the regioselectivity of the title reaction.

All geometries were optimized using (U)B3LYP[13]/3-21G(d),[14] followed by single-point calculations at the (U)B3LYP/6-31G(d)[14] level of theory.[15] All calculations were carried out with the Gaussian 09 program.[16] The armchair (n,n) SWNTs (n = 5−12) were represented by the 9-layer finite models, $C_{18n}H_{4n}$, which fulfill the complete Clar network.[17,18]

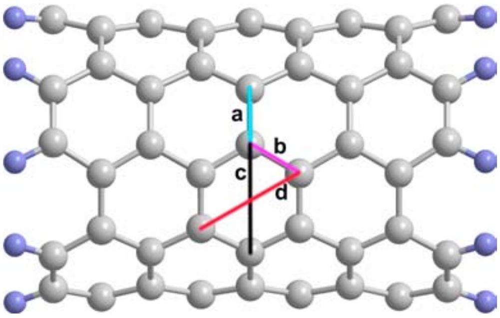


Figure 1. The 9-layer finite model ($C_{90}H_{20}$) tube representing an armchair (5,5) SWNT, in which there are four possible CA sites for benzyne. The **a** and **b** belong to the [2 + 2] CA while **c** and **d** are the [4 + 2] CA.

Figure 1 depicts the finite model of the armchair (5,5) SWNT. It is obvious that two kinds of nonequivalent C−C bonds are presented, the circumferential bond **a** and the axial bond **b**, implying two different [2 + 2] products can form. The calculated results revealed that both [2 + 2] CAs upon **a** and **b** are exothermic with reaction energies of −39.4 and −41.9 kcal/mol, respectively. The higher reactivity of the bond **b** is mainly ascribed to its shorter bond length (1.42 Å) compared with that of the bond **a** (1.45 Å).

On the other hand, two kinds of [4 + 2] products could be generated when benzyne is added to the **c** and **d** sites, respectively. However, these two kinds of [4 + 2] CAs are quite different: the CA upon site **c** is endothermic (35.5 kcal/mol), whereas the product over the site **d** is 27.2 kcal/mol lower than isolated reactants in energy. It is clearly demonstrated that [2 + 2] products are more favored than [4 + 2] products thermodynamically. The result can be explained by the large distances of two carbon atoms involved in the CA reaction in the sites **c** and **d** in [4 + 2] CAs. First, the reactive bond of benzyne is obviously elongated to react with two carbon atoms in the SWNT, which destroys the aromaticity of benzyne. Second, the bond lengths of two newly formed carbon bonds in the [4 + 2] products are much large, resulting in the weak interaction between benzyne and the SWNT. Compared with the site **d**, the CA over the site **c** not only needs much more energy to distort the SWNT to the CA product but also has lower interaction energy between benzyne and the SWNT, as **c** is circumferential. Indeed, the two newly formed C−C bonds in the product over **c** shows much larger bond lengths (1.65 Å) than those in the product over **d** (1.58 Å). Therefore, the site **c** exhibits the lowest reactivity among the four sites.

In order to unravel which cycloaddition type is kinetically preferred, we have searched for the transition states and possible intermediates of four CA reactions. The energy profiles of both [2 + 2] and [4 + 2] CAs have been outlined in Figures 2 and 3, respectively.

We first considered the [2 + 2] CA reactions and found that they follow a diradical mechanism via a singlet

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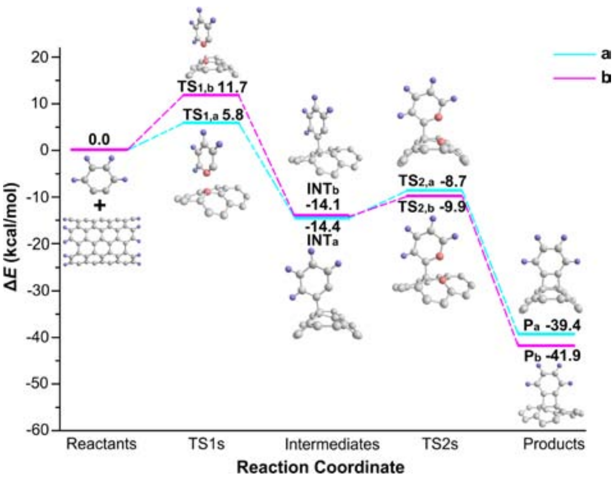

Figure 2. Energy profiles of the [2 + 2] CAs of benzyne and the armchair (5,5) SWNT.

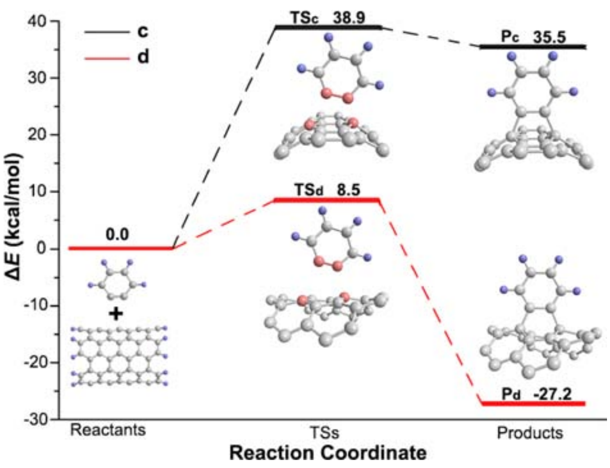

Figure 3. Energy profiles of the [4 + 2] CAs of benzyne and the armchair (5,5) SWNT.

diradical intermediate. As shown in Figure 2, the CA of bond **a** starts through $\mathbf{TS_{1,a}}$ (5.8 kcal/mol), forming the singlet diradical intermediate $\mathbf{INT_a}$. The transition states connecting $\mathbf{INT_a}$ and the product $\mathbf{P_a}$ have also been located, $\mathbf{TS_{2,a}}$, which is −8.7 kcal/mol. The activation energies from $\mathbf{INT_a}$ to $\mathbf{TS_{2,a}}$ is predicted to be 5.7 kcal/mol. The reaction mechanism is similar for the CA of the bond **b**. Clearly, the formation of the singlet diradical intermediate **INT**, rather than the ring-closing step, is the rate-determining step of the [2 + 2] cycloaddition upon SWNTs. Compared with the bond **a**, the rate-determining step for the CA upon the bond **b** is 11.7 kcal/mol high in energy, implying that the product $\mathbf{P_a}$ is more favored kinetically than the product $\mathbf{P_b}$.

The [4 + 2] CA reaction of benzyne to SWNTs, which belongs to the Diels−Alder reaction, takes the concerted mechanism. Indeed, [4 + 2] CA fulfills the Woodward−Hoffmann rule[19] and frontier orbital theory[20] (see Supporting Information). It is evident from Figure 3 that the concerted transition state $\mathbf{TS_c}$ leading to the product $\mathbf{P_c}$ is as large as 38.9 kcal/mol, while the $\mathbf{TS_d}$ which gives rise to the product $\mathbf{P_d}$ is 8.5 kcal/mol, in agreement with the thermodynamic trend discussed above in preference of $\mathbf{P_d}$ compared to $\mathbf{P_c}$. However, compared with that of $\mathbf{P_a}$, the activation energy of the overall CA reaction resulting in the $\mathbf{P_d}$ is still higher. Therefore, from both kinetic and thermodynamic points of view, [2 + 2] CAs are more preferable to the [4 + 2] ones.

To disclose the role of the SWNT diameter in the CA reactions, we have investigated CA reactions of benzyne to a series of armchair (*n*,*n*) SWNTs (*n* = 6−12). Noteworthy, the (12,12) SWNT has a diameter of 16.6 Å, which is quite close to the maximum diameter of SWNTs synthesized in the experiment.[8]

Figure 4 displays the reaction energies for both [2 + 2] and [4 + 2] CAs of benzyne to armchair SWNTs. It is clear that the SWNT diameter moderately influences the exohedral reactivity of the sidewalls of SWNTs toward benzyne. Interestingly, as the SWNT diameter increases, the predicted exothermicities of CAs upon the sites **a**, **b**, and **d** decrease, while the endothermicity of CA upon site **c** drops down. In fact, the bond lengths of two newly formed carbon bonds in the products **c** shorten gradually, which results in the strong interaction between benzyne and the SWNT. All the bond lengths of newly formed carbon bonds in products **a**, **b**, **c**, and **d** have been collected in the Supporting Information. However, for the SWNT with a given diameter, the [2 + 2] CA upon the bond **b** always shows the largest reaction energy over other CAs, indicating the high stability of the [2 + 2] product. Recently, Langa et al. theoretically investigated the reaction energies of CAs of benzyne with (7,7) and (10,10) SWNTs, showing similar results.[9]

Furthermore, we have calculated reaction energies of CAs of benzyne on zigzag (*n*,0) SWNTs (*n* = 7−12). Interestingly, for (*n*,0) (*n* = 7, 9, and 10) SWNTs, the [4 + 2] products are more stable than [2 + 2] ones; however, for other zigzag SWNTs [2 + 2] CAs are preferred over [4 + 2] CAs, indicating that CA type may even depend on whether the SWNT is metallic or semiconducting (see Supporting Information). The result here revealed that the CA reactions of benzyne on armchair SWNTs are quite different from those on zigzag SWNTs; for armchair SWNTs, the [2 + 2] product shows much higher stability over the [4 + 2] ones, which is independent of the SWNT diameter, while the CAs of benzyne upon zigzag SWNTs are very complex and the diameter plays an important role in determining the CA type.

Except for the reaction on the site **c**, the activation energies for the other three reactions rise along with the

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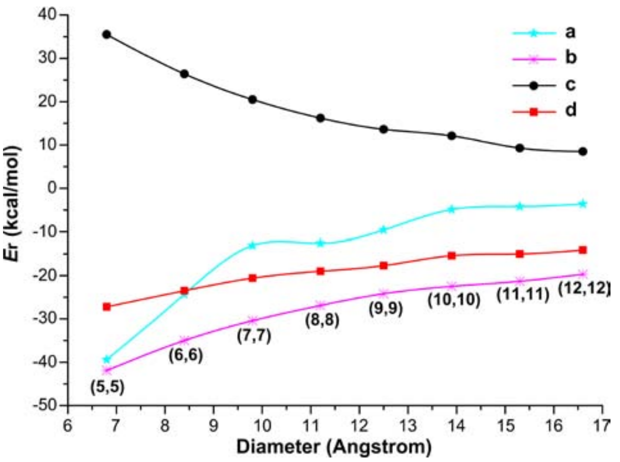

Figure 4. Reaction energy (E_r) for CA reactions of benzyne on (n,n) SWNTs versus diameters of (n,n) SWNTs (n = 5–12).

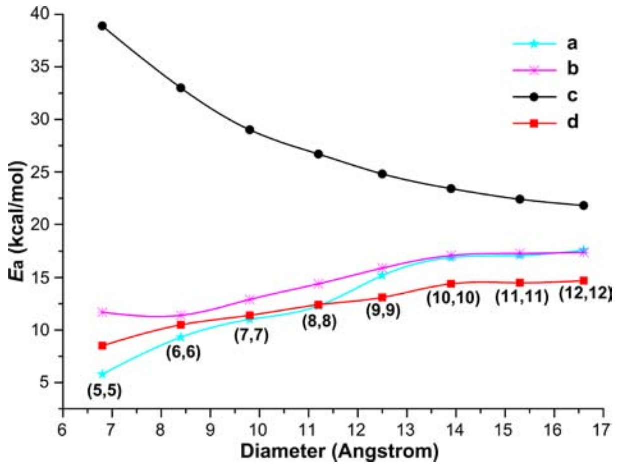

Figure 5. Activation energy (E_a) for CA reactions of benzyne on (n,n) SWNTs versus diameters of (n,n) SWNTs (n = 5–12).

armchair SWNT diameter, as shown in Figure 5. More importantly, as the SWNT diameter goes up, the activation energy of the [4 + 2] CA on the site **d** increases very slowly and becomes the lowest one since the SWNT diameter is larger than the (8,8) SWNT diameter (11.2 Å). Overall, the CA reactivity of the armchair SWNT sidewall toward benzyne follows the generally accepted rule; that is, the larger diameter the SWNT has, lower reactivity the armchair SWNT sidewall exhibits.

In conclusion, by means of quantum chemical calculations, we investigated the reaction mechanism and regioselectivity of [2 + 2] and [4 + 2] CAs of benzyne to armchair (n,n) SWNTs (n = 5–12). The [2 + 2] CA reaction follows the diradical mechanism, whereas the [4 + 2] CA reaction adopts the concerted mechanism. Even if the SWNT diameter increases, the [2 + 2] product over the bond **b** is always the most thermodynamically stable one among the four CA reactions. However, the SWNT diameter plays an important role in determining the kinetically favored CA type; that is, the [2 + 2] CA upon the bond **a** has the lowest energy barrier for small diameter SWNTs while the [4 + 2] CA over the site **d** gradually becomes kinetically favored for large diameter SWNTs. Our work provides a comprehensive understanding of the CAs upon SWNTs and encourages further study on the functionalized carbon nanotubes with various applications in nanodevices such as molecular paddle wheels.

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Supporting Information Available. Main frontier molecular orbitals for benzyne and SWNTs, reaction energies of benzyne with armchair (n,n) (n = 5–12) and zigzag (n,0) (n = 7–12) SWNTs, bond lengths of newly formed carbon bonds between benzyne and SWNTs, and Cartesian coordinates of the reactants, transition states, intermediates, and products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.