

# Stability of Supershort Single-Walled Carbon Nanotubes

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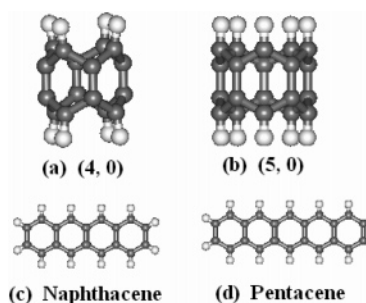
How short can single-walled carbon nanotubes (SWNTs) be? How stable are such supershort SWNTs (ss-SWNTs)? This work is the first to address these questions. On the basis of binding energy ( $E_B$ ), standard heats of formation ( $\Delta H_f^0$ ), and strain energy ( $E_S$ ), we found that SWNTs with only one benzene ring in the axial direction, which we refer to as supershort SWNTs (ss-SWNTs), can be thermodynamically stable. On the basis of the data of  $E_B$ ,  $\Delta H_f^0$ , and  $E_S$ , the relative stabilities of ss-SWNTs, fullerenes, polycyclic aromatic hydrocarbons, and butadiyne are discussed. This study has laid a theoretical foundation for the possible synthesis of ss-SWNTs.

## Introduction

It is well-known that single-walled carbon nanotubes (SWNTs) can be constructed from repeating translational units along the axial direction.<sup>1,2</sup> Naturally, the limiting case of SWNTs is only one benzene ring in the axial direction, namely, supershort SWNTs (ss-SWNTs). Although SWNTs have been synthesized for over 10 years,<sup>3,4</sup> the formation mechanism of SWNTs and controllable synthesis are still challenging subjects.<sup>5,6</sup> Supershort SWNTs represent the early configuration of SWNTs, which is fundamentally important for understanding of the formation mechanism.<sup>5,6</sup> Besides, the study of short SWNTs is of interest as single-electron transistors.<sup>7,8</sup> However, it is difficult to perform accurate quantum chemical calculations for SWNTs with several translation units, while such calculations can be carried out on ss-SWNTs with small diameters. Additionally, ss-SWNTs are three-dimensional benzene frameworks with open ends rather than planar polycyclic aromatic hydrocarbons (PAHs), closed fullerenes, or the extended structure of SWNTs. Supershort SWNTs can be viewed as bridging molecules, between PAHs, fullerenes, and SWNTs. Thus, the investigation of very short SWNTs is theoretically and experimentally significant for carbon nanotubes and related carbon materials. Two logical questions to ask are: How short can SWNTs be? And how stable are ss-SWNTs? In this work, the stability of ss-SWNTs is investigated by binding energy ( $E_B$ ), standard heats of formation ( $\Delta H_f^0$ ), and strain energy ( $E_S$ ) by using quantum chemical calculations.<sup>9</sup>

## Calculation Methods

Eight zigzag ss-SWNTs (ss-ZSWNTs), ( $n,0$ ) where  $n = 4-11$ , were investigated. Here, ss-ZSWNTs were chosen only due to their small unit cells. Linear PAHs (L-PAHs) with the same number of benzene rings have been selected as the reference molecules. Figure 1 presents the atomic structures of



**Figure 1.** Molecular structures of ss-ZSWNTs (4,0) and (5,0) and L-PAHs naphthalene and pentacene. The white spheres are hydrogen atoms, and the gray spheres are carbon atoms.

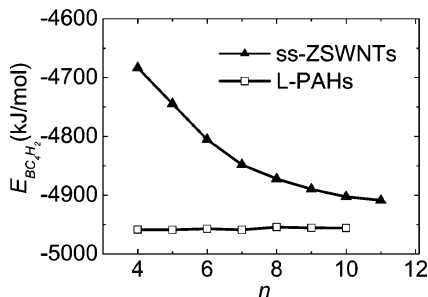
(4,0) and (5,0) ss-ZSWNTs and their unfolded L-PAH equivalents, naphthalene and pentacene. As shown in the figure, all dangling bonds of the carbon atoms are terminated with hydrogen atoms. The general formulas are  $C_{4n}H_{2n}$  for the ss-ZSWNTs and  $C_{4n+2}H_{2n+4}$  for the L-PAHs, respectively. The geometry optimizations and single-point energy calculations were performed at the HF/3-21G(d) and B3LYP/6-31G(d) theoretical levels, respectively. The total energies are thermally corrected by zero-point energies (ZPEs). The scale factors of the ZPEs for HF/3-21G(d) and B3LYP/6-31G(d) take the recommended values of 0.9409 and 0.9804.<sup>9</sup> All of the optimizations met the default convergence criteria setting in Gaussian 03. The stationary point geometries were fully optimized and characterized as minima (no imaginary frequency) by vibration frequency calculations. To improve the efficiency of calculations, a preoptimization was carried out with semiempirical calculations of AM1 for all investigated structures of ss-ZSWNTs and PAHs. All calculations were performed using Gaussian 03. The reported average error for B3LYP/6-31G(d)//HF/3-21G(d) is 33 kJ mol<sup>-1</sup> on the G2 molecule set; however, as a part of this error is due to systematic errors, the expected error for closely related species will be lower.<sup>9</sup>

The binding energy,  $E_B$ , is calculated relative to ground-state atoms contained in the investigated molecule; for instance, for  $C_xH_y$ ,  $E_B = E_{C_xH_y}^0 - (xE_C^0 + yE_H^0)$ . The standard heats of formation for PAHs and ss-ZSWNTs are calculated based on

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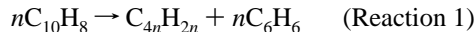
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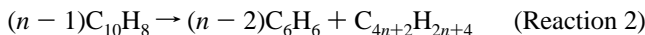


**Figure 2.** Binding energies per  $C_4H_2$  ( $E_{BC_4H_2}$ ) as a function of  $n$ .

hypothetical reactions proposed for ss-ZSWNTs as follows



and for L-PAHs



As can be seen, excluding the deviation of the hybridization of carbon atoms in ss-ZSWNT from the ideal  $sp^2$  hybrid,<sup>11</sup> the above-mentioned reactions are hyperhomodesmotic reactions,<sup>12</sup> which are supposed to provide a more extensive error cancellation.<sup>13</sup> The enthalpy changes for the hyperhomodesmotic reactions 1 and 2 are

$$\Delta H^1 = (E_{C_{4n}H_{2n}}^0 + nE_{C_6H_6}^0) - nE_{C_{10}H_8}^0 \quad (1)$$

and

$$\Delta H^2 = E_{C_{4n+2}H_{2n+4}}^0 + (n-2)E_{C_6H_6}^0 - (n-1)E_{C_{10}H_8}^0 \quad (2)$$

On the basis of  $\Delta H^1$  and  $\Delta H^2$ , the standard heats of formation for  $C_{4n}H_{2n}$  and  $C_{4n+2}H_{2n+4}$  can be calculated from the following equations

$$\Delta H^1 = \Delta H_{C_{4n}H_{2n}}^0 + n\Delta H_{C_6H_6}^0 - n\Delta H_{C_{10}H_8}^0 \quad (3)$$

and

$$\Delta H^2 = \Delta H_{C_{4n+2}H_{2n+4}}^0 + (n-2)\Delta H_{C_6H_6}^0 - (n-1)\Delta H_{C_{10}H_8}^0 \quad (4)$$

All single-point energy calculations are performed as described above at the level of B3LYP/6-31G(d)//HF/3-21G(d). The standard heats of formation for benzene and naphthalene,  $\Delta H_{C_6H_6}^0 = 82.9$  kJ/mol and  $\Delta H_{C_{10}H_8}^0 = 150.6$  kJ/mol, were obtained from the CRC handbook.<sup>10</sup>

## Results and Discussion

Figure 2 shows the binding energies per  $C_4H_2$  ( $E_{BC_4H_2}$ ) for ss-ZSWNTs and L-PAHs as a function of  $n$ . When  $n = 4-11$ ,  $E_{BC_4H_2}$  for L-PAHs changes slightly around  $-4957.0$  kJ/mol; for ss-ZSWNTs, however,  $E_{BC_4H_2}$  changes from  $-4683.4$  to  $-4908.9$  kJ/mol, suggesting that the stability increases with the increment of the diameter of ss-ZSWNTs, which is due to the decrease of strain energy; since with the increment of  $n$ , ss-ZSWNTs are apt to be planar and nonplanar distortion decreases immediately, which can be confirmed from the analysis of strain energy in the following. The increment of  $C_4H_2$  can be also described as the isomer butadiyne,  $HC\equiv C-C\equiv CH$  with  $E_B = -4579.0$  kJ/mol from a quantum chemical calculation at the

**TABLE 1: Standard Heats of ss-ZSWNTs and PAHs (kJ/mol)**

$n$	$C_{4n}H_{2n}$	$\Delta H_{f1}^0$	$\Delta H_{f(C_4H_2)}^0(n)$	$\Delta H_{f1}^0/4n$	PAHs	$\Delta H_{f2}^0$	$\Delta H_{f2}^0/n$
4	$C_{16}H_8$	1478.3	369.6	92.4	$C_{18}H_{12}$	323.8	81.0
5	$C_{20}H_{10}$	1542.4	308.5	77.1	$C_{22}H_{14}$	418.0	83.6
6	$C_{24}H_{12}$	1485.3	247.6	61.9	$C_{26}H_{16}$	512.1	85.3
7	$C_{28}H_{14}$	1434.4	204.9	51.2	$C_{30}H_{18}$	607.9	86.8
8	$C_{32}H_{16}$	1447.4	180.9	45.2	$C_{34}H_{20}$	701.9	87.7
9	$C_{36}H_{18}$	1469.1	163.2	40.8	$C_{38}H_{22}$	800.8	89.0
10	$C_{40}H_{20}$	1503.4	150.3	37.6	$C_{42}H_{24}$	898.1	89.8
11	$C_{44}H_{22}$	1585.1	144.1	36.0	$C_{46}H_{26}$	995.2	90.5

same level. This suggests that ss-ZSWNTs are more stable than butadiyne, even for (4,0) ss-ZSWNTs.

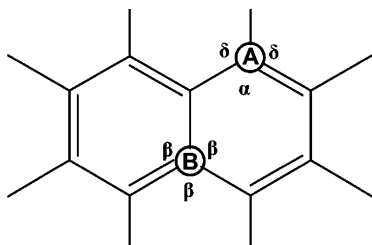
Table 1 presents the standard heats of formation of ss-ZSWNTs and L-PAHs. From Bakowies,<sup>14</sup>  $\Delta H_f^0$  can be expressed as the increments of carbon and hydrogen atoms ( $E_C$  and  $E_H$ ),  $\Delta H_{f1}^0(n) = 4nE_C(n) + 2nE_H(n)$  and  $\Delta H_{f2}^0 = (4n + 2)E_C(n) + (2n + 4)E_H(n)$  for ss-ZSWNTs and L-PAHs, respectively, where  $E_C$  and  $E_H$  are the contributions of carbon and hydrogen atoms to  $\Delta H_f^0(n)$ , respectively. Theoretically,  $E_C = 0$  kJ/mol and  $E_H = 0$  kJ/mol for bulk graphite and gaseous hydrogen, by definition; hence, in the above expressions,  $E_C \geq 0$  and  $E_H \geq 0$ . To compare the thermodynamic stability of clusters of different sizes,  $\Delta H_f^0$  needs to be averaged over a cluster with the same size. Here,  $\Delta H_f^0$  is averaged over  $C_4H_2$  by  $\Delta H_{f(C_4H_2)}^0(n) = 4E_C(n) + 2E_H(n) = \Delta H_{f1}^0(n)/n$  for ss-ZSWNTs and  $\Delta H_{f(C_4H_2)}^0(n) = [\Delta H_{f2}^0(n) - 2E_C(n) - 4E_H(n)]/n < \Delta H_{f2}^0(n)/n$  for L-PAHs. It is obvious from Table 1 that, in general,  $\Delta H_{f(C_4H_2)}^0(n)$  decreases with the increment of  $n$ , suggesting that the stability of ss-ZSWNTs increases with the increment of the molecule size, which is consistent with the above conclusion from  $E_B$ . In Table 1, the values of  $\Delta H_{f(C_4H_2)}^0(n)$  for ss-ZSWNTs are larger than those of L-PAHs, suggesting that L-PAHs are more stable than ss-ZSWNTs  $C_{4n}H_{2n}$ . However, with the increment of  $n$ , ss-SWNTs tend to be planar, and their stability will asymptotically approach that of the L-PAHs.

To compare the relative stability of ss-ZSWNTs and  $C_{60}$ ,  $\Delta H_f^0$  needs to be averaged over one carbon atom by  $\Delta H_{fC}^0 = [\Delta H_{f1}^0(n) - 2nE_H(n)]/4n < \Delta H_{f1}^0(n)/4n$ , as shown in Table 1; clearly,  $\Delta H_{fC}^0(n) < \Delta H_{f1}^0(n)/4n < 36.0$  kJ/mol when  $n > 11$ . For fullerenes  $C_{60}$ ,  $\Delta H_{fC}^0 = 44.3$  kJ/mol,<sup>15</sup> suggesting that ss-ZSWNTs with  $n \geq 9$  are more stable than  $C_{60}$ . To understand the stability of ss-SWNTs completely, we also investigated the source of destabilization of ss-SWNTs and extended the stability prediction of ss-ZSWNTs to a larger system for which accurate quantum chemical calculation is not feasible. In a previous study of  $C_{60}$ , the total strain energy ( $E_S$ ) was estimated to be approximately 100% of its heat of formation,<sup>16</sup> and  $E_S$  due to nonplanar distortion is estimated to 78% of the excess energy of the carbon atoms relative to graphite.<sup>17</sup> Similarly, the total strain energy calculations can be carried out on ss-SWNTs providing insights into their stability. From Bakowies<sup>14</sup> and Haddon,<sup>17</sup> it is possible to identify the two major sources of destabilization as out-of-plane and in-plane bending distortions. In terms of strain energy

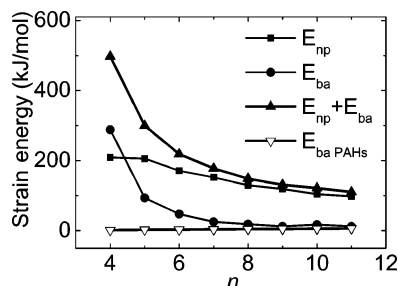
$$E_{ba} = \frac{1}{2}\kappa D^2 \sum (\theta_{ij} - \frac{2\pi}{3})^2 \quad (5)$$

$$E_{np} = \frac{1}{2}\kappa_\gamma D^2 \sum (\theta_{i\pi} - \frac{\pi}{2})^2 \quad (6)$$

where  $E_{np}$  is the strain energy due to the nonplanar distortions and  $E_{ba}$  is the strain energy due to bond-angle bending for the



**Figure 3.** Different carbon sites (A and B) and bond angles for the calculation of strain energy, using naphthalene as an example, according to refs 18 and 19.

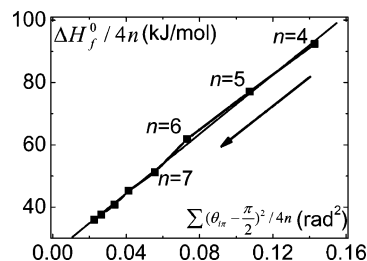


**Figure 4.** Strain energies of L-PAHs ( $\nabla$ ) and ss-ZSWNTs (solid symbols) as a function of  $n$ .

deviation of bond angles from the  $sp^2$  ideal;  $\kappa$  and  $\kappa_\gamma$  are force constants for angle bending and nonplanar distortion, respectively.  $D$  is the bond length; normally,  $D_{CC} = 1.42$  Å from the graphite structure. On the basis of the chemical environment, there are two identical carbon atoms in both L-PAHs and ss-ZSWNTs, marked as A and B as shown in Figure 3, and the different force constants have been taken from a force field<sup>18,19</sup>  $\kappa_\alpha = 0.7$ ,  $\kappa_\beta = 0.4$ ,  $\kappa_\delta = 0.35$ ,  $\kappa_{\gamma(C_3H)} = 0.20$ , and  $\kappa_{\gamma(C_4)} = 0.15$ , in units of mdyne/Å; this set of force constants was designed to describe the vibrations in aromatic molecules and had predicted reasonable results for fullerenes.<sup>14,16,17,20</sup> The definitions of  $\alpha$ ,  $\beta$ , and  $\delta$  are described in Figure 3, and the subscripts  $C_3H$  and  $C_4$  indicate two types of carbon-centered tetrahedrons.<sup>18,19</sup> In eq 6, the nonplanar distortion is quantitatively described by using the  $\pi$ -orbital axis vector (POAV),<sup>21</sup> which can provide a very logical and natural bridge between  $\sigma$ - $\pi$  separability assumed in planar conjugated systems and the realities of  $\pi$ -bonding in nonplanar geometries.<sup>22</sup> In this theory, there are six angles for one conjugated carbon atom, three among the  $\sigma$ -orbitals ( $\theta_{12}$ ,  $\theta_{23}$ , and  $\theta_{31}$ ) and three between the  $\sigma$ -orbitals and  $\pi$ -orbital ( $\theta_{1\pi}$ ,  $\theta_{2\pi}$ , and  $\theta_{3\pi}$ ), corresponding to  $\theta_{ij}$  and  $\theta_{i\pi}$  in eqs 1 and 2, respectively. Both angles  $\theta_{ij}$  and  $\theta_{i\pi}$  are obtained using the POAV package.<sup>21–23</sup>

Figure 4 presents  $E_S$  of L-PAHs and ss-ZSWNTs as a function of  $n$ . For L-PAHs,  $E_{np} = 0$  kJ/mol, and  $E_S$  is contributed to by  $E_{ba}$  and increases slightly with  $n$ . By fitting the data, we obtain,  $E_{ba} = 0.654n - 0.881$  kJ/mol, with a correlation coefficient of 0.999 and a standard error of 0.075 kJ/mol. For ss-ZSWNTs, with the increment of  $n$ ,  $E_{np}$ ,  $E_{ba}$ , and  $E_S$  decrease, and the  $E_S$  for ss-ZSWNTs has an overwhelming contribution from the out-of-plane distortion when  $n > 6$ . (This phenomenon has also been found in fullerenes.<sup>14,17</sup>) Hence, the destabilization of ss-ZSWNTs mainly arises from the nonplanar distortions; with increasing molecular diameter, ss-ZSWNTs become planar ( $\theta_{i\pi} \rightarrow 0$ ),  $E_{np}$  decreases immediately, and the stability of the ss-ZSWNTs is asymptotically approaching that of L-PAHs, which confirms the above conclusion.

From Figure 4, the nonlinear trend is due to the curvature effect for larger clusters. Hence, it is logical to correlate the thermodynamic stability with the average curvature of the



**Figure 5.** Average standard heats of ss-ZSWNTs ( $\Delta H_f^0/4n$ ) as a function of the average curvature.

cluster, which can be characterized by  $\sum(\theta_{i\pi} - \pi/2)^2/N$  (in our notation), where  $N$  is the total number of carbon atoms.<sup>14,16</sup> Similar analysis was carried out for fullerenes, and the standard heats of 30 fullerene clusters fall on a linear function,<sup>14</sup>  $\Delta H_f^0/N = 1248.9 \sum(\theta_{i\pi} - \pi/2)^2/N + 16.7$  kJ/mol. Fortunately, such a linear regression has also been found in ss-ZSWNTs, as shown in Figure 5, and average standard heats of formation,  $\Delta H_f^0/4n$ , are presented as a function of  $\sum(\theta_{i\pi} - \pi/2)^2/4n$ . By fitting the data in Figure 5, we obtained,  $\Delta H_f^0/4n = 476.5 \sum(\theta_{i\pi} - \pi/2)^2/4n + 25.3$  kJ/mol, with a correlation coefficient of 0.999 and a standard error of 0.909 kJ/mol. Obviously, for ss-ZSWNTs, the limit of  $\Delta H_f^0/4n$  is 25.3 kJ/mol, which is always bigger than that of L-PAHs;  $\Delta H_f^0/4n = 24.0 - 15.6/n$  kJ/mol, suggesting that ss-ZSWNTs are less stable than L-PAHs, even for larger clusters. Similar to fullerenes,<sup>14,17</sup> the expression suggests that  $\Delta H_f^0$  can be partitioned between a term related to the strain of pyramidalization of the conjugated carbon atoms and a term related to the number of  $\pi$ -bonds. Different from fullerenes,<sup>14,16,17</sup>  $\sum(\theta_{i\pi} - \pi/2)^2$  does not remain constant; hence when  $n > 6$ , the part from nonplanar distortion for  $\Delta H_f^0/4n$  is less than the contribution from the strain related to  $\pi$ -bonds, according to the expression of  $\Delta H_f^0/4n$ .

In the above discussion on the basis of  $\Delta H_f^0$ , we only suggested that for ss-ZSWNTs with  $n \geq 9$  they are more stable than  $C_{60}$ , and there is no further evidence to show the relative stabilities of larger fullerenes and ss-ZSWNTs. On the basis of the relationship between standard heats of ss-ZSWNTs ( $\Delta H_f^0/4n$ ) and the average curvature, we can further compare the relative stabilities between larger ss-ZSWNTs and fullerenes  $C_N$ . For spheroidal fullerenes,<sup>14,16</sup>  $\sum(\theta_{i\pi} - \pi/2)^2 \approx 2.418$  rad<sup>2</sup>; therefore, for  $C_{4n}$ ,  $\Delta H_f^0/N \approx 755.0/n + 16.7$  kJ/mol. With respect to ss-ZSWNTs, when  $n > 87$ , fullerenes are going to be more stable than ss-ZSWNTs with the same number of carbon atoms. This conclusion can be confirmed by MNDO results of fullerene; for ss-ZSWNTs, the limit of  $\Delta H_f^0/4n$  is 25.3 kJ/mol, which is a little bigger than that of  $C_{540}$  ( $\Delta H_f^0/540 = 20.0$  kJ/mol<sup>14</sup>). For ss-ZSWNT (11,0),  $\Delta H_f^0/44 = 36.0$  kJ/mol; therefore, on a per atom basis, when  $n > 11$ ,  $25.3 < \Delta H_f^0/4n < 36.0$  kJ/mol, which is very close to larger fullerenes (such as, 38.9 kJ/mol for  $C_{140}$ , 32.4 kJ/mol for  $C_{180}$ , and 27.8 kJ/mol for  $C_{240}$ <sup>14,16</sup>).

## Conclusion

In conclusion, the results in the present work demonstrate that ss-ZSWNTs are less stable than L-PAHs but more stable than butadiyne and normal fullerenes, providing the theoretical basis for the possible synthesis of ss-ZSWNTs since fullerenes have been synthesized readily. As bridging molecules, the proposed ss-ZSWNTs fill the gap between L-PAHs, fullerenes, and extended SWNTs. Extensive studies on aromaticity can be carried out using the analogy as we used it in this work, which

would possibly open a new area of carbon physics and chemistry. The work in this paper will also be fundamentally significant in helping to understand the formation mechanism and controllable synthesis of SWNTs (such as by seeded synthesis) and short SWNTs for use as nanoscale molecular devices.

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