

# Bond-Curvature Effect of Sidewall [2+1] Cycloadditions of Single-Walled Carbon Nanotubes: A New Criterion To the Adduct Structures

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A unique property, bond curvature  $K$ , is proposed as a universal criterion for structures and reactivities of sidewall [2+1] cycloadditions of SWCNTs. B3LYP/6-31G\* calculations for cycloadditions on various types of SWCNTs show that the binding energies of the open structures and the changes in C–C bond lengths of the 3MR structures increase linearly with  $K$ . When  $K$  is large, the open structure is formed, whereas when  $K$  is small, the formation of the configuration with a three-membered ring (3MR) is favorable. A boundary of  $K$  for producing different structures is about  $1.5 \text{ nm}^{-1}$  for the tubes with moderate radii. The cycloaddition of  $\text{CCl}_2$  on any C–C bond of zigzag tubes with smaller  $K$  values will lead to adducts with 3MR structures, which clarifies the contradiction between the experimental phenomenon and previous theoretical predictions.

## 1. Introduction

Single-walled carbon nanotubes (SWCNTs) exhibit interesting electronic, mechanical, and structural properties,<sup>1,2</sup> making them promising for applications in various fields such as chemical sensors and nanometer-scale electronic devices.<sup>3–6</sup> The experimental and theoretical investigations show that the sidewall of SWCNT has a higher curvature-induced chemical reactivity than that of the flat graphite.<sup>7–9</sup> Consequently, the chemical functionalization of open ends and sidewalls of SWCNTs would play a vital role in tailoring their properties. One of the most-promising approaches to purifying SWCNTs and expanding their application areas is the chemical derivatizations.<sup>10–14</sup> Among these, covalent

sidewall functionalizations, especially the [2+1] cycloaddition of C–C bond on the tube wall, may increase their solubility<sup>15–19</sup> and improve their bioactivity and biocompatibility etc.<sup>20,21</sup> Therefore, the investigation for the [2+1] cycloaddition has been an important subject for the covalent sidewall chemistry of carbon nanotubes.<sup>22–24</sup>

The [2+1] cycloadditions of dichlorocarbene  $\text{CCl}_2$ ,<sup>10,25,26</sup> Bingel  $(\text{COOEt})_2\text{C}$ , and its derivations,<sup>27</sup> as well as (*R*)-oxycarbonylaziridino<sup>28</sup> have been achieved experimentally. According to the dramatic changes in the optical spectra of SWCNTs, Hu<sup>26</sup> et al. considered the local structures of adducts attached to dichlorocarbene to be three-membered

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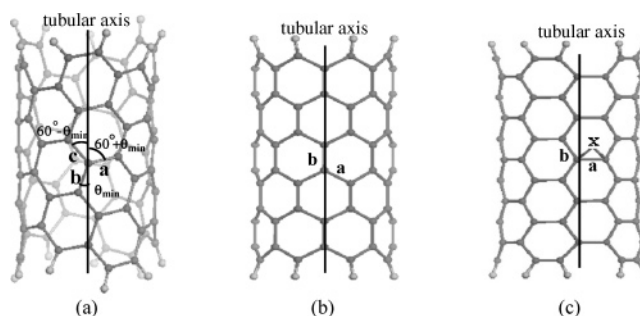
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- (1) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. *Carbon Nanotubes*; Springer: Berlin, 2001.
- (2) Dai, H. *Surf. Sci.* **2002**, *500*, 218–241.
- (3) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A.; *Science* **2000**, *287*, 1801–1804.
- (4) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622–625.
- (5) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787–792.
- (6) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787–1800.
- (7) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105–1113.
- (8) Tada, K.; Furuya, S.; Watanabe, K. *Phys. Rev. B* **2001**, *63*, 155405–155408.
- (9) Gülseren, O.; Yildirim, T.; Ciraci, S. *Phys. Rev. Lett.* **2001**, *87*, 116802–116805.
- (10) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95–98.
- (11) Wong, S. S.; Joselevich, E.; Woolley, A. T.; Cheung, C. L.; Lieber, C. M. *Nature* **1998**, *394*, 52–55.
- (12) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, *103*, 4318–4322.

- (13) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.
- (14) Chen, Q.; Dai, L.; Gao, M.; Huang, S.; Mau, A. *J. Phys. Chem. B* **2001**, *105*, 618–622.
- (15) Sun, Y.-P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002**, *35*, 1096–1104.
- (16) Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2004**, *108*, 11151–11159.
- (17) Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. *Adv. Mater.* **2005**, *17*, 17–29.
- (18) Hirsch, A.; Vostrowsky, O. *Top. Curr. Chem.* **2005**, *245*, 193–238.
- (19) Georgakilas, D.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760–761.
- (20) Pantarotto, D.; Partidos, C. D.; Graff, R.; Hoebeke, J.; Briand, J.-P.; Prato, M.; Bianco, A. *J. Am. Chem. Soc.* **2003**, *125*, 6160–6164.
- (21) Alvaro, M.; Atienzar, P.; de la Cruz, P.; Delgado, J. L.; Garcia, H.; Langa, F. *J. Phys. Chem. B* **2004**, *108*, 12691–12697.
- (22) Chen, Z. F.; Nagase, S.; Hirsch, A.; Haddon, R. C.; Thiel, W.; Schleyer, P. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1552–1554.
- (23) Barone, V.; Heyd, J.; Scuseria, G. E. *Chem. Phys. Lett.* **2004**, *389*, 289–292.
- (24) Lu, X.; Chen, Z. F. *Chem. Rev.* **2005**, *105*, 3643–3696.
- (25) Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science*, **2003**, *301*, 1501–1501.
- (26) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893–14900.
- (27) Coleman, K. S.; Bailey, S. R.; Fogden, S.; Green, M. L. H. *J. Am. Chem. Soc.* **2003**, *125*, 8722–8723.
- (28) Holzinger, M.; Abraham, J.; Whelan, P.; Graupner, R.; Ley, L.; Hennrich, F.; Kappes, M.; Hirsch, A. *J. Am. Chem. Soc.* **2003**, *125*, 8566–8580.

rings (3MR) with a cyclopropane configuration. So far, there have been several reports regarding theoretical investigations of the additions of oxygen,<sup>22–24,29–32</sup> carbene,<sup>22,32</sup> dichlorocarbene,<sup>33,34</sup> and nitrene<sup>22,35</sup> on the sidewall of SWCNTs. However, in terms of the prediction for ultimate structures, some controversies still exist. Lu<sup>36</sup> et al. showed by using ONIOM method that when dichlorocarbene, silylene, germylene, and oxycarbonylnitrene were added to the sidewall of an armchair (5,5) SWCNT, epoxide-like structures of adducts were formed. Recently, by the full optimization for the structure of SWCNTs on the basis of the critical theoretical method, Chen et al. suggested that the breaking of conjointed C–C bond is possible and that the epoxide-like structures are not energetically favorable.<sup>22</sup>

The results obtained from the theoretical calculations on the B3LYP/6-31G\* level have a higher reliability;<sup>22</sup> however, several cruces related to the [2+1] cycloadditions are still puzzling. For example, why are the structures of [2+1] adducts derived from experiments different from those predicted theoretically?<sup>22,34</sup> How do we find a proper index that predicts the reactivities and adduct structures, etc.? Many authors take the strength of the C–C bond,<sup>22</sup> the tube diameter (or tubular curvature),<sup>32</sup> the pyramidalization angle ( $\theta_p$ ), and the  $\pi$ -orbital misalignment angle ( $\phi$ )<sup>7–9</sup> as criteria for predicting the configurations of [2+1] adducts; however, these criteria are not universal. In the present work, we will see that, in many cases, the short (or more double-bond character<sup>22</sup>) C–C bonds favor the formation of 3MR structures; on the contrary, the long C–C bonds are broken, which is where the opened structure is formed during the [2+1] cycloaddition. The tubular diameter is also not a good criterion, because it cannot distinguish the different C–C bonds in a given SWCNT and can be used only for the comparisons of the adduct structures involving the C–C bonds with  $\theta = 90^\circ$  ( $\theta$  is the C–C bond obliquity angle, as presented in Figure 1) in different SWCNTs. Although the values of  $\theta_p$  and  $\phi$  have been proven to be a useful index for describing the local reactivity of the fullerenes,<sup>7–9</sup> they are not perfect parameters for the SWCNTs, because it is impossible to estimate an opened cycloaddition structure with the broken C–C  $\sigma$  bond. Therefore, finding a suitable criterion to discriminate the chemical reactivities and structures of the same or different SWCNTs is still a problem awaiting a solution. In practice, the precise characterization of the structure of the adduct has become a bottleneck for the study of sidewall cycloaddition.<sup>22,24</sup> In addition, up to now, there is still a lack of systemic and critical theoretical



**Figure 1.** Nonequivalent C–C bonds in the (a) chiral, (b) zigzag, and (c) armchair SWCNTs; X expresses species in [2+1] cycloadditions.

investigations for [2+1] cycloadditions of SWCNTs with different types and sizes, especially for the chiral SWCNTs that possess the most common SWCNT structure.<sup>37</sup>

Here, we report a critical theoretical study on the basis of the first principle method for the structures, energies, and their varying rules of [2+1] sidewall cycloadditions on all kinds of the SWCNTs, including the chiral, armchair, and zigzag tubes. A new criterion, bond curvature, which can estimate the [2+1] adduct structures for both the same and different SWCNTs, is proposed in this work, and the contradiction of the cycloaddition structures predicted by the experiments and the theoretical calculations is elucidated.

## 2. Definition of Bond Curvature and Computational Model

Figure 1 shows the nonequivalent C–C bonds of different types of SWCNTs.  $\theta$  is an acute angle between the tubular axis and the C–C bond on the plane of the unfolded SWCNT, defined as the C–C bond obliquity angles or the bond angles. The minimum  $\theta_{\min}$  is just the chiral angle of a SWCNT, and the other C–C bond angles are equal to  $60^\circ - \theta_{\min}$  and  $60^\circ + \theta_{\min}$ .

For the [2+1] cycloaddition, the curvature of SWCNT<sup>32</sup> (or point curvature) that expresses only the curvature of every carbon atom on the tubular circumference does not exactly reflect the strain energies of various C–C bonds. Bond curvature, a new indicator proposed in this work, may effectively estimate the strain energy of a certain C–C bond, and the [2+1] cycloaddition is just sensitive to the C–C bond curvature.

Bond curvature  $K$  is defined as the average curvature of the corresponding arc of a C–C bond in the SWCNT. As shown in Figure 2, the terminal tangents of the arcs of the  $C_1$ – $C_2$  bond and its projected bond  $C'_1$ – $C'_2$  on the tubular circumference lie in planes M and N, respectively. The formula of bond curvature  $K$  of the  $C_1$ – $C_2$  bond can be derived from the curvature of arc  $C'_1$ – $C'_2$  on the circumference with tubular radius  $R$  (see part 1 of the Supporting Information for details).

$$K = \frac{\phi}{C_1C_2} = \frac{\phi' \sin^2 \theta}{C'_1C'_2} = \frac{\sin^2 \theta}{R}$$

From the above formula of  $K$ , it can be seen that  $K$  is related to the values of  $\theta$  and  $R$ . For the C–C bonds of a given SWCNT,  $K$  changes only with  $\theta$ , and for the bonds with the same  $\theta$  among different SWCNTs,  $K$  changes with  $R$ .  $K$  relates only to a given C–C bond in this work, so it can express the strain energy  $E_s$  of

(29) Sorescu, D. C.; Jordan, K. D.; Avouris, P. *J. Phys. Chem. B* **2001**, *105*, 11227–11232.

(30) Lu, X.; Zhang, L.; Xu, X.; Wang, N.; Zhang, Q. *J. Phys. Chem. B* **2002**, *106*, 2136–2139.

(31) Dag, S.; Gülseren, O.; Yildirim, T.; Ciraci, S. *Phys. Rev. B* **2003**, *67*, 165424/1–10.

(32) Lu, J.; Nagase, S.; Zhang, X.; Maeda, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Akasaka, T.; Yu, D.; Gao, Z.; Han, R.; Ye, H. *J. Mol. Struct. (THEOCHEM)* **2005**, *725*, 255–257.

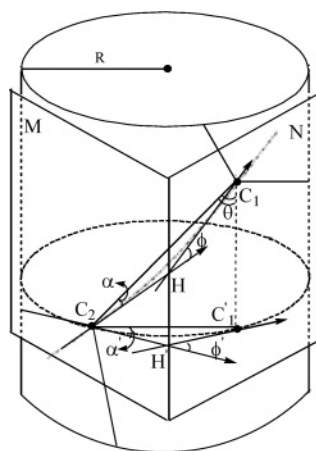
(33) Li, R. F.; Shang, Z. F.; Wang, G. C.; Pan, Y. M.; Cai, Z. S.; Zhao, X. Z. *J. Mol. Struct. (THEOCHEM)* **2002**, *583*, 241–247.

(34) Zhao, J. J.; Chen, Z. F.; Zhou, Z.; Park, H.; Schleyer, P. R.; Lu, J. P. *Chem. Phys. Chem.* **2005**, *6*, 598–601.

(35) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002–4005.

(36) Lu, X.; Tian, F.; Zhang, Q. *J. Phys. Chem. B* **2003**, *107*, 8388–8391.

(37) Miyauchi, Y.; Chiashi, S.; Murakami, Y.; Hayashida, Y.; Maruyama, S. *Chem. Phys. Lett.* **2004**, *387*, 198–203.



**Figure 2.** Three-dimensional sketch map for the definition of the bond curvature ( $K$ ); also see part 1 of the Supporting Information for details.

the C–C bond,<sup>38</sup> namely  $E_S = aK$ , where  $a$  is a proportionality factor.

The binding energies  $E_b$  for the [2+1] cycloaddition can be calculated according to the following expression

$$E_b = E_{\text{tube}} + E_X - E_{\text{tube-X}}$$

where  $E_{\text{tube-X}}$  is the total energy of the tube–adsorbate system and  $E_X$  ( $X = \text{O}, \text{CH}_2, \text{NH}, \text{SiH}_2, \text{or } \text{CCl}_2$ , etc.) and  $E_{\text{tube}}$  are the energies of an isolated  $X$  species and the pristine tube, respectively.

The optimized structures and binding energies were obtained by the hybrid density functional theory (DFT), namely Becke's three parameter hybrid functional,<sup>39</sup> B3LYP method was employed in the present work. For all atoms considered, the standard 6-31G\* basis sets were used. All the calculations were performed with the Gaussian 03 package.<sup>40</sup> On the basis of the method mentioned above, we obtain a series of results of various O/SWCNT derivatives, and  $\text{CH}_2$ ,  $\text{NH}$ , and  $\text{SiH}_2$  adducts for (6,2) and (6,3) SWCNTs, as well as  $\text{CCl}_2$  adducts for (20,0) and (22,0) SWCNTs. During the calculations, the SWCNTs are simulated by a section of the tube, and the dangling C–C bonds at the two ends of the fragment are saturated by H atoms. For the chiral SWCNTs, one unit cell is selected except for the (6,5) tube, for which a fragment with 100 carbon atoms is chosen because there are too many carbon atoms in the unit cell. In [2+1] cycloadditions, the C–C bond a, b, or c in the middle-exohedral sidewalls of the SWCNTs (Figure 1) is considered. For example, the C–C bonds a, b, and c of the chiral SWCNT (6,3)(C78H18) (Figure 1a), the C–C bonds a and b of the zigzag (8,0)(C96H16) (Figure 1b) and the armchair (5,5)-(C110H20) (Figure 1c) participated in the cycloadditions (also see Tables 1 and 2). Furthermore, to investigate the adsorptions of O atom on the periodical zigzag SWCNTs, we also have carried out some additional calculations within the framework of DFT with a plane wave basis set and pseudopotentials (see the Supporting Information for the details of the calculations).

The cycloaddition of O,  $\text{CH}_2$ ,  $\text{NH}$ ,  $\text{SiH}_2$ , and  $\text{CCl}_2$  on the sidewall of SWCNT may result in two types of the C–C bonds on the reaction site, namely the broken C–C bond in the opened C–X–C configuration and the C–C bond in the closed 3MR formed with X, which are denoted by type I and type II, respectively, in this work. For the cycloaddition of the formation of the type I adduct,

the binding energies  $E_b(\text{I})$  can be rewritten as the following simplified expression

$$E_b(\text{I}) = E_X + E_{\text{C-C}} + E_S + E'_{\text{SWCNT}} - (2E_{\text{C-X(I)}} + E_X + E'_{\text{SWCNT}}) = E_{\text{C-C}} + E_S - 2E_{\text{C-X}} \quad (\text{I})$$

where  $E_{\text{C-C}}$  and  $E_{\text{C-X}}$  are the binding energies of the C–C bond and the C–X bond, respectively;  $E_S$  is the strain energy of the C–C bond; and  $E'_{\text{SWCNT}}$  is the energy of a fictitious SWCNT from which the C–C bond participating in the [2+1] cycloaddition is removed. Because the values of  $E_{\text{C-C}}$ ,  $E_{\text{C-X}}$ , and their difference  $\Delta E = E_{\text{C-C}} - 2E_{\text{C-X}}$  are fixed, it could be expected that there is a linear relationship between  $E_b(\text{I})$  and  $E_S$  or  $K$ , namely  $E_b(\text{I}) = \Delta E + aK$ .

For the binding energy of the formation of type II adduct

$$E_b(\text{II}) = (E_{\text{C-C}} - E'_{\text{C-C}}) + (E_S - E'_S) - 2E_{\text{C-X}} \quad (\text{II})$$

where  $E'_{\text{C-C}}$  and  $E'_S$  are the C–C bond energy and the strain energy of the adduct, respectively.  $|2E_{\text{C-X(I)}}| > |2E_{\text{C-X(II)}}|$  and  $(E_{\text{C-C}} - E'_{\text{C-C}}) + (E_S - E'_S) \approx 0$  because of their counteraction, so in general,  $E_b(\text{II}) < E_b(\text{I})$ , and there is not a simple relationship between  $E_b(\text{II})$  and  $K$ . A linear relationship may exist between the change in the C–C bond length ( $\Delta R_{\text{C-C(II)}}$ ) and  $K$ , because the value of  $K$  will increase along with a reduction in the C–C bond length.

### 3. Results and Discussion

**3.1. X/SWCNT System with Moderate  $R$ .** Because SWCNTs used in the chemical modifications are mainly HiPCO tubes with moderate diameter (7–14 Å), the cycloaddition rule of these SWCNTs will be especially considered. On the basis of the calculated results for various C–C bonds of all types of SWCNTs, we established two linear relationships between  $E_b(\text{I})$  and  $K$  and  $\Delta R_{\text{C-C(II)}}$  and  $K$  (Figures 3 and 4, or Tables 1 and 2). However,  $\Delta R_{\text{C-C(I)}}$  of the type I bond and  $E_b(\text{II})$  of the formation of the type II adduct vary irregularly with increasing  $K$  (Tables 1 and 2).

From Tables 1 and 2, it can be seen that  $E_b(\text{I})$  is larger than  $E_b(\text{II})$  as a whole and that the larger  $K$ , the easier the C–C bond is broken. A boundary value of  $K$  for determining whether the C–C bond is broken or not is obtained, namely  $K \approx 1.5 \text{ nm}^{-1}$ . Hence, it is favorable to form the type I adduct as  $K > 1.5 \text{ nm}^{-1}$ , whereas the type II structure is obtained as  $K < 1.5 \text{ nm}^{-1}$ .

It is worth noting that, according to our results, whether the C–C bond is broken or not is not directly relative to the bond length or strength. As an example, for the cycloaddition of O on a (6,1) tube, the C–C bond with a short length of 1.414 Å ( $K = 0.068 \text{ nm}^{-1}$ ) is not broken, and a C–C bond with a long distance of 1.439 Å ( $K = 2.429 \text{ nm}^{-1}$ ) is destroyed. On the other hand, there also exist cases in which the short C–C bond is broken whereas the long C–C bond is kept. For instance, in the (6,3) tube, the C–C bond with a length of 1.435 Å ( $K = 0.344 \text{ nm}^{-1}$ ) is preserved; however, another strong C–C bond with a length of 1.429 Å ( $K = 3.101 \text{ nm}^{-1}$ ) is broken.

It is also obvious that the tube diameter is not a good index for judging whether the C–C bond is broken. A typical example is that in a given SWCNT, such as the (6,1) tube mentioned above, the breaking and nonbreaking of C–C bonds can coexist. Another example is that, although the tube diameter of the (6,2) tube (0.564 nm) is smaller than that of

(38) Robertson, D. H.; Brenner, D. W.; Mintmire, J. W. *Phys. Rev. B* **1992**, 45, 12592–12595.

(39) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652.

(40) Frisch, M. J.; et al.; *Gaussian 03*, Gaussian Inc.: Pittsburgh, PA, 2003.

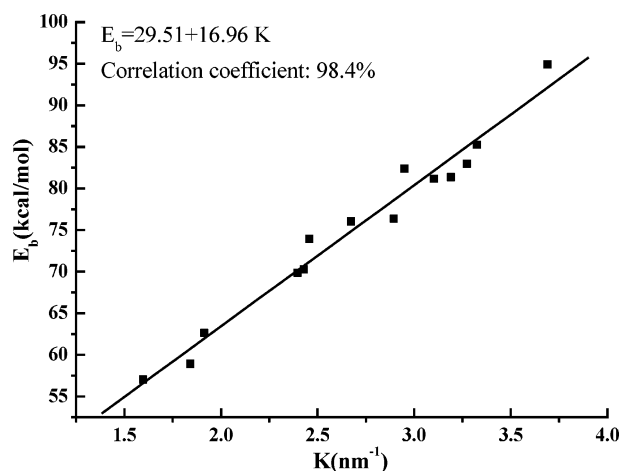


**Table 1. Tubular Radius ( $R$ ), Bond Angles ( $\theta$ ), Bond Curvature ( $K$ ), Lengths of C–C Bonds before ( $R_{c-c}^0$ ) and after ( $R'_{c-c}$ ) Cycloaddition, Changes in C–C Bond Lengths ( $\Delta R_{c-c}$ ), and Binding Energies ( $E_b$ ) of the Formation of the Type I Adduct for the Cycloaddition of the O Atom on Various SWCNTs**

	$R$ (nm)	$\theta$ (deg)	$K$ (nm <sup>-1</sup> )	$R_{c-c}^0$ (Å)	$R'_{c-c}$ (Å)	$\Delta R_{c-c}(I)$ (Å)	$E_b(I)$ (kcal/mol)
(12,0) (C <sub>120</sub> H <sub>24</sub> )	0.470	60.00	1.596	1.422	2.097	0.675	57.03
(6,2) (C <sub>100</sub> H <sub>16</sub> )	0.282	46.10	1.841	1.433	2.123	0.690	58.93
(10,0) (C <sub>100</sub> H <sub>20</sub> )	0.392	60.00	1.913	1.425	2.109	0.684	62.63
(8,0) (C <sub>96</sub> H <sub>16</sub> )	0.313	60.00	2.396	1.428	2.125	0.697	69.87
(6,1) (C <sub>168</sub> H <sub>14</sub> )	0.257	52.41	2.429	1.439	2.154	0.715	70.28
(6,6) (C <sub>132</sub> H <sub>24</sub> )	0.407	90.00	2.457	1.432	2.118	0.686	73.95
(6,5) (C <sub>100</sub> H <sub>22</sub> )	0.373	87.00	2.673	1.430	2.111	0.681	76.03
(6,4) (C <sub>148</sub> H <sub>20</sub> )	0.341	83.41	2.894	1.421	2.096	0.675	76.36
(5,5) (C <sub>110</sub> H <sub>20</sub> )	0.339	90.00	2.950	1.437	2.127	0.690	82.39
(6,3) (C <sub>78</sub> H <sub>18</sub> )	0.311	79.11	3.101	1.429	2.114	0.685	81.17
(6,0) (C <sub>84</sub> H <sub>12</sub> )	0.235	60.00	3.191	1.443	2.179	0.736	81.35
(6,2) (C <sub>100</sub> H <sub>16</sub> )	0.282	73.90	3.273	1.431	2.141	0.710	82.98
(6,1) (C <sub>168</sub> H <sub>14</sub> )	0.257	67.59	3.325	1.442	2.177	0.735	85.25
(4,4) (C <sub>88</sub> H <sub>16</sub> )	0.271	90.00	3.690	1.447	2.139	0.692	94.91

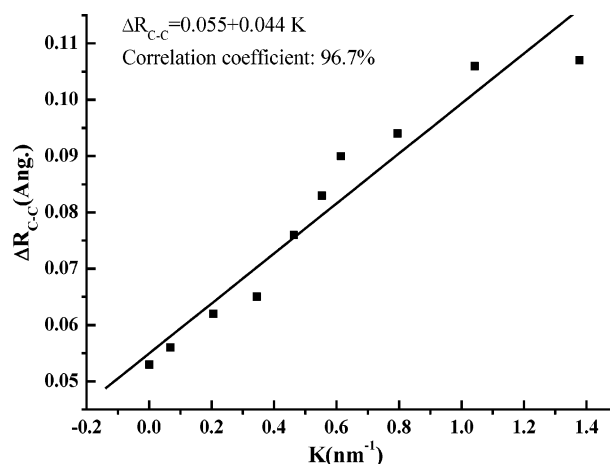
**Table 2. Tubular Radius ( $R$ ), Bond Angles ( $\theta$ ), Bond Curvature ( $K$ ), Lengths of C–C Bonds before ( $R_{c-c}^0$ ) and after ( $R'_{c-c}$ ) Cycloaddition, Changes in Adduct Lengths ( $\Delta R_{c-c}$ ), and Binding Energies ( $E_b$ ) of the Formation of the Type II C–C Bond for the Cycloaddition of the O Atom on Various SWCNTs**

	$R$ (nm)	$\theta$ (deg)	$K$ (nm <sup>-1</sup> )	$R_{c-c}^0$ (Å)	$R'_{c-c}$ (Å)	$\Delta R_{c-c}(II)$ (Å)	$E_b(II)$ (kcal/mol)
(6,0) (C <sub>84</sub> H <sub>12</sub> )	0.235	0	0	1.416	1.469	0.053	72.58
(6,1) (C <sub>168</sub> H <sub>14</sub> )	0.257	7.59	0.068	1.414	1.470	0.056	64.56
(6,2) (C <sub>100</sub> H <sub>16</sub> )	0.282	13.90	0.205	1.428	1.490	0.062	49.57
(6,3) (C <sub>78</sub> H <sub>18</sub> )	0.311	19.11	0.344	1.435	1.500	0.065	42.02
(6,4) (C <sub>148</sub> H <sub>20</sub> )	0.341	23.41	0.463	1.430	1.506	0.076	46.13
(6,5) (C <sub>100</sub> H <sub>22</sub> )	0.373	27.00	0.553	1.423	1.506	0.083	47.97
(6,6) (C <sub>120</sub> H <sub>24</sub> )	0.407	30.00	0.614	1.417	1.507	0.090	51.26
(6,5) (C <sub>100</sub> H <sub>22</sub> )	0.373	33.00	0.795	1.424	1.518	0.094	48.42
(6,4) (C <sub>148</sub> H <sub>20</sub> )	0.341	36.59	1.042	1.435	1.541	0.106	45.18
(6,3) (C <sub>78</sub> H <sub>18</sub> )	0.311	40.89	1.378	1.421	1.528	0.107	56.15

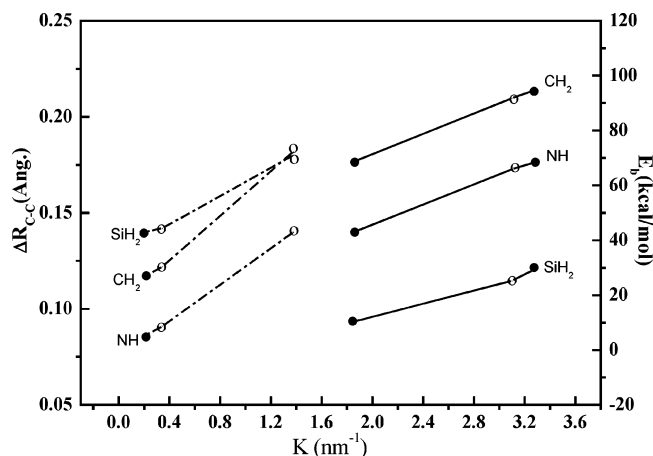
**Figure 3.** Variation in the binding energy ( $E_b$ ) as a function of bond curvature for the formation of the type I adduct during the cycloaddition of the O atom.

the (6,4) tube (0.682 nm), the C–C bond of the former ( $K = 0.205$  nm<sup>-1</sup>) is kept but the C–C bond of the latter ( $K = 2.894$  nm<sup>-1</sup>) is broken.

In the research,<sup>7–9</sup> authors suggest that the magnitude of the misalignment angle for  $\pi$ -orbital overlap,  $\phi$ , could reflect the SWCNT's reactivity. However, there exists a contradiction between the  $\phi$  value of a C–C bond of an armchair tube along the tubular circumference and the reactivity, because the  $\phi$  value is zero but the reactivity of this C–C bond is strongest in the armchair tube, as seen in this work and others.<sup>22,32</sup> Furthermore, the cycloaddition of the O atom at the C–C bond with  $\theta = 90^\circ$  in the armchair SWCNT (5,5) shows an opened structure, whereas the 3MR is produced when the cycloaddition takes place at the other

**Figure 4.** Variation in the change of C–C bond length ( $\Delta R_{c-c}$ ) as a function of bond curvature for the formation of the type II adduct during the cycloaddition of the O atom.

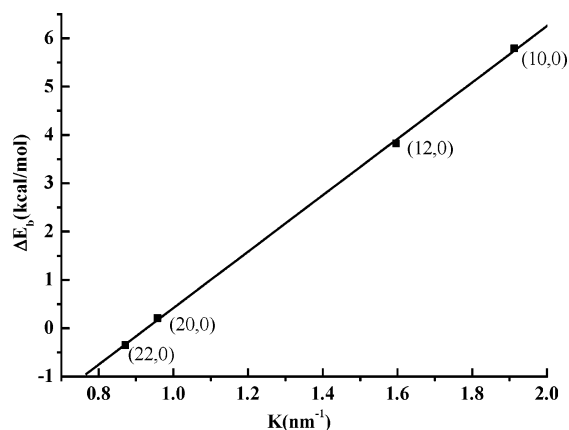
C–C bonds with  $\theta = 30^\circ$ , which implies that the C–C bond with  $\theta = 90^\circ$  exhibits a higher [2+1] cycloaddition reactivity. This conclusion contradicts the result deduced from the criterion of  $\phi$ , because the  $\phi$  value of the C–C bond with  $\theta = 90^\circ$  is equal to zero and is obviously less than that of the other C–C bond with  $\theta = 30^\circ$ .<sup>7–9</sup> Moreover, in general, the C–C bond with  $\theta = 60^\circ$  in a zigzag SWCNT (10,0) forms an open structure and the C–C bond with  $\theta = 30^\circ$  in the (5,5) SWCNT tends to create 3MR structures; however, the values of  $\theta_p$  and  $\phi$ <sup>7–9</sup> of the former are less than those of the latter. Therefore, the parameter  $\phi$ , which is localized and does not consider  $\sigma$ -bonding, is obviously difficult to determine for the adduct structures and reactivities on SWCNTs.



**Figure 5.** Variations in the binding energy ( $E_b$ ) for the formation of the type I adduct (solid line) and the change in C–C bond length ( $\Delta R_{C-C}$ ) for the formation of the type II adduct (dashed line) as functions of bond curvature for the cycloadditions of  $\text{CH}_2$ ,  $\text{SiH}_2$ , and  $\text{NH}$  on (6,2) (denoted by filled circles) and (6,3) tubes (denoted by hollow circles).

According to the structural character of SWCNTs,  $K$  involving the two parameters  $R$  and  $\theta$  can solely determine the types of the C–C bonds and predict the reactivities of C–C bonds and adduct structures for both the same and different SWCNTs, so it is universal. In practice, both  $\pi$ -delocalized and  $\sigma$ -bonding interactions of the C–C bond are considered in  $K$ , so  $K$  along the tubular circumference of the armchair tube is maximal. Of course, it exhibits a high chemical reactivity. Therefore, compared with the above criteria that have been usually adopted in many studies,  $K$  is more suitable for estimating the reactivity and structure of the SWCNT. Herein, what is meant by the high reactivity is the favorable reaction in binding energy, namely thermodynamically, as in many previous works.<sup>7–9,24</sup> Of course, there may be various kinetic mechanisms of the reaction for different types of SWCNTs; for instance, concerning the presence of the density of state close to the Fermi level, the metallic tubes have a higher reactivity than the semiconducting ones,<sup>41</sup> and simultaneously, the  $\sigma$ – $\pi$  mixing caused by high curvature obviously affects the band structures of SWCNTs in this band region.<sup>42,43</sup>

Figure 5 shows the cycloadditions of  $\text{CH}_2$ ,  $\text{NH}$ , and  $\text{SiH}_2$  on the sidewall of the (6,2) and (6,3) tubes; a similar rule found in the cycloaddition of O is also observed. The boundary between the formations of adduct types I and II is close to  $K = 1.5 \text{ nm}^{-1}$ . Here, the reason only the (6,2) and (6,3) tubes are considered is that, according to the results from the cycloaddition of the O atom, the boundary for the formations of two types of C–C bonds is expected to be between the (6,2) and (6,3) tubes. For the addition of the O atom, there are two type I and one type II structures for the (6,2) tube, whereas there are one type I and two type II structures for the (6,3) tube. It must be pointed out that when  $\text{SiH}_2$  is added to the sidewall of the (6,2) tube, only one C–C bond is broken, and the corresponding  $E_b$  is specially



**Figure 6.** Variation in the difference in binding energy ( $\Delta E_b$ ) between the formations of two types of adducts as a function of bond curvature for the cycloaddition of the O atom on some zigzag SWCNTs with large radii.

small (see the Supporting Information, Table S3). This may be related to the singlet ground state (The other X species except  $\text{SiH}_2$  and  $\text{CCl}_2$  are in the triplet ground states).

**3.2. X/SWCNT System with Large or Small  $R$ .** From Tables 1 and 2, it can be seen that, for the cycloadditions on the SWCNTs with moderate  $R$  values, the C–C bonds with  $\theta = 30^\circ$  in the armchair tube or  $\theta = 0^\circ$  in the zigzag tube are not destroyed, whereas those bonds with  $\theta = 90^\circ$  in the armchair tube or  $\theta = 60^\circ$  in the zigzag tube are broken. This conclusion is in agreement with Chen's calculation results.<sup>22</sup> However, for the SWCNTs with  $R < 0.2 \text{ nm}$  and  $R > 0.7 \text{ nm}$ , some attention must be paid to the cycloadditions on the C–C bonds with  $\theta = 30^\circ$  in the armchair tubes and  $\theta = 60^\circ$  in the zigzag tubes. Our results (see the Supporting Information, Tables S1 and S2) show that, for the C–C bonds of the armchair tubes with  $R < 0.2 \text{ nm}$ , such as the O/(2,2) and O/(3,3) systems, it is easy to form the open structures even for the C–C bond with  $\theta = 30^\circ$ ; for the zigzag tubes with  $R > 0.7 \text{ nm}$ , such as the O/(20,0) and O/(22,0) systems, it is also possible to form the 3MR structures for the C–C bond with  $\theta = 60^\circ$ .

It must be pointed out that, for the cycloaddition on SWCNTs with larger or smaller  $R$  values, the boundary of  $K$  should be properly extended. For instance, the competition between the structures of the type I and II adducts formed on the (3,3) armchair tube or the zigzag tubes from (10,0) to (22,0) may occur for  $0.9 \text{ nm}^{-1} < K < 1.9 \text{ nm}^{-1}$  (see the Supporting Information, Table S1 or S2). The structural ambiguity in this  $K$  region may be related to the distortion of the SWCNTs with these sizes. Figure 6 displays the variation in the difference of binding energies ( $\Delta E_b$ ) between the formations of two types of structures from (10,0) to (22,0) SWCNTs, and the positive value of  $\Delta E_b$  means the formation of the type I adduct is favorable. The middle point of the  $K$  interval is close to  $1.5 \text{ nm}^{-1}$ , and a similar result is also obtained for the periodic zigzag tube (see the Supporting Information, Figure S2).

From the calculated results for the  $\text{CCl}_2$ /SWCNT system (see the Supporting Information, Table S4), it also can be seen that the experimental observation<sup>26</sup> that the local structure of  $\text{CCl}_2$ /SWCNT is 3MR occurs in any bond of the zigzag SWCNTs ( $n,0$ ) with smaller  $K$  ( $n \geq 20$ ) and

(41) Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science*, **2003**, *301*, 1519–1522.

(42) Gülsiren, O.; Yildirim, T.; Ciraci, S. *Phys. Rev. B* **2002**, *65*, 153405/1–4.

(43) Zólyomi, V.; Kürti, J. *Phys. Rev. B* **2004**, *70*, 085403/1–8.

maybe in that in the middle of the competition region  $K$ . Because of the especially large  $K$  of the C–C bonds participating in the reaction, the theoretical prediction derived from the calculations for the  $\text{CCl}_2$  cycloadditions on the (9,0) and (10,0) tubes led to open structures.<sup>34</sup> According to the  $K$  effect, for the armchair or chiral SWCNT, if only the 3MR configuration is obtained for the cycloaddition of  $\text{CCl}_2$ , it requires a tube with a very large diameter, which is extremely unstable.

### Conclusions

Bond curvature  $K$  proposed in this work can well-describe the local structures of the [2+1] cycloaddition for various C–C bonds of both the same and different SWCNTs, including the chiral, armchair, and zigzag SWNTs. The boundary value of  $K$  for the formation of the opened or 3MR adduct is approximately equal to  $1.5 \text{ nm}^{-1}$  for the tube with moderate  $R$ , and the values of  $E_b(\text{I})$  and  $\Delta R_{\text{C-C}}(\text{II})$  increase

linearly with  $K$ . Several criteria, such as C–C bond strength (or length), tube diameter, and  $\pi$ -orbital misalignment angle, are not appropriate for determining the structure of the adduct because of various deficiencies. Our results indicate that only for the zigzag tube with smaller  $K$  will the cycloaddition of  $\text{CCl}_2$  on any C–C bond lead to the adducts with 3MR structure, which clarifies the contradiction between the experimental phenomenon<sup>26</sup> and previous theoretical predictions.<sup>24, 34</sup>

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**Supporting Information Available:** Derivation of the bond-curvature  $K$  and some detail results about the [2+1] cycloaddition. This material is available on the Web at <http://www.pubs.acs.org>. CM060563V