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Chemical Anisotropies of Carbon Nanotubes and Fullerenes Caused by the Curvature Directivity

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Abstract: The directional-curvature theory is developed as a rational basis for the strain energy and the chemical reactivity in single-walled carbon nanotubes (SWCNTs) and fullerenes. The directional curvature K_D and its mean K_M, derived from this theory, cover the overall curvatures of their bonds and atoms and break through the limitations of the pyramidalized-angle θ_p approach, which is only available to atomic curvature. The directional-curvature theory demonstrates that K_D and K_M depend directly on the strain or reactive binding energies of the bonds and atoms and that there is approximate curvature conservation in SWCNTs and fullerenes. Application of this theory to addition reactions of various SWCNTs and fullerenes shows that the slope of the straight line between the strain or binding energies and K_D is close to a constant, which helps clarify the puzzle as to why some functionalizations of C_{70} occur at the relatively flat midsection.

Keywords: anisotropy · fullerenes · nanotubes · reaction mechanisms · reactivity · strain energy

Introduction

Since fullerenes[1] and carbon nanotubes,[2] new types of carbon material different from graphite and diamond, were discovered, they have exhibited interesting electronic, electric, mechanical, and structural properties and stimulated extensive research into their chemical functionalization.[3] Experimental and theoretical investigations show that fullerenes and single-walled carbon nanotubes (SWCNTs) have higher curvature-induced chemical reactivities than flat graphite[4] and have a different chemical anisotropy from graphite and diamond.[5] Research into the strain or curvature, which is considered to be the source of their higher reactivity, has become an important aspect of the chemistry of SWCNTs and fullerenes. Theoretical research into the correlation of curvature with the reactive mechanisms, up until now, remains at the level of isolated atoms[4b–c,5a] and is deficient in various directional curvatures, hence the reactivity of the bond and the inherent relation of the curvature of the atom and bond cannot be considered correctly. Consideration of the whole curvature of these carbon clusters is indispensable to rationally estimate the reactivities of the atoms and bonds.

The formation of SWCNTs or fullerenes with various frameworks includes two orbital–interaction processes. First, the orbitals of isolated carbon atoms are hybridized to sp^x (type: σ; s/p orbital ratio: 1:x) and sp^y (type: π; s/p orbital ratio: 1:y). Second, the multifarious carbon tubes or cages are formed by different routes between the hybrid orbitals of the adjacent atoms. The second precedence is the crux of the formation and anisotropic reactivity of the SWCNTs or fullerenes with a specific structure (Figure 1).

The pyramidized-angle (θ_p) concept[4b,6] indicates the orbital hybridization of isolated atoms; however, it only considers the first step, so that the second step, the formation of SWCNTs and fullerenes, exceeds the capacity of this approach. The misalignment angle based on pyramidization also does not represent the second step correctly. Therefore, the pyramidization approach to carbon atoms merely represents the mean reactivity of the vertex atom of the fullerene or SWCNT. This approach has undergone grave difficulty in describing the reactivities and adduct structures of the different directional C–C bonds on SWCNTs.[5a–b] Furthermore,

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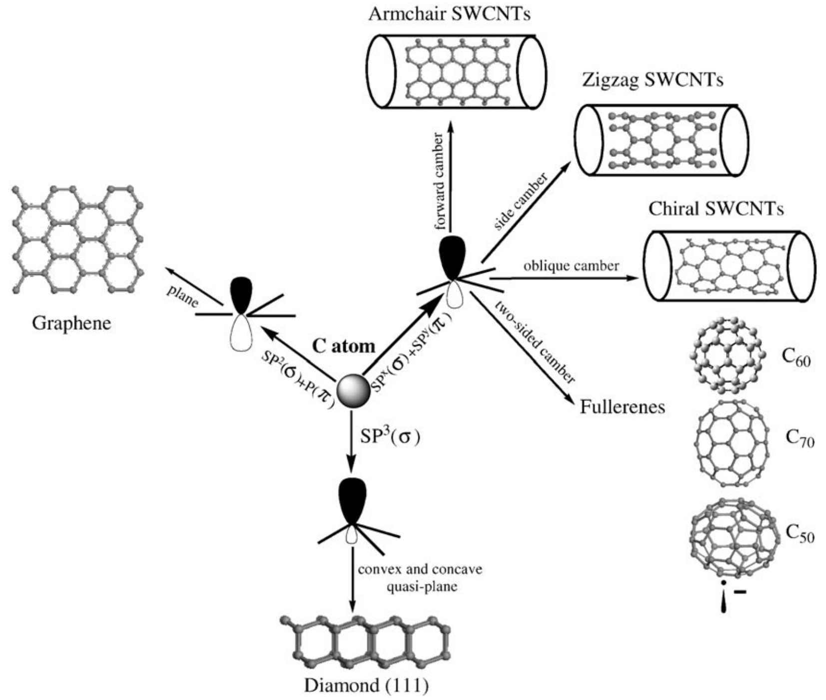

Figure 1. SWCNT, fullerene, graphene, and diamond formed by various routes.

the pyramidization approach also does not have the proper criterion for the reactivities of fullerenes with anisotropic curvature, which encompasses most of the known fullerenes. For example, the tubular radii and θ_p value of SWCNTs (5,5) and (9,0) are very close, whereas the curvatures and reactivities of the C–C bonds on the circumference of the (5,5) tube are much greater than those of the axis bonds of the (9,0) tube because of the different routes of formation.[5b,7] The reactivities of the variously oriented C–C bonds in the (5,5) or (9,0) tubes are also obviously different as a result of the different oblique angle θ[5b] of the C–C bonds, although their θ_p values are equal. Diamond and C_{20} also have similar θ_p values, whereas their structures are quite distinct. From the addition reactions of benzyne, dichlorocarbene, and sulfonyl azides to C_{70},[5c–e] it has been found that the sites on C_4–C'_4 (i.e., C_7–C_8 in IUPAC numbering) with smaller pyramidalized angles have higher reactivities than those with larger θ_p values. The [2+1] addition of an oxygen atom to C_{50} does not occur at the equator with the largest θ_p value.[8]

The bond-curvature approach[5b] was successfully used to explain the reactivities of the C–C bonds of SWCNTs; however, this approach needs to be extended and enriched to predict the reactivities of the fullerenes and vertex sites of SWCNTs. To describe the oriented curvature and the anisotropic chemistry of SWCNTs and fullerenes generated by various routes of formation, we have developed, herein, a unified, directional-curvature theory that evaluates the strain energies and reactivities of the vertices and bonds.

Directional-Curvature Theory of SWCNTs and Fullerenes

The direction of the curvature of the σ framework camber of SWCNTs or fullerenes is in the normal direction of the camber, the orientation of which is the π hybrid orbital relative to the σ framework formed by the delocalized interaction of the hybrid orbitals of the isolated atoms. Hence, the curvature of the camber can be regarded as a unified mathematical representation of the geometry and inherent stress of the dangling hybrid orbital on the vertex or the arc of the camber relative to the σ framework of these carbon clusters as viewed by delocalization.

The curvatures of the arcs that correspond to the C–C bonds and the vertex carbon atoms of the SWCNTs or fullerenes are defined as the directional curvature K_D and its mean K_M, respectively. Based on the delocalization of the curved π conjugated system[5b] and the Euler formula in differential geometry[9] for the C_a–C_b bonds with biterminal oblique angles θ_i,[5b] K_D can be defined by Equation (1) and for the vertex atom i, the curvature may take the mean of the $K_D(i)$ for θ_i, namely, K_M, which is given by Equation (2):

$$K_D = \frac{1}{2}\sum_{i=a,b}(K_{i1}\sin^2\theta_i + K_{i2}\cos^2\theta_i) \tag{1}$$

$$K_M = \frac{2}{\pi}\int_0^{\frac{\pi}{2}} K_D(i)d\theta_i = \frac{1}{2}(K_1 + K_2) \tag{2}$$

where K_{i1} and K_{i2} and K_1 and K_2 are the principle curvatures of carbon atom i (see the Supporting Information). Equations (1) and (2) include the whole curvature of the vertices and the bonds of the various SWCNTs or fullerenes. In practice, others may be simplified greatly except for the curvature of the ellipsoidal fullerenes, which should be calculated by Equations (1) and (2). For example, in the SWCNTs, because K_1 is equivalent to $1/R$ (see the Supporting Information) and $K_2=0$ and $\theta_a=\theta_b$, K_D is defined by Equation (3):

$$K_D = \frac{\sin^2\theta}{R} \tag{3}$$

where R is the radius of the SWCNT. Equation (3) is the bond curvature K of the SWCNTs,[5b] and the K_M value for

Table 1. The curvature parameters of SWCNTs in the formation of the adducts with the opened C–C bond.

SWCNTs	Atoms					Bonds					
	R [nm]	K_M [nm^{-1}]	θ_p [°]	$\sum_j K_M$ [nm^{-1}]	Reactivity	θ [°]	K_D [nm^{-1}]	E_b [kcal mol^{-1}] O/SWCNT	E_b [kcal mol^{-1}] CH_2/SWCNT[a]	E_b [kcal mol^{-1}] NH/SWCNT[a]	Reactivity
(11,0)	0.431	1.16	4.70	22.10		60.00	1.742	71.89			
(6,2)	0.282	1.77	7.17	22.07		46.10	1.841	73.20	68.38	42.71	
(8,8)	0.542	0.92	3.73	22.13		90.00	1.844	78.86			
(9,0)	0.352	1.42	5.75	22.17		60.00	2.129	79.43			
(8,0)	0.313	1.60	6.48	22.16		60.00	2.396	82.14			weak
(6,1)	0.257	1.95	7.90	22.14	$\approx K_M$	52.41	2.429	85.48			↓
(6,6)	0.407	1.23	4.98	22.17	or	90.00	2.457	89.42			
(7,0)	0.274	1.82	7.40	22.20	$\frac{1}{2R}$	60.00	2.737	86.81			
(6,4)	0.341	1.47	5.95	22.05		83.41	2.894	93.27			
(5,5)	0.339	1.47	5.95	22.14		90.00	2.950	96.79			strong
(6,3)	0.311	1.61	6.52	22.13		79.11	3.101	96.98	91.86	65.96	
(6,0)	0.235	2.13	8.63	22.07		60.00	3.191	95.12			
(6,2)	0.282	1.77	7.17	22.16		73.90	3.273	97.81	94.62	68.27	
(6,1)	0.257	1.95	7.90	22.20		67.59	3.325	100.33			
(4,4)	0.271	1.85	7.49	22.20		90.00	3.690	104.50			

[a] The binding energies are given on the basis of the cluster model.[5b]

the vertices of SWCNTs can be obtained from Equation (2) or the average of the K_D value with θ_{min} and $60° \pm \theta_{min}$,[5b] namely from Equation (4)

$$K_M = \frac{1}{2R} \tag{4}$$

hence, the vertex curvatures of SWCNTs with a given radius are identical everywhere. For the spherical fullerenes, such as C_{60}, K_D and K_M are given by Equation (5):

$$K_D = K_M = \frac{1}{R_S} \tag{5}$$

because $K_1 = K_2 = 1/R_S$ (see the Supporting Information), where R_S is the radius of spherical fullerenes.

It can be seen, from the above discussion, that the curvatures of various directions are different from those of the isolated atoms in SWCNTs and that for the great majority of fullerenes $K_D \neq K_M$, except for the spherical fullerenes. In other words, as the SWCNTs or fullerenes are formed, the σ and π hybrid orbitals of a central carbon atom (set as C_1) may be changed from the original sp^x (σ) and sp^y(π) hybrid orbitals obtained by POAV analysis[6] to new σ and π hybrid orbitals as a result of various curvatures of the C_1–C_n ($n = 2$, 3, and 4) bonds between C_1 and its adjacent atoms C_2, C_3, or C_4. At the same time, the $\theta_{\sigma\pi}$ value (or $\theta_p + \pi/2$) of the C_1 atom will be changed correspondingly. For example, for an armchair SWCNT with a moderate radius, the $\theta_{\sigma\pi}$ value for C_1 obtained from the σ bond angles $\sphericalangle C_n$-C_1-C_n', obtained on the basis of the POAV approach,[6] comes close to equal. However, the practical $\theta_{\sigma\pi}$ value (set as $\theta_{\sigma\pi}'$) may be obviously different because of the curvature directivity. The θ_p' value (or $\theta_{\sigma\pi}' - \pi/2$) of C_1 along the C_1–C_n bond (set as C_1–C_2) of the circumference is twice as large as the original θ_p value, and the θ_p' value along the C_1–C_3 or C_1–C_4 bonds is one half of the θ_p value. These $\theta_{\sigma\pi}'$ values will create a set of new σ and π hybrid orbitals of the C_1 atom under orthonormal conditions.

The variance of the $\theta_{\sigma\pi}$ value caused by the curvature or strain led to increasing ($\theta_{\sigma\pi}$ value decreased) or decreasing ($\theta_{\sigma\pi}$ value increased) bonding interactions between the π hybrid orbitals of the C_1 and C_n atoms, and at the same time, the σ bond between C_1 and C_n is changed reasonably. From the point of view of energy, the SWCNTs or fullerenes will tend to stabilize, but there is a larger difference in the activities of various C_1–C_n bonds; for example, the reactivity of the circumference C_1–C_2 bond is obviously stronger than that of the axis C_1–C_3 or C_1–C_4 bonds. From the correlation of the directional curvature with the calculated binding energies and experimental results (see Table 1, Table 2, and reference [5]), it must be admitted that the directional-curvature method is reasonable, though the direct experimental measurement of the $\theta_{\sigma\pi}'$ or $\theta_{\sigma\pi}$ values is difficult.

The hybrid-orbital recombination inevitably leads to the anisotropy of the chemistry; however, the chemistry of the graphene and diamond is isotropic, because the hybrid orbitals are not changed. This behavior is just the chemical outcome of the directional-curvature theory.

The Directional-Strain Energy Derived from the Directional Curvature

The recombination of the atomic hybrid orbitals in SWCNTs and fullerenes is carried out according to their curvatures, which can be used to represent the interactional energy of these hybrid orbitals relative to a single sheet of graphite, as the SWCNT or fullerene increases the bonding energy and, at the same time, bears a corresponding strain energy that comes from the curved structure. Based on a continual elastic model,[10] the strain energy or work E_s re-

Table 2. The curvature parameters for oxygen addition to fullerenes.

Fullerenes	Atoms						Bonds						
	Atomic types	R_S [nm]	K_M [nm^{-1}]	θ_p^e (θ_p^s) [°]	$\sum_i K_M^2$ [nm^{-1}]	Reactivity	Bond types	K_D [nm^{-1}]	θ_p^e(B) [°]	r [nm]	E_b [kcal mol^{-1}]	Reactivity opened C–C bond	Reactivity closed C–C bond
C_{60}	1	0.352	2.84	11.50	483.9		[6,6][a]	2.84		0.138	76.33		[b]
							[5,6][a]	2.84		0.145	78.25	[b]	
	1		3.109	12.59			1(C_1–C'_1)[5,6]	3.141	9.72	0.1452	78.18	[b]	
	2		2.804	11.36		strong	2(C_1–C_2) [6,6]	2.805		0.1397	75.89		[b]
C_{70}	3		2.601	10.53	484.8	↑	3(C_2–C_3) [5,6]	2.779	9.45	0.1448	75.74		
							4(C_3–C'_3) [6,6]	2.899		0.1389	75.30		[b]
	4		2.426	9.83			5(C_3–C_4) [5,6]	2.236	8.80	0.1450	70.43		
						weak	6(C_4–C'_4) [5,6]	2.799	8.11	0.1434	76.97	[b]	
	5		2.375	9.62			7(C_4–C_5) [6,6]	2.226		0.1421	63.46		
							8(C_5–C'_5) [6,6]	2.769		0.1471	89.02		[b]
	1		2.538	10.28		weak	1(C_1–C'_1)[5,6]	2.520		0.1465	80.11		
	2		2.892	11.71			2(C_1–C_2) [6,6]	2.861		0.1390	81.76		[b]
C_{50}	3		3.256	13.19	485.0	↓	3(C_2–C_3) [5,6]	2.964		0.1469	88.31	[b]	
							4(C_3–C'_3) [6,6]	2.816		0.1415	69.58		[b]
	4		3.535	14.32		strong	5(C_3–C_4) [5,6]	3.669		0.1417	82.80	[b]	
							6(C_4–C'_4) [5,5]	2.913		0.1470	73.48		

[a] [6,6] or [5,6] ring fusion. [b] Reaction is favorable.

quired to bend a bar with moment M through an angle ϕ is given by Equation (6):

$$E_s = \frac{1}{2} M \times \phi = \alpha \frac{\sin^2\theta}{R} = \alpha K_D \tag{6}$$

where $\phi = \frac{r_{C-C}}{R}\sin^2\theta$,[5b] or more generally, $\phi = r_{C-C} K_D$, in which r_{C-C} is the corresponding arc of the C–C bond, and α may be taken approximately as a constant because M does not significantly affect the π orbital, which is the dominant contributor to E_b. Thus, the mean E_s (E_{sM}) is equal to αK_M.

Equation (6) develops a relation in which the strain energy depends directly on K_D or K_M. The directional-curvature theory allows the curvature to represent the strain energy or the difference of the binding energy E_b of the SWCNT or fullerene relative to the graphite sheet E_{bg}, as given by Equation (7) or Equation (8):

$$E_b = E_{bg} + E_s = E_{bg} + \alpha K_D \tag{7}$$

$$\begin{aligned} E_b &= E_T(C_n) + E_X - E_T(C_n + X) \approx E_T(C_n') + E_C + E_s + E_X \\ &\quad -(E_T(C_n' + E_{C-X} + E_X) = (E_C - E_C' - E_{C-X}) + E_X = E_{bg} + E_s \end{aligned} \tag{8}$$

where $E_T(C'_n)$ is the energy of a fictitious SWCNT or fullerene from which the carbon atom or C–C bond participating in the reaction has been removed; E_C and E'_C are the energies corresponding to the carbon atom or bond before and after the reaction; and E_X and E_{C-X} are the energies of applied species x and the binding energy of the bond C–X, respectively.

In the sidewall additions of H and Al atoms on the vertices of zigzag[11] and armchair[12] SWCNTs and of O, CH_2, NH, and SiH_2 species on the C–C bonds with different θ values for the various types of SWCNTs,[5b] the linear relationships between E_b and $1/R$, θ_p, or $\frac{\sin^2\theta}{R}$ have been seen, respectively.

The Relationship of K_D with the Bond Curvature K and the Pyramidalized Angle θ_p

From Equations (1), (3), and (5) deduced from Equation (1), it can be seen that K_D is the same as the bond curvature K and its extension to the SWCNTs and fullerenes. It can be also proved that the K_M values from Equations (2), (4), and (5) represent the curvatures that correspond to the θ_p value of the vertex atoms of SWCNTs and fullerenes, respectively.

Figure 2 is the projection of the bonds that adjoin a vertex carbon atom on the circumference of an armchair SWCNT. The ΔC_1-C_2-C_3 of the bottom plane is close to an equilateral triangle, thus giving Equation (9) and Equation (10)

$$K_M = \frac{1}{2R} = \frac{\sin\frac{\phi}{2}}{r} \approx \frac{\phi}{2r} = \frac{2\theta_p}{r} \tag{9}$$

$$K_D = 2K_M \sin^2\theta = \frac{4\theta_p}{r}\sin^2\theta \tag{10}$$

where r is the C–C bond length of about 0.142 nm.

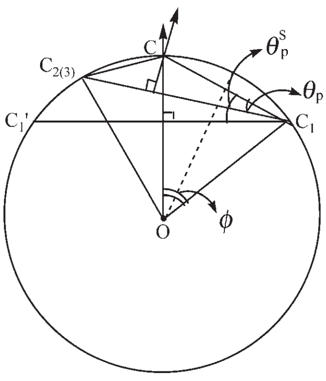

Figure 2. The projected frame of the bonds on the circumference of an armchair SWCNT.

In Equation (9), $\theta_p=\phi/4$ and, simultaneously, may be regarded as the mean of the radial and axial θ_p value, in which the former is $\phi/2$ and the latter zero as a result of orbital delocalization. Furthermore, $\theta_p=\frac{r}{4R}=\frac{a}{4\sqrt{3}R}$ (a is the length of the repeat unit) can be also obtained, which is identical to the result reported by Kleiner and Eggert.[13] The K_M and θ_p values are only dependent on the tubular radius R, and the θ_p values obtained from K_M are also consistent with the result of Haddon and co-workers,[5a] but the tedious calculation is not required; besides, the vertex curvatures obtained from the K_M and θ_p values are identical as well. Equations (9) and (10) may be spread to other SWCNTs or fullerenes if only the circular section in Figure 2 is taken as the corresponding curvature circle. Therefore, the relationship of K_D (or K_M) with θ_p in the zigzag or chiral SWCNTs can be also represented by Equations (9) and (10), whereas those of the spherical fullerenes are given by Equation (11):

$$K_M = K_D = \frac{2\theta_p{}^s}{r} \tag{11}$$

where $\theta_p{}^s$ is the pyramidalized angle of the vertices in the spherical fullerenes. For the ellipsoid fullerenes, those are given by Equation (12) and (13):

$$K_M = \frac{1}{r}(\theta_{p1}{}^e + \theta_{p2}{}^e) = \frac{2\theta_p{}^e}{r} \tag{12}$$

$$K_D = \frac{1}{r}\sum_{i=a,b}(\theta_{p1}{}^e\sin^2\theta_i + \theta_{p2}{}^e\cos^2\theta_i) \tag{13}$$

where $\theta_p{}^e$, $\theta_{p1}{}^e$, and $\theta_{p2}{}^e$ are the corresponding pyramidalized angles of the vertex, K_1 and K_2, on the ellipsoid fullerenes, respectively. It is evident from Equations (9)–(13) that the θ_p, $\theta_p{}^s$, or $\theta_p{}^e$ values may represent the K_M value of the vertices in SWCNTs and fullerenes, although they are not enough to represent the directional curvatures K_D (see Table 1), except for the spherical fullerenes, and that the $\theta_p{}^s$ value is equal to twofold θ_p, as the R values are equal. For example, as a result of the close R values, $\theta_p \approx 6°$ for the (5,5), (6,4), and (9,0) tubes and $\theta_p{}^s \approx 12°$ for C_{60}.

It can be found from Equation (9) that the sum of the curvatures of the vertices in the SWCNTs with i atoms is given by Equation (14)

$$\sum_i K_M = m\sum_j K_M = m\sum_j \frac{\phi}{2r} = m\frac{\pi}{r} = 22.13\,m(nm^{-1}) \tag{14}$$

where j and m are the atomic number in the circumference camber fragment with continuous C–C bonding and the repeated number of the camber fragment along the tubular axis, respectively. Therefore, there is also an approximate curvature conservation in SWCNTs as m is an infinite or the same certain value (see Table 1 and the Supporting Information). The curvature conservation in fullerenes may be obtained by an approach used by Haddon[4b] and $\sum_i K_M{}^2$ (or $\sum_i \theta_p{}^2$; see Table 2). Unfortunately, the curvature conservation of SWCNTs cannot be represented by this approach.

Theoretical Calculations of the Directional Curvature and Prediction of Reactivity

The directional-curvature theory allows a universal method that estimates the reactivities of the vertices and bonds of SWCNTs and fullerenes to be developed (see Tables 1 and 2). The K_D and K_M values given in Tables 1 and 2 are calculated from the above-mentioned equations and the differential-geometry approach based on optimized structures. For SWCNTs and fullerenes, periodic[14] and molecular[15] DFT methods were applied to optimize the structures and calculate the binding energies, respectively (see the Supporting Information for details).

As an illustration of the directional-curvature theory, the calculated results for various SWCNTs with moderate R values show that there is a linear relationship between the E_b and E_s or K_D values; for example, $E_b = e_{bg} + \alpha K_D = 45.45 + 16.26\,K_D$ for the addition of oxygen (Figure 3). The intercept of the line could be regarded as the binding energy of the addition of oxygen onto the graphene plane; hence, the strain energy $E_s = \alpha K_D$ in SWCNTs accounts for about 100% of the excess energy of the cured structure relative to graphene.[11]

Similar results can be obtained from different computational models and methods.[5b] It is noteworthy that the slopes α are very similar for the various models, computational approaches, or adducts. For example, from the cluster model and DFT-B3LYP method[5b] $\alpha = 16.96$ kcal nm mol^{-1} for the addition of oxygen and $\alpha = 16$–18 kcal nm mol^{-1} for various adducts O, CH_2, or NH with triplet ground states. The α values are also equal for the vertex additions of H and Al atoms.[11] It can also be seen from Tables 1 and 2 that the conservation of $\sum_i K_M$ in various types of SWCNTs or of $\sum_i K_M{}^2$ in various types of fullerenes occurs, and that the latter is approximately equal to the square of the former. In

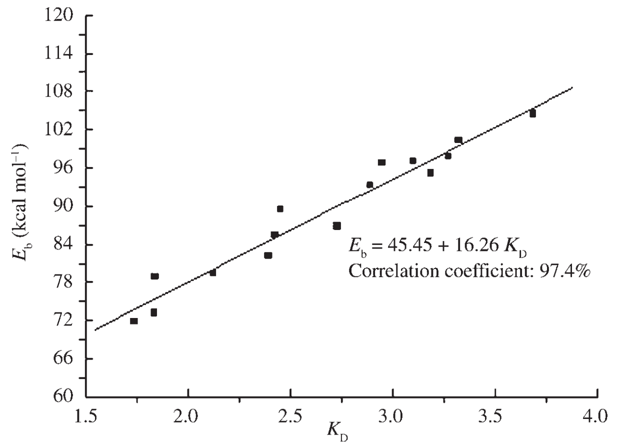

Figure 3. Variation of the binding energy (E_b) as a function of the K_D value of oxygen adducts with an opened C–C bond on SWCNTs.

addition, the θ_p (or θ_p^s, θ_p^e) values obtained from K_M and Niyogi et al.[5a] are close.

As distinct from SWCNTs, the C–C bonds in fullerenes may result from either [6,6] or [5,6] ring fusion (see the Supporting Information and Table 2 for oxygen addition to fullerenes) and the change in the bond length is larger. In general, the E_b value of the bonds with the [6,6] ring fusion or the shorter bond lengths are less because larger energies are required to break these bonds. The anisotropy of the chemistry of C_{60} may be expressed by the different reactivities of the various bonds of the [6,6] and [5,6] ring fusions, the vertices, or the bonds of the distorted C_{60}. The bonds of the [5,6] ring fusion are more reactive than those of the [6,6] ring fusion.[16] This case can be also seen from the calculated results for the defect SWCNT.[17]

The calculated results of the K_D values for C_{70} (see Table 2 or the Supporting Information) rationally explain the addition[5e] of sulfonyl azides to C_{70} that occur at the C_1–C_1' and C_4–C_4' bonds (i.e., C_2–C_3 and C_7–C_8 according to the IUPAC numbering). These bonds (C_1–C_1' and C_4–C_4') with [5,6] ring fusion have the largest K_D values or binding energies for the formation of the fulleroids with an open C–C bond structure.

Up until now, no one has succeeded in explaining the puzzle of the higher reactivity of the C_4–C_4' bond at the relatively flat midsection, our approach based on the theory of K_D contributes to clarifying this dilemma. In fact, the K_D value is not simply equal to the average of the biterminal atomic K_M value of the bond, and it is also not equal to the curvature obtained by the average $\theta_p^e(B)$ of the θ_p^e value relative to the bonds in the POAV2 analysis[6] (see Table 2), thus the K_D value may be larger, even if the biterminal K_M, θ_p^e, or $\theta_p^e(B)$ values are less. This reason is why the θ_p^e value could not correctly describe the reactivities of the C–C bonds with various orientations and sites.

The K_D value also indicates that the adducts of C_{70} oxidoannulenes with an open C–C bond structure formed at the C_1–C_1' and C_4–C_4' bonds are favorable.[18] The especially large E_b value of the equatorial C_5–C_5' bond may relate to the largest bond length, and the absence of adduct C_5,C_5'–$C_{70}O$[19] may be attributed to kinetic factors as the electronic state of the equatorial carbon atoms is very small at the HOMO/LUMO (see the Supporting Information).

There is also an approximate linear relationship between the E_b and K_D values for the bonds of the [5,6] ring fusion with the close C–C bond length in C_{70} (Figure 4). For the vertex reactivity of C_{50}, the results predicted from the K_M and θ_p^e values are the same, hence the [1+1] addition of a Cl atom onto C_{50} occurs preferably at C_4, which is consistent with the experimental results.[19] However, the reactivities predicted by the K_D and θ_p (or K_M) values for the addition at the C–C bonds are different. For the [2+1] addition of an oxygen atom onto C_{50}, the C_2–C_3 or C_3–C_4 bonds with the larger K_D value is preferable to the C_4–C_4' bond, which is consistent with the results calculated by Xu et al.[8]

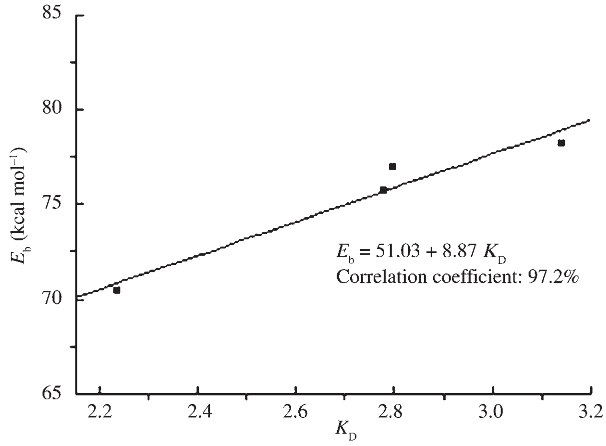

Figure 4. Variation of the binding energy (E_b) as a function of the K_D value for the bonds with [5,6] ring fusion during the addition of an oxygen atom.

Conclusion

The higher reactivities of SWCNTs and fullerene relative to graphite stem from their curvatures. Their variously curved frameworks are formed in two steps, which include the hybridization of the vertex atomic orbitals and bonding between these hybrid orbitals, in which the former is embodied in the mean property of the curvature and the latter in the directional property of the curvature. The directional-curvature theory, developed for the first time herein, covers the mean and directional properties of the curvatures of SWCNTs and fullerenes and allows a unified approach to manifest the strain energies of the vertices and bonds in SWCNTs and fullerenes. The pyramidized angle θ_p can not be used to explain the anisotropy of the chemistry of SWCNTs and fullerenes, and the curvature theory contributes to overcoming this difficulty. The theory, in essence, reveals that the K_D and K_M values have an inherent relation to the bond curvature K and pyramidized angle θ_p and demonstrates that there are approximate curvature conservations in SWCNTs and fullerenes.

Prediction of the binding energies or the corresponding reactivities, which depend directly on the strain energies or K_D (K_M) values, has been verified by a series of theoretical calculations and experiments. It must be pointed out, as the proportional relation is used for the reactivity of the bonds of fullerenes, that consideration of some factors, such as, bonds with [6,6] or [5,6] ring fusion and obviously different lengths, should be required. The surface of many nanoclusters are formed by various orientations of the dangling orbitals relative to the σ framework, thus the directional-curvature theory will be conducive to the study of their reactive mechanisms.[20]

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[20] The derivation of the directional curvature and further details of selected results are given in the Supporting Information.

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