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Research Article

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Density Functional Study of Functionalization of Carbon Nanotubes with Carbenes

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Abstract: DFT calculations have been performed on the interactions of carbon nanotubes and carbenes, in order to perform a comparative study of the sidewall functionalization of the two classes of nanotubes, i.e. armchair and zigzag. The systematic investigation of cycloaddition of both zigzag and armchair carbon nanotubes with $:CX_2$ (where X = H, F, Cl, Br, I) has been undertaken. The models selected for zigzag and armchair CNT are (10,0) and (6,6), respectively, since they have comparative radii (~8 Å). The bond lengths and binding energies of products are analysed in great detail. The band gaps of these non periodic structures are investigated and correlated with the electronic behavior of 'armchair' and 'zigzag' nanotubes. Our results also confirm the previous studies that armchair nanotubes are thermodynamically more stable than zigzag nanotubes. On comparison of armchair carbon nanotubes with zigzag nanotubes, it is found that trends towards carbenic reactivity are the same in both the cases.

The dependence of addition of carbenes on the diameter of the carbon nanotubes is also investigated. The models used for nanotubes in this study range from (3,3) to (10,10). Their reactions with $:CH_2$ have been studied with first principles DFT calculations. An attempt to rationalize the diameter effects is made on the basis of the structures of the nanotubes. It seems that diameter dependence of the reactivity is because of different pyramidalization and π-orbital misalignment angles in different carbon nanotubes. This leads to higher local strain for tubes of smaller diameter that can be partially relaxed by sidewall addition.

Keywords: Carbon Nanotubes, Carbenes, DFT, Armchair, Zigzag

1. INTRODUCTION

In recent years, scientists have tried to exploit the outstanding electronic, thermal and mechanical properties of carbon nanotubes and their unique one-dimensional structures to engineer new materials with exciting potential applications. However, they have to contend with various difficulties arising from the poor processibility of these carbon allotropes, mainly because of their intrinsic poor solubility in organic and aqueous solvents, which makes their characterization difficult. The majority of the

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investigations on carbon nanotubes have, therefore, been carried out with an insoluble form of solid state material. Issues also arise from the difficulty in separating metallic and semiconducting carbon nanotubes; so the majority of investigations have been carried out on undefined mixtures of the two types of nanotubes with widely different properties. Also, pristine nanotubes tend to agglomerate in polymer hosts, leading to weakening in the chemical strength of these composite materials [1]. The lack of interfacial bonding of the SWNTs with the matrix material leads to fibre pullout during stress and eventually catastrophic failure.

Chemical functionalization is the way out of the difficulties in handling and applicability of carbon nanotubes [2]. This is of two types: non covalent and covalent. In non covalent sidewall modification, such as wrapping of the nanotubes with surfactants, the sp^2 hybridized structure of carbon nanotubes is not disrupted, but covalent side wall functionalization involves attachment of functional groups or aliphatic carbon chains to the nanotubes via chemical bonds. Hence, the sp^2 structure of the nanotube is altered, and the optical and electronic properties are also changed significantly. Recently, this method has been increasingly used to tailor the interaction of the nanotube with other entities, such as a solvent or a polymer matrix, and thus is a useful tool in areas like nanobioelectronics, hydrogen storage, polymer composite science and molecular scale mechanics [3,4].

Chemical functionalization has various advantages: it can dramatically increase the solubility of nanotube material, and chemically modified carbon nanotubes can easily be fixed on a surface via chemical bonds from the surface to the nanotube. Organic molecules like dyes, proteins or nucleic acids may be coupled with functionalized nanotubes for sensor applications. Sidewall functional groups can react with polymers, thus providing "handles" for dispersion in host polymers. This also provides exfoliation in bundles, thus improving the mechanical properties of nanocomposites and polymers [2]. Chemical modification prevents bundling and increases the specific surface area for gas adsorption. Even for interconnection purposes in nanoscale circuits, suitable functionalization provides an attractive method to link individual tubes to form more complex networks. Due to all these reasons, covalent functionalization of carbon nanotubes (CNTs) has been attracting much research interest, both at experimental and theoretical levels.

The first experiments on nanotubes functionalization started from the fluorination of single-walled nanotubes (SWNTs), followed by a substitution reaction of fluorinated SWNTs in solution. Direct functionalization to the surface of SWNTs by various functional groups has been reported since then. Recently, it was found that the direct functionalization of SWNTs with organic groups is possible using reactive species such as carbenes, nitrenes and radicals. A very good example of this is a study which demonstrated that especially stable solutions of functionalized SWCNTs are formed from the addition of nucleophilic carbenes [5]. More recently, the functionalization of SWCNTs with carbenes has been increasingly investigated because it provides an efficient route to form novel carbon nanotube compounds.

Since there are experimental limitations to handling both carbenes and carbon nanotubes, not much data are available regarding the mechanistic and electronic aspects of carbene-CNT interactions. Previous theoretical studies on carbene-CNT interactions limit themselves to explain the energy profiles of simple cycloadditions. No effort, to the best of our knowledge, has been made in the direction of investigating the effects of electronegativity and changing the substituents on carbenes, except a theoretical investigation that deals with alkyl substituted carbenes [6].

Thus, in light of the rapid progress in this field and the potential applications, we feel that it is highly desirable to investigate the interactions between SWNTs and carbenes from a theoretical point of view. Such knowledge should be useful not only to explain the nature of interactions between SWNTs and

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functional groups, but also to further functionalize SWNTs by other functional groups as well as for building nanodevices for new materials. Hence, in view of all this, we tried to investigate the covalent functionalization of carbon nanotubes with carbenes and suggest some novel methods to improve their processibility. It will be shown that an understanding of the factors that can facilitate chemical functionalizations of SWCNTs may suggest further synthetic applications.

2. COMPUTATIONAL DETAILS

In this work, single-walled carbon nanotubes were chosen as model reactants. Also, out of the three types of nanotubes, that is, armchair, zigzag and chiral, the most thermodynamically stable one is the armchair single walled carbon nanotube [6], so a comparative study of the sidewall functionalization of the two stable classes of nanotubes, i.e. armchair and zigzag, was performed in this work. Thus, in an effort to gain insight into the substituent effects, the systematic investigation of cycloaddition of both zigzag and armchair carbon nanotubes with $:CX_2$ (where X= H, F, Cl, Br, I) was undertaken. The models selected for zigzag and armchair CNT are (10,0) and (6,6) respectively. The dangling bonds at both ends were terminated by hydrogen, yielding $C_{80}H_{20}$ and $C_{72}H_{24}$ as formulas for zigzag and armchair nanotube, respectively. The initial diameters of the zigzag and armchair nanotubes were 7.83 and 8.14 Å, respectively, and the lengths of each are approximately 7 Å.

Previous theoretical studies suggested that the much popular approach for larger systems, i.e. the ONIOM (B3LYP:AM1) technique [7], which combines a low- and high-level theory to allow a more realistic treatment of the system, is not suitable for the nanotube systems [3,8]. Among other methods tried are semiempirical and Hartree-Fock calculations. However, semiempirical methods, though good for describing some of the properties of the nanotubes, mostly give unreliable estimates of geometries and energies [9]. In our experience too, at the stage of initial optimization, the AM1 method gave unreasonable geometries, though PM3 performed a little better. Therefore to obtain accurate information, the density functional approach (DFT method) was applied.

The $DMol^3$ [10] program package was used to carry out all calculations within the generalized gradient approximation (GGA) of the Perdew-Wang-91 (PW91) exchange-correlation potential functional [11]. All-electron calculations were employed to model the cores. The double numerical basis set plus polarization functions (DNP), which is the numerical equivalent of the Gaussian 6-31G* basis set, was used for all the calculations. The DNP basis set has been widely used in the theoretical calculations of SWNT systems, including covalent functionalizations of SWNTs. The numerically derived basis sets also have many advantages. Firstly, the molecule can be dissociated exactly to its constituent atoms. Secondly, use of numerical orbitals reduces basis set superposition effects (BSSE) [11] and it becomes possible to describe even weak bonds. Compared with the plane-wave basis set, DNP basis sets tend to overestimate the binding energy. This overestimation is compensated for by the GGA method, which is known to reduce the over-binding effects caused by the local density approximation (LDA).

The geometries of all the nanotubes, carbenes and nanotube-addend (carbene) systems were fully optimized at the GGA-PW91/DNP level of theory. The studies were performed on nonperiodic structures in which dangling bonds at both ends were terminated by hydrogen bonds. Mulliken population analysis was used to obtain the charge on each atom and to determine and interpret the electron densities. Spin unrestricted calculations were performed. The geometry optimization convergence thresholds for energy change, maximum force, and maximum displacement between optimization cycles were set at 2.0×10^{-5} Ha, 0.004 Ha $Å^{-1}$ and 0.005 Å, respectively, so that the optimization stopped when the energy convergence was satisfied, along with either the displacement or gradient criterion.

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3. RESULTS AND DISCUSSION

3.1 Bond Lengths And Adsorption Energy

3.1.1 The SWCNT (10,0) system

Two types of bonds are available for addition of the carbene to carbon nanotubes, axial and circumferential. For the (10,0) and (6,6) carbon nanotubes, the axial bond was selected and the corresponding carbenes were oriented accordingly. For all the five cases studied, it was found that the carbon atom C of the carbene adopts sp^3 hybridization and forms chemical bonds with two of the carbon atoms on the carbene axis, which are pulled outwards indicating a radial deformation. This suggests that cycloaddition is a generic feature of carbon nanotube-carbene chemistry. The lengths of the newly formed bonds and the original C_1-C_2 bonds and binding energies in each case are given in Table 1.

Table 1. Bond lengths (Å) and adsorption energies (kcal mol^{-1}) for $:CX_2$ attached to the (10,0) carbon nanotube.

Carbene	C_1—C	C_2—C	C_1--C_2	Adsorption energy, E_{ads}
$:CH_2$	1.515	1.516	1.536	-77.1
$:CF_2$	1.496	1.496	1.568	-9.9
$:CCl_2$	1.528	1.529	1.534	8.7
$:CBr_2$	1.482	1.484	1.541	64.7
$:CI_2$	1.487	1.489	1.541	70.0

The adsorption (or binding) energies of the carbenes adsorbed on SWNTs were calculated using equation (1):

$$E_{ads} = E_{SWNT+:CX_2} - (E_{SWNT} + E_{:CX_2}) \quad (1)$$

where E_{ads} stands for the total adsorption energy of the carbenes on SWNT, whereas $E_{SWNT+:CX_2}$, E_{SWNT} and $E_{:CX_2}$ stand for the total energies of the carbene adsorbed SWNT, pristine SWNT, and the single carbene, respectively. A negative $E_{ads}(n)$ corresponds to a stable adsorption structure. All the carbenes form the expected cycloaddition product (Fig. 1), but the adsorption energies are negative only for the case of $:CH_2$ and $:CF_2$. Figure 1 shows the product of the functionalization of (10,0) CNT with $:CH_2$, and all carbenes yield similar structures.

An analysis of Table 1 reveals that the most stable adsorption structure is that with $:CH_2$. Most others do not form stable adsorption products. The adsorption energy is plotted versus the period number of X in $:CX_2$ in Table A3 of the Electronic Supplementary Information (ESI). It can be seen that there is a kink at dichlorocarbene. This is in accord with a previous study on the addition of dichlorocarbene to CNTs [12]. On analyzing the preferred multiplicities of the addition products, we find that only the dichloro and dibromo compounds have triplet multiplicities in their ground states. The adsorption energies can be fit to a fourth-degree polynomial from $:CH_2$ to $:CI_2$.

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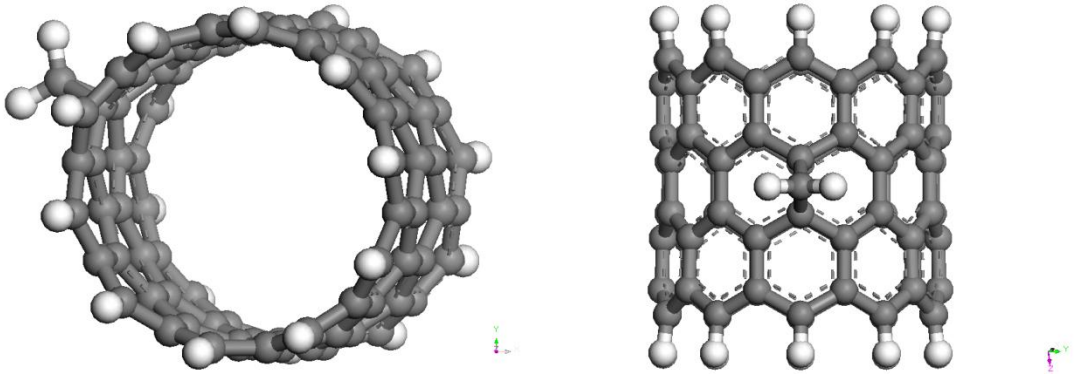

Figure 1. Two views of the product of the functionalization of (10,0) CNT with :CH_2.

We sought to explain the variation of the adsorption energies with the size of the carbene by considering the natures of the carbene moieties. The relative stabilities of the carbenes with respect to methylene can be deciphered in terms of the energies of the following isodesmic reactions:

$$:CX_2 + CH_4 \rightarrow :CH_2 + CH_2F_2$$

The calculated reaction energies for :CF_2, :CCl_2, :CBr_2, and :CI_2 are 66.1, 58.4, 62.5 and 52.7 kcal mol^{-1}, respectively. These results also suggest that :CCl_2 displays an unusual instability, as its reaction energy is lower than those observed for :CF_2 and :CBr_2, instead of being the mean of the values obtained for these two carbenes. The XCX bond angles are calculated as 100.7°, 103.8°, 109.1°, 109.8° and 112.0°, respectively, for X = H, F, Cl, Br, and I. Clearly the bond angles also reflect the sp^3 hybridization and triplet multiplicities of the chloro and bromo compounds, in which the central carbon atoms are surrounded by four electron domains rather than the three domains in the other systems. This favors the adsorption, resulting in less endothermic adsorption than expected.

The calculated Mulliken charges on the carbene carbon are -0.151, 0.403, -0.146, 0.032, and -0.217, showing an anomalous behavior for F, for which the charge on the carbon is highly positive due to the enormous electron-withdrawing power of fluorine. The populations on the carbene carbon orbitals are given in Table 2. The population of the carbon 2*s* orbital increases monotonically from :CH_2 to :CI_2, with the exception of :CCl_2, which shows an anomalously large population. For :CF_2, the population of the 2*p* orbital is the least due to electron withdrawal, but this is compensated for partially by more back bonding to the vacant 3*d* orbital of carbon.

Table 2 Populations on the carbene carbon atoms in the various carbenes.

Orbital	:CH_2	:CF_2	:CCl_2	:CBr_2	:CI_2
C (1s)	2.000	2.001	2.001	2.000	2.000
C (2s)	1.719	1.756	1.870	1.779	1.862
C (2p)	2.340	1.728	2.174	2.115	2.300
C (3d)	0.024	0.113	0.064	0.045	0.032

To understand the differences in the bonding behavior of the carbenes, we plotted the electrostatic potential map for :CH_2. The 0.017 au contour value for the electron density was plotted and the

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electrostatic potential was mapped on this surface (Fig. 2). The map is colored in reverse rainbow, i.e. the blue areas signify negative potential values, which are the sites of electrophilic attack, and red areas have highest positive potential values, and are the sites of nucleophilic attack.

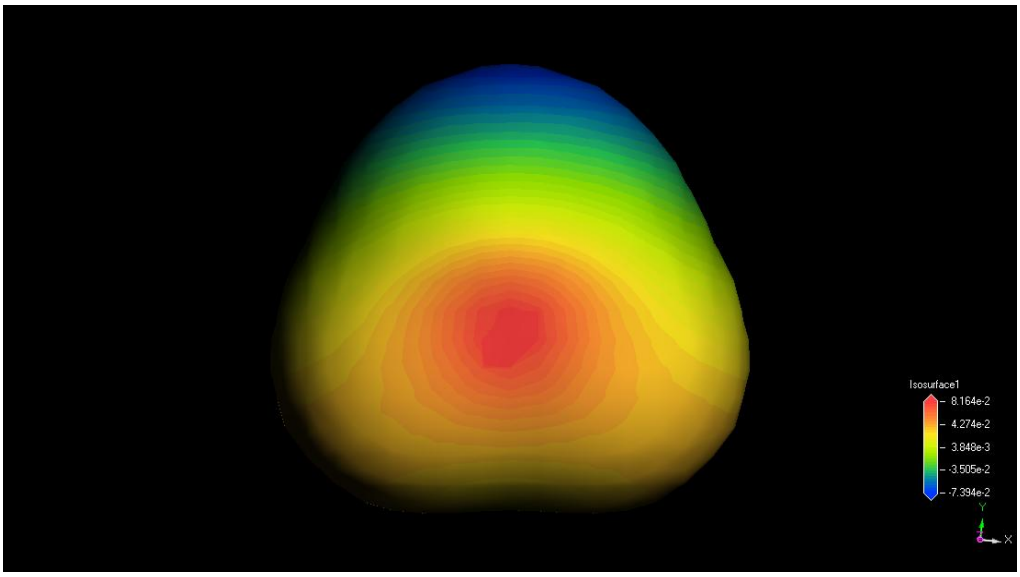

Figure 2. Electrostatic potential map of :CH_2

The electrostatic potential maps for the :CX_2 are displayed in Figure A4 of the ESI. The volumes encompassed by the 0.017 au electron density contours increase from 24.6, 33.9, 57.7, 69.6 and 88.2 $Å^3$ in order, respectively. In each case, the positive potentials lie close to the carbon atom, but with increasing atomic number, the positive potential at the carbon becomes smaller in magnitude and moves away to the end regions of the halogen atoms along the C-X bond vectors for X = Cl, Br and I. Moreover, the range of potential values varies in each case (-0.039 to 0.060 au for :CF_2, -0.050 to 0.040 au for :CCl_2, -0.044 to 0.048 au for :CBr_2, and -0.045 to 0.050 au for :CI_2). Thus, the range is largest for :CH_2, and smallest for :CCl_2, which also has the smallest positive potential value amongst all the carbenes. The positive potential areas are most diffuse for dichlorocarbene. Thus all :CX_2, except when X = F, exhibit a positive electrostatic end-cap along the C-X bond. All carbenes also have a negative electrostatic potential in the π-region [13]. The adsorption energies of Table 1 are found to follow the same order as the negative potentials.

Table 3. Bond lengths (Å) and adsorption energies (kcal mol^{-1}) for :CX_2 attached to the (6,6) carbon nanotube.

Carbene	C_1--C	C_2—C	C_1--C_2	Adsorption energy, E_{ads}
:CH_2	1.490	1.490	2.135	-106.9
:CF_2	1.496	1.496	2.238	-35.8
:CCl_2	1.509	1.509	2.210	-10.2
:CBr_2	1.497	1.497	2.215	34.7
:CI_2	1.489	1.489	2.203	64.8

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3.1.2 The SWCNT (6,6) system

Now, comparing this with the armchair carbon nanotube (6,6), the trend towards carbenic reactivity is almost the same, although the adsorption energies are much more negative (Table 3). However, :CCl_2 shows a more than expected negative value. The difference in the adsorption energies compared to the (10,0) case can be traced to the breaking of the axial C-C bond of the carbene on which adsorption takes place.

This can be explained if one considers the valence tautomerization of an aromatic, 6-methano[10]annulene (**1**) and the cyclopropane derivative bisnorcaradiene (**2**), which can result from carbene addition to the central bond of naphthalene [14].

1 **2**

All the previous experimental and computational studies suggest that the preference for closed versus open structures depends on the substituent *R* at the methano bridge. One may think that, since the naphthalene unit is also embedded in the SWNT sidewall, open structures might be expected to form, irrespective of the addition site and the tube chiral angle. However, a balance between strain in the pristine tube and in the reaction products on the one hand, and homoconjugative stabilization on the other appears to determine the structure. The C bonds hold the tubular structure and are strained, more so in armchair than in zigzag tubes. Therefore, the C-C bonds of the armchair nanotube break on bridging to give open products, which can additionally enjoy homoconjugative stabilization.

Table 3 shows that the most stable adsorption structure is that with :CH2. Among the dihalocarbenes, the strongest adsorption is with :CF2 as was the case with zigzag nanotubes. On comparing the adsorption energies of (10,0) and (6,6) nanotubes, it is found that the trend in adsorption energies for both the zigzag and armchair nanotubes is the same. Despite general geometric similarities, the adsorption energy values reveal a very important feature, i.e. the dependence of adsorption energy on the electronic structure of the nanotube. It is found that the adsorption on semiconducting, i.e. zigzag nanotubes, is consistently weaker than on metallic nanotubes. Thus the adsorption of the carbene is dependent on tube chirality, which is a prerequisite for separation of metallic and semiconducting nanotubes. Also, the shortest distances of the carbenes from the (10,0) SWNT surface are significantly larger for :CH2 than those for the (6,6) SWNT surface. This fact further shows that the adsorption of carbenes on metallic SWNTs is much stronger than on semiconducting nanotubes. Thus, this is a very important finding with respect to the commercial viability of studying carbene-CNT interactions.

The separation of SWNTs according to their electronic structure has attracted much attention [3]. In many cases, metallic SWNTs are separated from semiconducting SWNTs and enriched in the supernatant due to stronger interaction between metallic SWNTs and adsorbates. However, the inverse separation of semiconducting from metallic SWNTs is often observed [15], but in this case we have found that the carbenes do not prefer inverse separation.

3.1.3 Comparison with a simple unsaturated analogue

To specifically study the effect of the sidewall of the carbon nanotube, the carbene reactivity was compared with that for a conjugated system of four rings ($C_{16}H_{10}$) (assuming that the effect of the carbene on the nanotube extends to four rings). It is found that the trend for carbenic reactivity towards the CC of

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a $C_{16}H_{10}$ molecule is the same as that towards the sidewall of the carbon nanotube. The binding energies show an upward trend as is observed for both the zigzag and armchair cases. The magnitude of the binding energy for $:CH_2$ and $:CF_2$ is the same as that for the zigzag tube. For $:CCl_2$, the adsorption energy is intermediate between the two, but the adsorption energies for $:CBr_2$ and $:CI_2$ are much smaller than the values calculated for the sidewalls of the nanotubes. This observation can be explained if we consider the fact that the repulsions between the $:CX_2$ species and the sidewall of SWCNT are smaller than those between the $:CX_2$ and a $C_{16}H_{10}$ planar molecule.

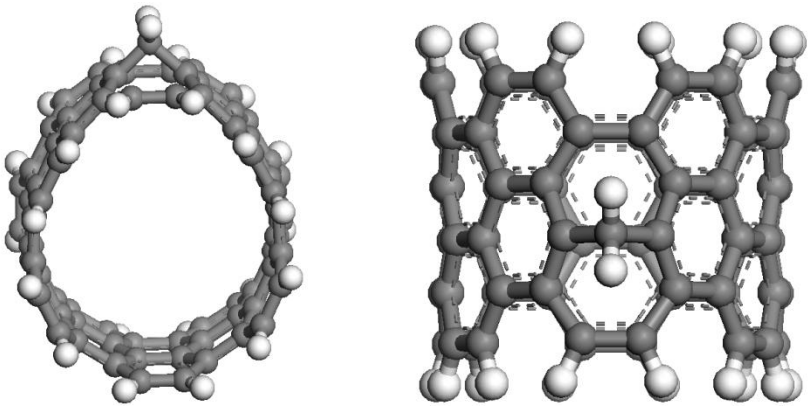

Figure 3. The adsorbed structures on the (6,6) functionalized SWCNT: Two views of the $:CH_2$ adsorbed structure.

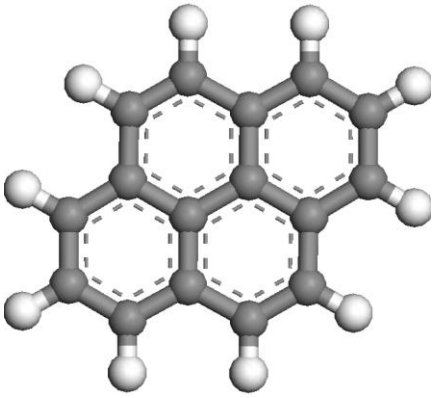

Table 4. Bond lengths (Å) and adsorption energies (kcal mol^{-1}) for $:CX_2$ attached to the $C_{16}H_{10}$ unsaturated analogue.

Carbene	C_1---C	C_2---C	C_1---C_2	Adsorption energy, E_{ads}
$:CH_2$	1.482	1.482	2.175	-78.1
$:CF_2$	1.482	1.482	2.219	-9.1
$:CCl_2$	1.495	1.495	2.170	-3.3
$:CBr_2$	1.482	1.482	2.161	8.3
$:CI_2$	1.509	1.509	1.663	15.4

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The weaker adsorption in the case of $:CI_2$ is also evident from the fact that in this case the C-C bond of the nanotube does not break, and it forms an addition, rather than an insertion, product. Moreover, the distance of the $:CI_2$ species from the nanotube is also largest in this case.

The conjugated system also loses its planar character on adsorption of the carbene (see Fig. 4) and takes on a pyramidal shape.

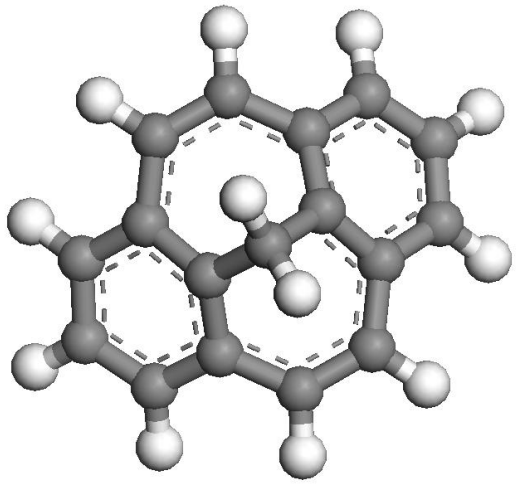

Figure 4. Carbenes adsorbed on the unsaturated analogue.

3.2 Mulliken Charge Analysis

3.2.1 The (10,0) SWCNT system

The Mulliken population analysis of (10,0) CNT functionalized with the various carbenes is given in Table 5. It can be seen that the partial charges on the nanotube carbons are negligible, but the carbene carbon shows a large variation in charges. For example, the charge is highly positive in the case of $:CF_2$, and less positive in the case of $:CBr_2$, but for the other carbenes, the situation is reversed.

Table 5 Population analysis of (10,0) CNT functionalized with carbenes

$:CX_2$	Charge		
	$C_{1,2}$	C	$X_{1,2}$
$:CH_2$	0.019	-0.225	0.066
$:CF_2$	-0.017	0.458	-0.317
$:CCl_2$	-0.069	-0.115	-0.001
$:CBr_2$	-0.068	0.235	-0.207
$:CI_2$	-0.045	-0.050	-0.088

Charge transfer is the main mechanism in changing the electronic structures of the tube. Thus, we studied the charge transfer on adsorption of carbene on SWNTs, and the amounts of charge transfer to the carbene are 0.093, 0.176, 0.117, 0.179 and 0.226, respectively, for $:CH_2$, $:CF_2$, $:CCl_2$, $:CBr_2$, and $:CI_2$. The charge transfer is thus dependent on the electronic structure of the carbene, just as the adsorption energies were. The least charge transfer to the carbene is in the case of $:CCl_2$, which is seen to show anomalous behavior. An interesting finding is the largest charge transfer in the case of $:CI_2$, in spite of the fact that

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iodine is less electronegative than chlorine. This leads us to think that electronegativity is not the only criterion to decide the amount of charge transfer. Another deciding factor could be the π electron donating capacity of the halogen atom. In the case of $:CCl_2$, it seems that the π electron donation overcomes the σ withdrawing capacity.

3.2.2 The (6,6) SWCNT system

The Mulliken charges on selected atoms in the carbene functionalized (6,6) SWCNTs are given in Table 6.

Table 6. Mulliken charges on selected atoms in functionalized (6,6) SWCNT

$:CX_2$	$C_{1,2}$	C	$X_{1,2}$
$:CH_2$	-0.105	-0.033	0.058
$:CF_2$	-0.160	0.690	-0.326
$:CCl_2$	0.077	-0.366	0.019
$:CBr_2$	0.038	0.049	-0.187
$:CI_2$	0.056	-0.206	-0.063

A careful analysis of the charges (Table 6) reveals a very important similarity. In this case, too, the nanotube carbons have negligible charges, except in the case of $:CF_2$. There is a large positive charge on the carbene carbon in the case of $:CF_2$ because of the electron-withdrawing character of fluorine. In the case of $:CCl_2$ and $:CI_2$, the carbon of the carbene has much more negative charge than the carbons of the nanotube. This is in contrast to the electron deficient character of carbenes and electron rich nature of carbon nanotubes. A possible explanation could be that, after the formation of the cyclopropane ring, due to the inductive effect of the highly electronegative halogen atoms, the carbon of the carbene withdraws negative charge towards itself.

It is more instructive to analyze the charge transfer from the nanotube to the carbene. The calculated values of the charges transferred to the carbenes from the (6,6) SWCNT are -0.083, -0.038, 0.328, 0.325, 0.332, respectively, for $:CH_2$, $:CF_2$, $:CCl_2$, $:CBr_2$, and $:CI_2$.

Thus, in the most stable configuration of carbene-SWCNTs, the charge transfer from the (6,6) SWCNT to the carbenes is much larger than that to the (10,0) SWCNT, particularly in the case of $:CCl_2$, $:CBr_2$ and $:CI_2$. The carbenes, $:CH_2$ and $:CF_2$, seem to be electron donating and responsible for charge transfer to the metallic nanotubes. However, the other three carbenes display an opposite behavior, and withdraw enormous amount of charge from the nanotube, even though the corresponding halogens, Cl, Br and I are less electronegative than F.

The chemical interactions involving large charge transfer should be sensitive to the energy gap of the CNT and therefore can be used for discriminating between semiconducting and metallic CNTs. We propose that methylene, for which the charge transfer from the (10,0) carbon nanotube is the least, can be used as a reagent to separate zigzag and armchair nanotubes because its charge transfer is opposite in direction for the (6,6) nanotube. Thus the electrical properties of metallic nanotubes are relatively sensitive to molecular adsorption compared to semiconducting nanotubes.

Several groups have suggested the application of nanotubes as miniature sensors for chemical and biological applications. Sensing gas molecules is critical to environmental monitoring, control of chemical processes, space missions, and agricultural and medical applications. One of the possible mechanisms includes charge transfer from adsorbed species. The interactions between carbenes and

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SWNTs in our study can help us in finding the mechanisms of molecular sensing with nanotube molecular wires. Upon exposure to molecules such as carbenes, the electrical resistance of a semiconducting SWCNT is found to dramatically increase or decrease. This serves as the basis for nanotube molecular sensors. On the basis of our observation, carbenes adsorbed on the surface of nanotubes can be suggested as novel nanosensors because of the large charge transfer involved in the case of metallic nanotubes.

3.3 Bandgaps

As seen in the previous sections, charge transfer seems to be the main mechanism governing the extent of adsorption. In the case of the (10,0) SWCNTs, the carbenes act as electrophiles and accept charge from the nanotube surface. While this is also true for the (6,6) SWCNTs in the case of the heavier halogens, the charge transfer is in the opposite direction for $:CH_2$ and $:CF_2$. Moreover, the extent of charge transfer is larger in the case of the (6,6) SWCNTs. To understand these differences in reactivities, we calculated the orbital occupancies of the frontier molecular orbitals, because these can give a clue about the metallic or semiconducting nature of the nanotube.

3.3.1 The (10,0) SWCNT system

We first calculated the orbital occupation for the pristine nanotube. It was found that the Fermi level is at -3.71 eV. The highest orbital that is occupied by 2 electrons has an energy of -5.09 eV. This is followed by eight MOs occupied by 6 electrons (Table 7).

Table 7. Fermi and orbital energies (eV) of the frontier orbitals of the (10,0) SWCNT

System	Fermi energy	Orbital energy (occupation)								
SWCNT(10,0)	-3.71	-5.09 (2.00)	-3.88 (1.57)	-3.88 (1.56)	-3.77 (1.25)	-3.70 (0.96)	-3.49 (0.34)	-3.49 (0.33)	-	-
$+:CH_2$	-3.68	-5.04 (2.00)	-4.59 (2.00)	-3.84 (1.52)	-3.75 (1.25)	-3.74 (1.23)	-3.67 (0.96)	-3.62 (0.80)	-3.40 (0.23)	-2.95 (0.01)
$+:CF_2$	-3.81	-5.17 (2.00)	-4.72 (2.00	-3.96 (1.50)	-3.90 (1.34)	-3.86 (1.18)	-3.80 (0.96)	-3.74 (0.78)	-3.53 (0.23)	-3.11 (0.01)
$+:CCl_2$	-3.87	-5.21 (2.00)	-4.77 (2.00)	-4.00 (1.46)	-3.99 (1.41)	-3.91 (1.16)	-3.86 (0.97	-3.80 (0.76)	-3.58 (0.22)	-3.21 (0.02)
$+:CBr_2$	-4.03	-5.36 (2.00)	-4.94 (2.00)	-4.17 (1.46)	-4.16 (1.44)	-4.08 (1.15)	-4.02 (0.96)	-3.96 (0.75)	-3.76 (0.22)	-3.41 (0.02)
$+:CI_2$	-4.10	-5.40 (2.00)	-4.99 (2.00)	-4.26 (1.51)	-4.22 (1.41)	-4.14 (1.14)	-4.09 (0.95)	-4.04 (0.75)	-3.82 (0.22)	-3.52 (0.03)

Table 7 shows that the Fermi energies become more negative down the group. The exception is $:CH_2$, which has a higher Fermi energy than expected. Similarly, the energy of the last orbital that is fully occupied by two electrons decreases with increasing atomic number of X in $:CX_2$, but for $:CH_2$ alone this energy is higher than that for the pristine CNT. Interestingly, in all functionalized carbenes, eight orbitals are used for the occupation of eight electrons, but in the pristine nanotube, the eight electrons occupy only six orbitals.

3.3.2 The (6,6) SWCNT system

Table 8 gives the calculated orbital occupancies for the (6,6) SWCNT system. It is seen that the pristine

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nanotube has molecule-like energy levels. The band gap is extremely small (~0.8 eV) and is characteristic of a metallic nanotube. However, on functionalization, the last two electrons get distributed between two orbitals because of mixing with the carbene orbitals. The band gap also reduces to ~0.7 eV.

Table 8. Fermi and orbital energies (eV) of the frontier orbitals of the (6,6) SWCNT

System	Fermi energy	Orbital energy (occupation)		
SWCNT(6,6)	-	-3.94 (2.00)	-3.14 (0.00)	-
+:CH_2	-3.52	-4.98 (2.00)	-3.86 (1.85)	-3.17 (0.15)
+:CF_2	-3.65	-5.12 (2.00)	-3.99 (1.85)	-3.30 (0.15)
+:CCl_2	-3.66	-5.12 (2.00)	-4.01 (1.86)	-3.31 (0.14)
+:CBr_2	-3.79	-5.15 (2.00)	-4.14 (1.86)	-3.44 (0.14)
+:CI_2	-3.87	-4.86 (2.00)	-4.20 (1.84)	-3.53 (0.16)

A comparison of Tables 7 and 8 reveals that both show (10,0) and (6,6) systems show similar behavior, and the Fermi energy becomes more negative with increasing atomic number of the halogen in the carbene. The (6,6) SWCNT has higher Fermi energy as compared to the (10,0) system. This is consistent with the fact that the former is a metallic nanotube, while the latter is semiconducting.
One can now correlate these findings with our earlier results with respect to adsorption energies and charge transfer. It was found that the adsorption is stronger for the metallic nanotubes. This is related to the larger amount of charge transfer to the vacant orbital of the carbene that is possible for the metallic nanotubes, which have higher Fermi energy levels. Higher reactivity of metallic tubes has been observed with various moieties [16,17].

3.4 Diameter effects

SWCNTs are made up of the sp^2-bonding network of carbon atoms, and the difference of the reactivity can be deeply related to the local curvature. Understanding the dependence on diameter is very important for controlling the amount of adsorbed species, and the ability to control this adsorption would be useful in controlling CNT properties. Not only is the reactivity of chemical reactions diameter dependent, the selectivity of certain addition reactions has been reported to be diameter dependent as well [2,18-21]. Thus selectivity of the reaction has been a hot topic right from the start and, as explained before, the major effects seem to be tube species and diameter.

The results of the previous sections revealed that there is stronger adsorption on the (6,6) nanotube, and :CH_2 shows the strongest interaction. Therefore, in this section, we study the influence of tube diameter for zigzag carbon nanotubes for methylene adsorption.

3.4.1 Binding energy per atom for carbon nanotubes of different diameters functionalized with methylene

To understand the effect of diameter on the (*n*,*n*) SWCNT, we constructed such nanotubes, with *n* ranging from 3 to 10, each CNT having a length of 7.38 Å. We discovered interesting effects including strong variations of binding energy per atom as a function of diameter. The magnitude of the binding energy per atom of nanotubes increases monotonically with increasing tube diameter (Table 9). Since nanotubes are obtained by rolling up a graphene sheet, the resultant distortions generate structures with the bond lengths deviating from the ideal value. The smaller the diameter, the higher is the curvature and the deviations are larger. This explains why, with increasing diameter, the binding energy tends towards a constant value (~ -2410 kcal mol^{-1}) in an exponential curve. As the strain releases, the stability increases

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to the value for graphene.

Table 9. Binding energy per atom (kcal mol^{-1}) for carbon nanotubes of different diameters (Å) functionalized with methylene

SWCNT (n,n)	Formula	Diameter	Binding energy per carbon
3,3	$C_{36}H_{12}$	4.07	-2304.2
4,4	$C_{48}H_{16}$	5.42	-2350.2
5,5	$C_{60}H_{20}$	6.78	-2375.2
6,6	$C_{72}H_{24}$	8.14	-2388.9
7,7	$C_{84}H_{28}$	9.49	-2397.1
8,8	$C_{96}H_{32}$	10.85	-2402.4
9,9	$C_{108}H_{36}$	12.20	-2405.9

3.4.2 Adsorption of methylene

In order to investigate the possible diameter selectivity of the chemical reactions of carbenes with nanotubes, we analyzed the bond lengths and adsorption energies of methylene adsorbed on nanotubes of different diameters.

The adsorption energies decrease with increasing diameter. All the carbenes form cycloaddition products, except the (5,5) CNT, which forms an insertion product, as inferred from the large C_2---C distance of 2.525 Å as opposed to the average (~1.5 Å). The structures of both SWCNTs and graphite are made up of the sp^2-bonding network of carbon atoms, and the difference of the reactivity in carbene addition is therefore deeply related to the local curvature. Our results strongly suggest that the carbene addition, which induces the structure deformation from sp^2 to sp^3-like bonding, depends on the diameter of SWCNTs.

As the reactant carbon atoms shift from three to four coordinate, the local preferred geometry correspondingly shifts from planar to tetrahedral. Furthermore, any local conjugation is broken and the carbon atoms rehybridize from sp^2 to sp^3. The energy required to induce such curvature is called strain energy. Previous theoretical studies [22] indicated that the strain energy scales inversely with diameter, therefore it is expected that small diameter nanotubes with greater strain can be functionalized more easily than the larger ones. The adsorption energy data (Table 9) also supports this. The most stable adsorption structure is that with the least diameter. Thus an addition reaction can take place with carbon atoms in the nanotube transformed from sp^2 to sp^3 hybridization. The reactivity is correlated with the extent of this hybridization transformation.

Second, it turns out that in SWNT sidewalls, *p*-orbital misalignment between adjacent carbon atoms plays a larger influence in determining overall reactivity. This misalignment, associated with bonds at an angle to the tube circumference (i.e., bonds that are neither parallel to nor perpendicular to the tube axis) is the origin of torsional stain in nanotubes, and the relief of this strain controls the extent to which addition reactions occur with nanotubes. Since *p*-orbital misalignment as well as pyramidalization scale inversely with tube diameter, smaller diameter tubes are expected to be more reactive than larger diameter tubes as is shown by our data.

In all cases, an insertion product is formed, since the C-C bond of the nanotube is found to break. On the other hand, the bond distance of the adsorbed carbene from the nanotube decreases with increasing nanotube diameter.

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3.4.3 Mulliken charges

Careful analysis of Mulliken charges (Table 10) reveals that, whether for very small or for very large diameter nanotubes, the charge distributions are exactly similar.

Table 10. Mulliken charges on the atoms of the nanotubes of different diameter functionalized with :CH_2.

CNNT (*n*,*n*)	C_1	C_2	C	H_1	H_2
3,3	0.011	0.014	-0.200	0.060	0.063
4,4	0.014	0.014	-0.214	0.061	0.062
5,5	0.018	0.020	-0.227	0.066	0.070
6,6	0.020	0.020	-0.229	0.067	0.070
7,7	0.017	0.018	-0.228	0.067	0.070
8,8	0.014	0.014	-0.223	0.069	0.071
9,9	0.013	0.013	-0.222	0.068	0.071

There is charge transfer from the surface of the nanotubes to the carbenes and this is in the range of 0.077 (for the (3,3) tube) to 0.092 (for the (6,6) nanotube). The other nanotubes show in-between values.

The charge transfer data reveals that for (4,4) to (7,7) nanotubes, maximum charge is transferred from the nanotube to the carbene.

3.4.4 Bandgaps

The first report on curvature-related effects on bandgaps was obtained experimentally [23] using low-temperature (about 5 K) scanning tunneling spectroscopy (STS). Prior STS experiments [24,25] confirmed that nanotubes could be either metallic (with no bandgap) or semiconducting (with a band gap of hundreds of millivolts). Our observations (Table 11) show that, for narrow carbon nanotubes, the effect of curvature can convert nanotubes expected to be semiconductors to metals, as the bandgap decreases with decreasing diameter. The notable exception is (3,3), which has a larger bandgap than all other nanotubes studied.

Table 11. Bandgaps (eV) of nanotubes of different diameters functionalized with methylene

SWCNT (*n*,*n*)	HOMO	LUMO	Bandgap
3,3	-4.113	-2.571	1.542
4,4	-3.682	-3.135	0.547
5,5	-3.847	-3.179	0.668
6,6	-3.881	-3.154	0.727
7,7	-3.994	-3.124	0.870
8,8	-4.035	-3.109	0.926
9,9	-4.066	-3.102	0.964

4. CONCLUSIONS

The trend towards carbenic reactivity is the same both for armchair and zigzag nanotubes, though the adsorption is stronger in the former case.

Charge transfer is the main mechanism in changing the electronic structure of the tube. The

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chemical interactions involving large charge transfer are sensitive to the energy gap of the CNT and therefore can be used for discriminating between semiconducting and metallic CNTs. $:CH_2$ can be used as a reagent for the separation of metallic and semiconducting nanotubes based on the analysis.

One of the possible mechanisms includes charge transfer to and from the adsorbed species. The interactions between carbenes and SWNTs in our study can help us in finding the mechanisms of molecular sensing with nanotube molecular wires. Also, carbenes adsorbed on the surface of nanotubes can be suggested as novel nanosensors because of the large charge transfer involved in the case of metallic nanotubes.

The binding energy per carbon atom of armchair carbon nanotubes increases in magnitude exponentially with increasing tube diameter. Though the pattern for binding energy per BN unit is almost the same for the boron nitride nanotubes [26], the values of binding energy per unit are different. Methylene forms an insertion product with all armchair carbon nanotubes.

The reactivity is correlated with the extent of hybridization transformation denoted by the pyramidalization angle θ_P and *p*-orbital misalignment. Both of these scale inversely with tube diameter, and hence smaller diameter tubes are more reactive than larger diameter tubes.

SUPPORTING INFORMATION

Figures S1-16 are included in the supporting information.

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