Computational Studies of Carbon Nanotube–Hydrocarbon Bond Strengths at Nanotube Ends: Effect of Link Heteroatom and Hydrocarbon Structure

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Abstract: Semiempirical and density functional electronic structure theory methods were used to study SWNT-X−R bond strengths, where the single-walled carbon nanotube (SWNT) had an armchair or zigzag structure, the link heteroatom X was O, N(H), or S and the hydrocarbon chain R was CH_2CH_3, $CH(OH)CH_3$, $CHCH_2$, or $CH(CF_3)CH_3$. In all systems the hydrocarbon was bonded to the end of the nanotube. The SWNT-X−R bond (that is, the bond joining the link atom to the hydrocarbon) is more than 0.4 eV stronger for armchair than for zigzag nanotubes with the same diameters, irrespective of whether O, N, or S are used as link atoms or whether OH, C=C, or CF_3 groups are present in the hydrocarbon chain. This raises the possibility for selective manipulation of armchair/zigzag nanotubes using a variety of link atoms and hydrocarbon structures. The SWNT-O−$CH(CF_3)CH_3$ bond is weaker than the SWNT-O−CH_2CH_3 bond (for both armchair and zigzag nanotubes), while inclusion of a double bond in the ethyl chain increases the bond strengths. Also, SWNT-S−CH_2CH_3 and SWNT-N(H)−CH_2CH_3 bonds are stronger than SWNT-O−CH_2CH_3 bonds.

Keywords: carbon · chirality · computer chemistry · nanotubes · separation

Introduction

Although carbon nanotubes have a diverse range of potential technological applications, the interest in single-walled carbon nanotubes (SWNTs) stems mainly from their use as components in nanoelectronic circuitry.[1] For example, metallic SWNTs can be used for interconnects, and semiconducting nanotubes can be used as transistors. However, current production methods are not able to precisely control the structure (diameter and chirality) of the SWNTs, and mixtures of metallic and semiconducting nanotubes that have a range of chiralities are grown.[1] It is therefore important to separate nanotubes from each other based on their properties and/or chiralities. This has been achieved, to a certain extent, by suspending SWNT mixtures in single-stranded DNA[2] or octadecylamine[3] solutions. In the latter prodecure, the octadecylamine binds more strongly to the semiconducting nanotubes and, in this way, the semiconducting tubes can selectively be retrieved from the mixture. Similarly, Chen et al., have shown that metallic SWNTs can be selectively separated from a suspension of mixed nanotubes by the addition of bromine,[4] and Krupke et al. have shown one can separate metallic and semiconducting nanotubes using alternating current dielectrophoresis.[5] In addition, Iijima and co-workers have shown that irradiation of a mixture of SWNTs can selectively remove nanotubes that have band gap energies similar to the irradiation wavelength.[6]

Since these separation methods are based either on the electrical properties or diameters of the nanotubes, they cannot distinguish between nanotubes with similar electrical properties and diameters. For example, these methods cannot separate (5,5) armchair from (9,0) zigzag SWNTs since both are metallic and have similar diameters. Calculations by Basuik and co-workers[7,8] and from our group[9,10] have shown that it may be possible to separate armchair and zigzag SWNTs (with similar diameters) by derivatization at the nanotube ends. Basuik and co-workers focused on amidation and esterification at SWNT ends, whereas we studied the homolytic bond cleavage of ether bonds linking the nanotube and a methyl chain. In both studies there was a large difference in bond energies for the armchair and zigzag nanotubes (more than 0.4 eV for homolytic ether bond cleavage).

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The dependence of the SWNT–alkyl bond strength on nanotube chirality is relevant for chiral-selective manipulation and purification. Since armchair nanotubes have stronger ether bonding to alkyl groups than zigzag nanotubes,[9] the zigzag nanotube–alkyl bond breaks at lower energies than the armchair SWNT–alkyl bond. Hence, by ramping the temperature of a SWNT solution—or of a substrate that supports a mixture of nanotubes—one can, in principle, separate the zigzag and armchair nanotubes or place a nanotube with the desired chirality at a specified site on a substrate.

In developing end-selective methods based on SWNT functionalization, obvious links between the SWNT and the reactive group (e.g., hydrocarbon) involve the oxygenated functionalities that are formed in the purification processes of carbon materials, such as carbonyl, carboxyl, or hydroxyl.[11,12] Less obvious, but still very important, is the consideration of other heteroatom linkers such as nitrogen (secondary amines) or sulfur (thioethers). Two reasons are that 1) nitrogen and sulfur are less electronegative than oxygen and 2) these heteroatoms, in contrast to disubstituted oxygen, offer further potentially structure-selective reactions. For example, secondary amines can react with electrophiles to give positively charged products with four substituents.[13] Similarly, thioethers can be oxidized to sulfoxides with introduction of sulfur-centered chirality and to sulfones,[14] a functional group that offers additional structure-selective elimination reactions.[14,15]

It is also important to consider several combinations of SWNT-X–R structures, where'X' is the link atom (O, N, or S) and'R' the hydrocarbon, in order to pick the most promising candidates for the more time-consuming experimental studies. The reactivity of an indicator/reactive group (X–R) depends on both the identity of the link heteroatom and on the "hydrocarbon chain" bonded to the heteroatom, as different types of carbon atoms (sp^3 alkyls, sp^2 alkenyls, sp^2 aryls) have different electronic properties and thus affect the X–R bond reactivity. The hydrocarbon structures considered here are $R = CH_2CH_3$, $CH(OH)CH_3$, $CHCH_2$, and $CH(CF_3)CH_3$ since they present a range of functional groups that have electron-withdrawing and -donating properties.

Herein we present theoretical PM3 semiempirical and density functional theory (B3LYP) calculations of the SWNT-X–R bond strengths. Experimental investigations of these types of systems are presently being started in our group. The experimental preparation of these systems depends on the available tube material. SWNTs terminated with phenolic hydroxyl groups can be alkylated directly, whereas nanotubes terminated with carboxyl groups have to be transformed into phenolic tubes by, for example, a Bayer–Villiger type oxidation[16–19] prior to alkylation. Introduction of N(H)–R or S–R requires either carbonyl-terminated SWNT material which can be reacted with N or S nucleophiles,[13,14] or high-purity pristine SWNTs that can be treated with electrophilic reagents developed for addition reactions for less reactive alkenes.[20–24]

Results and Discussion

The SWNT-X–R bond (that is, the bond between the link atom X and the hydrocarbon R) is the weakest bond in the SWNT-hydrocarbon system for all structures considered, and is therefore the bond that breaks at the lowest energy.[25] This bond, which is the focus of the calculations presented here, determines the stability and rate of decay of the SWNT-hydrocarbon systems. (As discussed in reference [9], there is no barrier for SWNT-O–CH_3 bond formation, and we assume that this also holds for the other link atoms and hydrocarbons studied here.)

The SWNT-X–R bond strengths are calculated from fairly short nanotubes. Calculations of (n,0) zigzag nanotubes were based on 4n nanotube carbon atoms (for example, see Figure 1b for the (10,0) nanotube), and those of (n,n) armchair nanotubes included 6n nanotube carbon atoms. In contrast to carbon nanotube electrical properties,[26–28] SWNT-X–R bond strengths are not sensitive to the nanotube length. This was validated by calculating bond energies (using both PM3 and B3LYP methods) for (5,5) and (10,0) nanotubes with X = O, N(H), and $R = CH_3$, CH_2CH_3, and $CH{=}CH_2$ for nanotubes of different lengths (up to 160 nanotube carbon atoms—which yields a 1.4 nm nanotube—were included in the calculations). The change in bond strengths that results from an increase in nanotube lengths was less than 4.5 % in all cases. This insensitivity of bond strengths on the length of the SWNT has, in fact, been assumed in previous work (for example, in reference [29] the energy of C–H bonds at nanotube ends was calculated for a short nanotube and *assumed* to be constant for all nanotube lengths) and our calculations confirm that this assumption is valid. The trends and differences in bond strengths reported here are thus also valid for the longer SWNTs that are obtained experimentally.

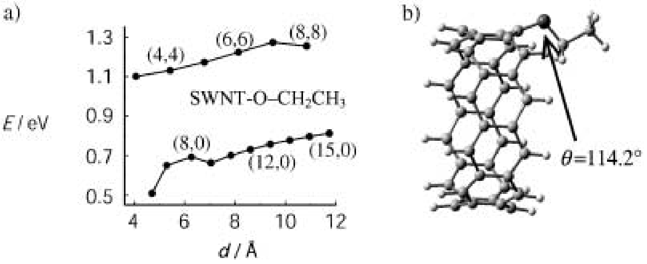

Figure 1. a) PM3 SWNT-O-CH_2CH_3 bond energies E for a series of (n,n) armchair and (n,0) zigzag nanotube structures as a function of their diameter d. The bond energies of the armchair structures are approximately 0.4 eV larger than those of the zigzag structures with similar diameters. b) PM3 minimum energy structure of the (10,0) SWNT-O-CH_2CH_3 system.

Figure 1a shows PM3 SWNT-O–CH_2CH_3 bond strengths for a series of armchair and zigzag nanotubes, and Figure 1b shows a typical optimized SWNT-O–CH_2CH_3 structure (the (10,0) nanotube is shown). There is a large difference in bond energies, of about 0.4 eV, between armchair and zigzag SWNTs with similar diameters. This is very similar to the difference in armchair and zigzag nanotube energies for the

SWNT-O−CH$_3$ bond reported previously,[9] showing this energy difference is not sensitive to an increase in the alkyl chain from one to two methyl groups. Calculations of longer alkyl chains showed that this energy difference is also valid for long-chain structures.

Although the *difference* in the armchair and zigzag SWNT-O−R bond strengths does not change when the length of the alkyl chain increases, the absolute bond strengths (for both the armchair and zigzag systems) decrease by about 0.4 eV when substituting the CH$_3$ with a CH$_2$CH$_3$ group (this can be seen by comparing Figure 1a with Figure 4 in reference [9]). For example, the SWNT-O−CH$_2$CH$_3$ bond energies for the (10,0) and (5,5) nanotubes are 0.702 and 1.18 eV, respectively, and the corresponding energies for the SWNT-O−CH$_3$ systems are 1.12 and 1.51 eV, respectively. Further increase in the alkyl chain length does not significantly change the bond energies, for example, the SWNT-O−(CH$_2$)$_3$CH$_3$ bond energy for the (10,0) nanotube is 0.695 eV (compared to 0.702 eV for the SWNT-O−CH$_2$CH$_3$ bond).

As discussed previously,[9] the SWNT-X−R bond strength is related to the SWNT edge energy (that is, the edge energy per carbon atom in the absence of functional groups and link heteroatoms). Density functional theory calculations yielded edge energies of 2.99 eV per edge atom for zigzag nanotubes and 2.20 eV per edge atom for armchair nanotubes.[28] The edge C atoms on zigzag nanotubes are thus more reactive than those on armchair nanotubes, which leads to stronger SWNT−X-R bonds for zigzag nanotubes than for armchair nanotubes. For example, the SWNT−O-CH$_2$CH$_3$ bond energies are 3.70 and 3.04 eV for (10,0) and (5,5) nanotubes, respectively. Our calculations show that stronger SWNT−X-R bonds are associated with weaker SWNT-X−R bonds (presumably because the link atom donates less electron density to the SWNT-X−R bond when it donates strongly to the SWNT−X-R bond). The SWNT-X−R bond is thus weaker for zigzag nanotubes than for armchair nanotubes. For example, the SWNT-O−CH$_2$CH$_3$ bond energies are 0.702 and 1.18 eV for (10,0) and (5,5) nanotubes, respectively. Since the difference in SWNT-X−R bond strengths between the armchair and zigzag nanotubes depends on the *nanotube chirality*, varying the link atoms and hydrocarbon structures is not expected to significantly affect this difference.

Figure 2 shows the SWNT-O−R bond energies for a series of armchair and zigzag nanotubes when R is CH(OH)CH$_3$, CH=CH$_2$, and CH(CF$_3$)CH$_3$. Although the inclusion of OH, C=C, or CF$_3$ groups in the hydrocarbon chain changes the absolute bond energies (discussed below), it does not significantly effect the *difference* in bond energies between the armchair and zigzag nanotube systems. All hydrocarbons give SWNT-O−R bond energies that are $\approx$0.4 eV larger for armchair than for zigzag nanotubes with similar diameters, as was the case for R = CH$_2$CH$_3$.

Although the *difference* between armchair and zigzag SWNT-O−R bond energies are insensitive to the hydrocarbon structure, the absolute energies are influenced by the presence of electron-donating and -withdrawing groups in the hydrocarbon chain. The most significant change occurs when C=C and CF$_3$ groups are included in the chain. The presence of the C=C double bond (compared to the C−C single bond in CH$_2$CH$_3$) increases the strength of the SWNT-O−R bond (compare Figure 1 and 2b), whereas exchanging an alkyl hydrogen (α to the SWNT-O−R bond) with a CF$_3$ group reduces the SWNT-O−R bond strength (compare Figure 1 and Figure 2c).

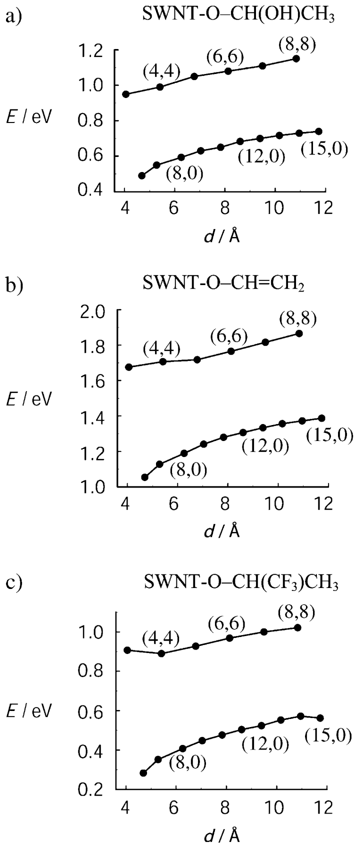

Figure 2. PM3 SWNT-O−R bond energies for a series of (n,n) armchair and (n,0) zigzag nanotube structures when R is a) CH(OH)CH$_3$, b) CH=CH$_2$, and c) CH(CF$_3$)CH$_3$. The bond energies for the armchair structures are approximately 0.4 eV larger than those of the zigzag structures, irrespective of the hydrocarbon structure.

B3LYP calculations confirm the trends in bond energies shown in Figure 2. For example, the B3LYP bond strengths for the SWNT-O−CH=CH$_2$ bond are 1.76 and 2.88 eV for the (10,0) and (5,5) nanotube structures, respectively.[10] This energy difference (1.12 eV) is very similar to the B3LYP energy difference for the SWNT-O-CH$_3$ system (where the (5,5) nanotube bond is 1.09 eV stronger than that for the (10,0) nanotube).[9] Also, similar to the PM3 results, the B3LYP (5,5) SWNT-O−R bond is stronger for R = CHCH$_2$ (2.88 eV) than for R = CH$_2$CH$_5$ (2.26 eV), while for R = CH(CF$_3$)CH$_3$ it is weaker (2.08 eV).

The increase in SWNT-O−R bond strength when including a double bond in the hydrocarbon chain is due to the increased delocalization of the free electron pairs on oxygen into the conjugated π system of the SWNT-O−CH=CH$_2$ complex. This electron delocalization is to both the SWNT-O and O−CH=CH$_2$ bonds, and thus both bonds are shortened and strengthened. For the SWNT-O−CH$_2$CH$_3$ complex, the saturated CH_2CH_3 alkyl chain does not promote electron delocalization to the O−CH_2CH_3 bond (although delocalization to the SWNT-O can still occur) and hence this bond is weaker than the O−CH=CH_2 bond. The calculations also show that the presence of the electron-withdrawing CF_3 group weakens the SWNT-O−$CH(CF_3)CH_3$ bond compared to the SWNT-O−CH_2CH_3 bond, which may be caused by the withdrawal of electron density from the O−$CH(CF_3)CH_3$ bond to the CF_3 group.

Figure 3a shows the SWNT-X−CH_2CH_3 bond energies for a series of armchair and zigzag nanotubes when the link atom X is S or N, and Figure 3b shows typical optimized structures. There is a slight reduction in the difference in SWNT-X−CH_2CH_3 bond energies between the armchair and zigzag nanotube systems compared with the ether bonded systems. Nonetheless, this energy difference—of just under 0.4 eV—is still substantial. The major effect of replacing the O link atom by S or N is the increase in the SWNT-X−CH_2CH_3 bond energies (compare Figure 1 and Figure 3), such that SWNT-S−CH_2CH_3 bonds are stronger than SWNT-N(H)−CH_2CH_3 bonds which, in turn, are stronger than SWNT-O−CH_2CH_3 bonds.

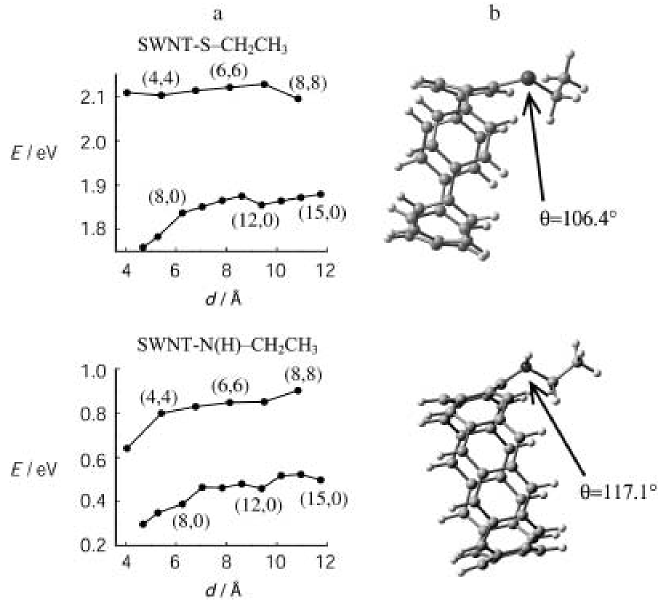

Figure 3. a) SWNT-S−CH_2CH_3 and SWNT-N(H)−CH_2CH_3 bond energies for a series of (*n*,*n*) armchair and (*n*,0) zigzag nanotube systems. The difference in bond energies between the armchair and zigzag structures with similar diameters is slightly less than 0.4 eV. b) PM3 minimum-energy structures of (5,5) SWNT-S−CH_2CH_3 and (10,0) SWNT-NH−CH_2CH_3.

The important trends shown in Figure 3 are validated by B3LYP calculations. For example, the difference in energy between (5,5) SWNT-N(H)−CH_2CH_3 (2.90 eV) and (10,0) SWNT-N(H)−CH_2CH_3 (1.53 eV) is large (1.37 eV). In contrast to the PM3 results, this is larger than the difference between (5,5) and (10,0) SWNT-O−CH_3 bond energies (1.09 eV). Also, similar to the PM3 trends, the N(H) and S link atoms yield stronger bonds than the O linkage. For example, the B3LYP bond energies for the (5,5) SWNT-X−CH_2CH_3 structure are 2.90, 2.39, and 2.26 eV for X = N(H), S, and O, respectively. It can be seen, however, that the ordering of the B3LYP bond energies for X = N(H) and S is opposite to that obtained from the PM3 calculations.

The PM3 and B3LYP results presented here show that the bond strengths of SWNT-X−R derivatives are larger for armchair than for zigzag nanotubes (≈0.4 eV from PM3 calculations and more than 1.0 eV from B3LYP). This energy difference has potential applications for separation and selective manipulation of armchair and zigzag nanotubes, and the present results show that this selective manipulation/separation can be achieved with a variety of functional groups and link atoms. In addition, since the SWNT-hydrocarbon bond strengths depend on the nanotube edge energies, it is expected that the difference in armchair and zigzag nanotube–functional group bond strengths will be valid for a diverse range of link atoms and functional groups. For example, independent studies indicate that chiral-dependent bond strengths are also found for COO and CON linkages.[7,8] Hence, link atoms and functional groups may be chosen and fine-tuned to optimize the separation/manipulation process, without losing the significant difference in SWNT-X−R bond energies between armchair and zigzag nanotubes.

Calculations of SWNT-X−R bond energies for nanotubes with other chiralities (not armchair and zigzag) are left for future studies. These results are important when determining if nanotubes with a specific chirality can be selectively manipulated in the presence of other nanotubes (or selectively separated from these nanotubes). Also, binding of link atoms and hydrocarbon chains to the nanotube sidewalls may also complicate practical implementation of selective nanotube manipulation/separation based on end-functionalization. As discussed previously,[9] when the functional group does not wrap around the nanotube, these sidewall bonds are far weaker than bonding to the nanotube ends, and they will thus be removed at far lower energies (leaving just the bonds between the functional groups and the nanotube ends).

Conclusion

The SWNT-X−R bond energies for armchair nanotubes are more than 0.4 eV larger than for zigzag nanotubes with similar diameters irrespective of whether O, N, or S is used as link atom or whether OH, C=C, or CF_3 groups are included in the hydrocarbon chain. This raises the possibility for selective manipulation/separation of mixtures of armchair and zigzag nanotubes using a variety of link atoms and hydrocarbon structures.

Even though the *difference* in SWNT-X−R bond strengths between armchair and zigzag nanotubes is not significantly influenced by the link atom and hydrocarbon structure, the absolute bond energies are. In particular, substitution of a CF_3 group on the C atom α to the SWNT-O−R bond decreases the bond strength, and inclusion of a double bond increases the bond strength. Also, SWNT-S−R and SWNT-NH−R bonds are stronger than SWNT-O−R bonds (for R = CH_2CH_3).

Methods and Models

The methods used here have been described previously.[9] Briefly, the Gaussian suite of programs[30] was used to obtain minimum energy (optimized) reactant (SWNT-X−R) and product (SWNT-X$^{\bullet}$ and $^{\bullet}$R) structures. Normal mode frequencies were determined to ensure that these structures are potential energy minima, and bond energies were calculated by subtracting the energy of the optimized reactant from the sum of the energies of the optimized products.

SWNT-X−R bond strengths were calculated by using both the PM3[31] semiempirical and density functional B3LYP/6–31G(d) electronic structure theories. The computational efficiency of the semiempirical model allows one to study a large range of SWNT-X−R systems thereby enabling the identification of trends in the bond strengths (for example, as a function of nanotube chirality, type of heteroatom and electron withdrawing/donating properties of the hydrocarbon). These *trends* were validated by determining the B3LYP bond strengths for a representative set of SWNT-X−R systems.

The PM3 semiempirical model, as opposed to other semiempirical theories, was chosen for this work since it gives reliable information of optical and electronic properties of carbon nanotubes.[32] In addition, previous comparisons of PM3 bond energies for small aryl-O−CH_3 and larger SWNT-O−CH_3, SWNT-O−C_2H_3 and SWNT-N(H)−C_2H_5 systems[9,10] with those calculated by using B3LYP/6–31G(d), MP2/6–31G(d), and MP2/6–311+G(2d,2p) confirmed that the PM3 method gives correct trends (and even semi-quantitative accuracy). Results from other research groups also show that the PM3 method yields the same trends in nanotube binding energies as Hartree Fock and density functional theory methods.[29] Comparison of the PM3 and B3LYP bond energies for the systems studied here, and that is presented above, confirms that the semiempirical calculations yield the correct trends for the SWNT-X−R bond energies.

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