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Effect of Tube Length on the Chemisorptions of One and Two Hydrogen Atoms on the Sidewalls of (3,3) and (4,4) Single-Walled Carbon Nanotubes: A Theoretical Study

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ABSTRACT: Density functional theory (B3LYP) calculations using 3-21G and 6-31G(d) basis sets were performed for four different lengths of (3,3) and (4,4) armchair single-walled carbon nanotubes to examine the effect of tube length on the chemisorption process. The significant changes in the C—C bond lengths by H-chemisorption are due to the change of hybridization of carbon atom(s) from sp^2 to sp^3 at the chemisorption site(s). In general, 3-21G basis set overestimates the bond distances and reaction exothermicities compared to 6-31G(d) basis set; however, both the basis sets reveal similar trend. The exothermicity for the addition of two H atoms is about 2–2.5 times that of one H chemisorption except for H (1,3) addition. The present study reveals that the positional preference for the chemisorption of two hydrogen atoms is not same for the armchair and zigzag type nanotubes. The reaction energies for hydrogen chemisorption on the surface of (3,3) nanotubes are substantially higher than for (4,4) SWNTs, probably due to the greater curvature and larger strain in the former case. The change of tube length has significant effect on the reaction energies of

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Key words: armchair nanotubes; zigzag nanotubes; hydrogen chemisorption; quantum chemical calculations; HOMO-LUMO energy gap

Introduction

Understanding the interactions of hydrogen atoms by two different mechanisms, namely physisorption and chemisorption, with single-walled carbon nanotubes (SWNTs) seems to be vital to achieve the hydrogen storage target of 6.5 wt% set by the United States Department of Energy. SWNTs show potential not only as hydrogen storage medium but for applications in diversified areas such as chemistry, material science, and biology, because of their shape and unique properties [1–6]. Dillon et al. first measured the hydrogen storage capacity of SWNTs using temperature-programmed desorption (TPD) spectroscopy [7]. The hydrogen storage capacities of carbon nanotubes have been widely investigated and debated [8–16].

The principal mechanism for hydrogen storage in carbon nanotubes was considered to be the physisorption process in the absence of doped catalysts [9, 10, 17, 18]. In this process, the aromatic bonding framework is not altered by the interaction of H₂ on SWNTs. On the other hand, hydrogen atoms bind to carbon atoms of nanotubes leading to strong C—H bonds in the chemisorption process, where the disruption of bonding network occurs because of changing of carbon atom hybridization from sp² to sp³. The investigations involving chemisorption of hydrogen atoms are limited compared to physisorption process [19–22]. Khare et al. reacted atomic hydrogen with nanotubes and demonstrated the formation of covalent C—H bonds [8].

In a recent study, Zhang et al. have shown the hydrogenation of SWNTs by means of H-plasma treatment [23]. They observed “swelling” in SWNT due to hydrogenation. They confirmed C—H bond formation by means of vibration band in the range of 2,750–3,000 cm^{−1}. Very recently, Yang et al. have examined the chemisorption of hydrogen at low occupancies (i.e. binding of 1 and 2 hydrogen atoms) on SWNTs [24]. They pointed out that binding energy of H atom depends on H occupancy, tube diameter and chirality. Moreover, exohedral binding of H is more favorable than endohedral binding because of easier conversion of sp² to sp³ hybrid-

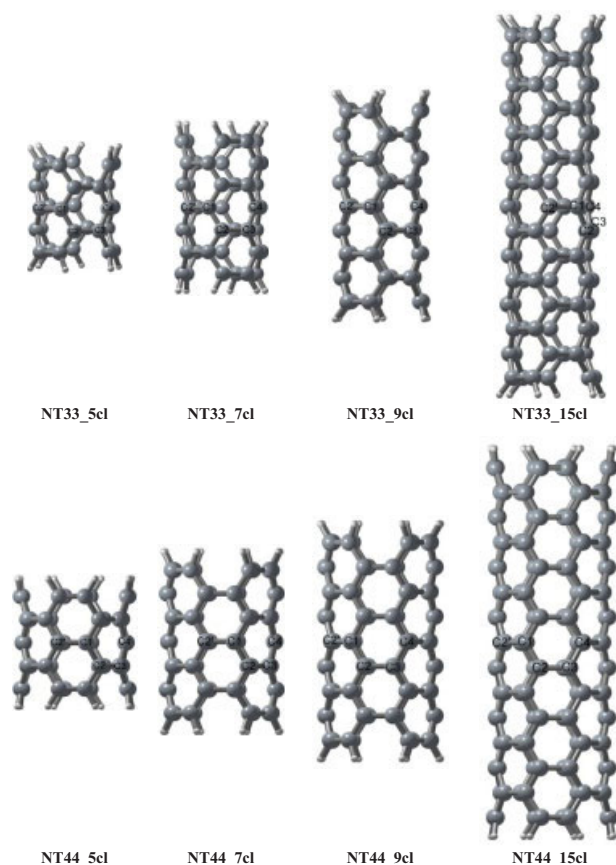
ization of carbon of exterior walls upon H binding [24].

Small diameter nanotubes have attracted much attention recently because of high curvature [25–28]. Physisorption of hydrogen on the small diameter armchair (3,3) and (4,4) SWNTs was investigated using quantum chemical calculations [29]. However, to our knowledge, studies on the chemisorption of hydrogen atoms on the external surface of these nanotubes have not been reported. Dai and coworkers have shown that smaller diameter nanotubes cut more easily than larger tubes in the hydrogenation process. Furthermore, smaller diameter nanotubes show higher reactivity compared to larger diameter tubes because of higher curvature and strain in the structures [23].

Recent studies of Dai and coworkers [23] and Yang et al. [24] have motivated the present work of computational investigation of single hydrogen chemisorption, the preference of the positions (i.e., 1–2, 1–2', 1–3 or 1–4 positions) for the chemisorption of two hydrogen atoms considering the small diameter armchair nanotubes of (3,3) and (4,4) with four different lengths as shown in Scheme 1. The addition of H atoms on the outer walls of SWNT (exohedral addition) has only been considered here because this has been reported to be more favorable than the addition on the inner wall of SWNT (endohedral addition) [24]. In this paper, we examined the reaction energies of hydrogen chemisorption, structural changes of SWNTs and HOMO-LUMO energy gap changes by chemisorption of hydrogen atoms, and the effect of tube length on these properties. The calculations have been performed using B3LYP functional with 3-21G and 6-31G(d) basis sets. We have assessed the performance of 3-21G versus 6-31G(d) basis sets for the structures and chemisorption energies.

Computational Details

The geometry optimizations of (3,3) and (4,4) SWNTs of four different lengths and their hydrogen chemisorbed structures were performed using B3LYP functional [30–32] employing 3-21G and



SCHEME 1.

6-31G(d) basis sets. The edges of nanotubes were terminated by hydrogen atoms. The atom numbers given in the structures shown in Scheme 1 indicate the positions of hydrogen atoms that are chemisorbed on the surface of SWNTs. Single hydrogen atom has been bound at C1. Two hydrogen atoms have been attached simultaneously at C1—C2, C1—C2', C1—C3, and C1—C4 positions for each of the structures. Harmonic frequency calculations performed at the B3LYP/6-31G(d) level for hydrogen chemisorbed SWNTs containing 5, 7, and 9 carbon layers yielded all real frequencies, indicating that these structures are minima. The frequency calculations could not be extended for hydrogen chemisorbed tubes containing 15 carbon layers since they were computationally prohibitive. All the calculations have been carried out using Gaussian03 suite of programs [33]. The reaction energies for hydrogen chemisorption (E_r) on the external surface of SWNTs have been calculated using the formula given below.

$$E_r = E_{\text{SWNT}+n\text{H}} - E_{\text{SWNT}} - nE_{\text{H}} \quad (1)$$

where $E_{\text{SWNT}+n\text{H}}$ denotes the total energy of hydrogen chemisorbed nanotube; n represents the number of hydrogen atoms chemisorbed; E_{SWNT} and E_{H} correspond to the energies of pristine nanotube and the hydrogen atom respectively. The reaction energy E_r can also be considered as hydrogen chemisorption energy.

Results and Discussion

The designations NT33 and NT44 are used to represent the (3,3) and (4,4) armchair nanotubes respectively. For these SWNTs, the notations 5c1, 7c1, 9c1, and 15c1 are used to denote 5, 7, 9, and 15 carbon layers (counted in axial direction) of SWNTs respectively. The positions where hydrogen atoms have been attached on the sidewalls are designated by numbers in parenthesis next to H; for instance, H(1,3) indicates that two hydrogen atoms have been chemisorbed to the atoms C1 and C3 of the nanotube structures.

GEOMETRICAL CHANGES BY CHEMISORPTION OF HYDROGENS

The bond distances in the vicinity of hydrogen chemisorption (C1—C2', C1—C2, C2—C3, and C3—C4) for the H-chemisorbed nanotubes and the corresponding distances of the bare tubes at the B3LYP/3-21G and B3LYP/6-31G(d) levels for (3,3) SWNTs are given in Table I and those for (4,4) SWNTs are provided in Table II. The bond lengths of bare SWNTs range from 1.41 to 1.5 Å. The geometrical data obtained at both levels indicate that one and two hydrogen atoms significantly alter the C—C bond lengths of nanotube in the region of hydrogen chemisorption. The significant changes in the C—C bond lengths by H-chemisorption are due to the change of hybridization of carbon atom(s) from sp^2 to sp^3 at the chemisorption site(s). For both (3,3) and (4,4) systems, B3LYP/3-21G level calculations predict the bond lengths similar to those obtained at the B3LYP/6-31G(d) level. However, there is slight overestimation of many of the bond distances at the former level. Chemisorption of hydrogen atoms leads to lengthening of the nearest C—C bonds in the H-chemisorbed region where the bond lengths are >1.5 Å. This indicates weakening of C—C bond in the region of hydrogen chemisorption and this weakening is higher in strained (3,3) nanotube compared to (4,4) SWNTs.

TABLE I

The important bond lengths (in Å) obtained at the B3LYP/3-21G and B3LYP/6-31G(d) levels for the hydrogen chemisorbed and pristine (3,3) nanotubes of different lengths.^a

Structures	B3LYP/3-21G				B3LYP/6-31G(d)			
	C1—C2'	C1—C2	C2—C3	C3—C4	C1—C2'	C1—C2	C2—C3	C3—C4
NT33_5cl	1.504	1.421	1.425	1.421	1.490	1.422	1.426	1.421
H(1)	1.588	1.526	1.374	1.451	1.575	1.523	1.378	1.451
H(1,2')	2.725	1.399	1.414	1.428	2.798	1.400	1.416	1.428
H(1,2)	1.558	1.566	1.550	1.385	1.551	1.562	1.547	1.388
H(1,3)	1.585	1.523	1.554	1.508	1.574	1.519	1.549	1.503
H(1,4)	1.581	1.526	1.345	1.525	1.570	1.521	1.351	1.521
NT33_7cl	1.419	1.440	1.483	1.440	1.419	1.439	1.473	1.439
H(1)	1.588	1.520	1.388	1.440	1.574	1.517	1.390	1.440
H(1,2')	1.714	1.495	1.445	1.443	1.710	1.492	1.442	1.442
H(1,2)	1.543	1.565	1.553	1.408	1.540	1.561	1.547	1.411
H(1,3)	1.559	1.526	1.559	1.523	1.552	1.523	1.554	1.521
H(1,4)	1.558	1.517	1.383	1.517	1.556	1.524	1.413	1.524
NT33_9cl	1.410	1.447	1.454	1.447	1.413	1.445	1.449	1.445
H(1)	1.563	1.525	1.412	1.448	1.558	1.522	1.413	1.447
H(1,2')	1.671	1.506	1.412	1.451	1.669	1.503	1.413	1.449
H(1,2)	1.550	1.574	1.555	1.403	1.547	1.569	1.548	1.405
H(1,3)	1.560	1.524	1.572	1.515	1.555	1.521	1.563	1.513
H(1,4)	1.563	1.516	1.369	1.516	1.564	1.521	1.380	1.521
NT33_15cl	1.473	1.425	1.431	1.425	1.464	1.426	1.430	1.426
H(1)	1.567	1.524	1.415	1.447	1.561	1.521	1.417	1.446
H(1,2')	2.630	1.400	1.420	1.423	2.697	1.400	1.421	1.423
H(1,2)	1.560	1.577	1.557	1.386	1.553	1.572	1.552	1.390
H(1,3)	1.572	1.517	1.572	1.515	1.564	1.516	1.565	1.512
H(1,4)	1.581	1.518	1.354	1.518	1.570	1.516	1.360	1.516

^a See Figure 1 and text for atom numbers and explanation of symbols.

The bond lengths of newly formed C—H bonds in the H-chemisorbed nanotubes are ~ 1.1 Å. The C2—C3 bond lengths in H(1,4) structures are less than 1.4 Å indicating that these bonds exhibit double bond characters. The addition of two hydrogen atoms to the nearest neighbor positions C1 and C2' (i.e., H(1,2') addition) leads to bond-breaking of C1—C2' (circumferential bond) in the structures NT33_5cl and NT44_5cl. Interestingly, the bond-breaking also occurred in H(1,2') addition of NT33_15cl, which is three times longer than the structure NT33_5cl. The distance between C1 and C2' in the above-mentioned structures is noticeably longer at B3LYP/6-31G(d) compared to B3LYP/3-21G level. It is important to mention that bond-breaking of C1—C2' does not occur in H(1,2') addition in 7cl and 9cl structures of both (3,3) and (4,4) SWNTs as well as NT44_15cl. However, the C1—C2' bonds in these cases are substantially elongated. The elongation of these C1—C2' bonds is

less in case of (4,4) compared to highly curved and strained (3,3) nanotubes. Although, two hydrogen atoms were added to the adjacent carbon sites in H(1,2') and H(1,2) additions, the elongation of C1—C2' bond is significantly higher in the hydrogen chemisorbed SWNTs of H(1,2') than C1—C2 bond in the hydrogen chemisorbed nanotubes of H(1,2).

A critical examination of the data provided in Tables I and II shows that the C1—C2' bond distances in the bare nanotube structures of NT33_5cl, NT33_15cl and NT44_5cl are 1.46–1.5 Å, which are longer than other bond distances in these structures and the corresponding bond lengths of rest of the bare nanotubes. These longer bond distances indicate much strain in that specific region of the tubes. Therefore, the chemisorption of two hydrogen atoms to the carbons of C1—C2' circumferential bonds (H(1,2') addition) leads to bond-breaking in order to release the strain. Arellano et al. has shown the scis-

TABLE II

The important bond lengths (in Å) obtained at the B3LYP/3-21G and B3LYP/6-31G(d) levels for the hydrogen chemisorbed and pristine (4,4) nanotubes of different lengths.^a

Structures	B3LYP/3-21G				B3LYP/6-31G(d)			
	C1—C2'	C1—C2	C2—C3	C3—C4	C1—C2'	C1—C2	C2—C3	C3—C4
NT44_5cl	1.464	1.424	1.423	1.424	1.455	1.424	1.423	1.424
H(1)	1.573	1.519	1.384	1.444	1.559	1.515	1.387	1.443
H(1,2')	2.650	1.397	1.415	1.434	2.705	1.398	1.417	1.434
H(1,2)	1.547	1.559	1.543	1.391	1.539	1.554	1.538	1.393
H(1,3)	1.564	1.516	1.540	1.511	1.555	1.511	1.534	1.506
H(1,4)	1.561	1.522	1.346	1.522	1.550	1.517	1.352	1.517
NT44_7cl	1.413	1.436	1.453	1.436	1.412	1.435	1.447	1.435
H(1)	1.543	1.521	1.426	1.444	1.536	1.517	1.424	1.443
H(1,2')	1.655	1.505	1.426	1.444	1.647	1.502	1.424	1.443
H(1,2)	1.532	1.562	1.544	1.409	1.527	1.558	1.536	1.411
H(1,3)	1.546	1.523	1.551	1.520	1.525	1.516	1.546	1.517
H(1,4)	1.541	1.519	1.380	1.519	1.533	1.514	1.382	1.514
NT44_9cl	1.408	1.441	1.430	1.441	1.409	1.440	1.427	1.440
H(1)	1.548	1.525	1.398	1.447	1.542	1.521	1.399	1.445
H(1,2')	1.637	1.511	1.400	1.448	1.628	1.508	1.400	1.446
H(1,2)	1.539	1.573	1.542	1.406	1.535	1.569	1.534	1.384
H(1,3)	1.546	1.517	1.540	1.517	1.537	1.517	1.539	1.520
H(1,4)	1.549	1.521	1.368	1.521	1.541	1.517	1.372	1.517
NT44_15cl	1.416	1.438	1.436	1.438	1.417	1.437	1.434	1.437
H(1)	1.551	1.524	1.405	1.446	1.545	1.520	1.406	1.445
H(1,2')	1.648	1.510	1.407	1.446	1.641	1.507	1.408	1.445
H(1,2)	1.541	1.573	1.542	1.404	1.536	1.569	1.537	1.406
H(1,3)	1.546	1.524	1.551	1.524	1.540	1.519	1.546	1.521
H(1,4)	1.552	1.521	1.371	1.521	1.546	1.517	1.376	1.517

^a See Figure 1 and text for atom numbers and explanation of symbols.

sion of C—C bond (the distance is 3.05 Å) of circumferential type upon chemisorption of hydrogen atoms, based on molecular dynamics simulations using local density approximation [21]. This sort of bond cleavage has been well documented for the addition of CH₂ and O with the circumferential C—C bond of armchair SWNTs [34–36].

REACTION ENERGIES OF HYDROGEN CHEMISORPTION

The reaction energies obtained using B3LYP functional with 3-21G and 6-31G(d) basis sets for the chemisorptions of single and two hydrogen atoms on the sidewalls of (3,3) and (4,4) SWNTs of 5, 7, 9, and 15 carbon layers are given in Table III. The reactions of single and two hydrogen chemisorptions on the surface of these armchair nanotubes are highly exothermic. In general, 3-21G basis set over-

estimates the reaction exothermicity of hydrogen chemisorption compared to 6-31G(d) basis set. However, the trend obtained using both the basis sets is similar. The reaction energies obtained at the B3LYP/6-31G(d) level for the hydrogen chemisorptions on the surface of (3,3) and (4,4) SWNTs of various lengths are depicted in Figure 1. The exothermicity for the addition of two H atoms is about 2 to 2.5 times that of one H chemisorption except for H(1,3) addition.

Figure 1 shows that change of tube length has significant effect on the reaction energies of hydrogen chemisorption. For both (3,3) and (4,4) systems, the addition of H(1,3) is thermodynamically less favored compared to H(1,2) and H(1,2') additions irrespective of the length of SWNTs. The least positional preference of H(1,3) addition among the chemisorptions of two hydrogen atoms considered for these (3,3) and (4,4) armchair

TABLE III

The reaction energy (E_r) calculated at the B3LYP/3-21G and B3LYP/6-31G(d) levels for the hydrogen chemisorption reactions on the sidewalls of (3,3) and (4,4) SWNTs of different lengths.^a

Tube length and addition site	(3,3) SWNT		(4,4) SWNT	
	B3LYP/3-21G	B3LYP/6-31G(d)	B3LYP/3-21G	B3LYP/6-31G(d)
5 carbon layers				
H(1)	-63.9	-62.1	-45.8	-42.3
H(1,2')	-162.6	-162.2	-136.2	-130.3
H(1,2)	-154.5	-149.2	-135.8	-127.9
H(1,3)	-109.6	-105.4	-86.4	-79.3
H(1,4)	-147.8	-140.9	-120.7	-112.4
7 carbon layers				
H(1)	-66.1	-65.6	-41.8	-38.6
H(1,2')	-129.0	-123.2	-114.7	-107.4
H(1,2)	-140.3	-134.9	-117.4	-110.1
H(1,3)	-104.8	-102.3	-67.8	-67.9
H(1,4)	-112.8	-113.9	-96.7	-90.4
9 carbon layers				
H(1)	-55.7	-53.5	-56.0	-52.0
H(1,2')	-136.2	-129.8	-123.1	-115.7
H(1,2)	-136.4	-131.4	-114.0	-107.2
H(1,3)	-97.0	-93.6	-76.0	-78.3
H(1,4)	-110.4	-114.0	-124.8	-115.2
15 carbon layers				
H(1)	-66.2	-62.2	-51.8	-47.8
H(1,2')	-149.2	-147.8	-119.3	-111.9
H(1,2)	-145.3	-139.3	-115.8	-108.9
H(1,3)	-106.8	-101.9	-82.8	-76.5
H(1,4)	-140.1	-132.9	-115.6	-105.8

^a All values are in kcal/mol.

SWNTs is different to the results reported for zigzag type nanotubes and graphene sheet [24]. Thermodynamically lower preference of adjacent positions than alternate carbon sites for the chemisorption of two hydrogen atoms on zigzag tubes and graphene sheet was attributed to the "crowding effect" by Yang et al. [24]. However, our current results on armchair nanotubes fail to support the reason of "crowding effect." Thus, the present study highlights that the positional preference for the chemisorption of two hydrogen atoms is not same for the armchair and zigzag type nanotubes. Figure 1 shows that in general, the reaction energies of hydrogen chemisorption on the surface of (3,3) nanotubes are substantially higher than for (4,4) SWNTs, probably due to the greater curvature and larger strain in the former case. The transition from sp^2 to sp^3 hybridization of carbon by hydrogen addi-

tion is easy in highly curved nanotubes, thus (3,3) SWNTs exhibit high exothermicity values.

Barone et al. considered smaller length nanotubes (one or two unit cells) for hydrogen chemisorptions [19]. They reported that the binding energies for single hydrogen chemisorption are quite similar when they doubled the nanotube length from one to two unit cells [19]. In comparison to NT33_15cl, the exothermicity for the chemisorptions of two hydrogen atoms is much higher in NT33_5cl albeit there is no significant change in the reaction energy for single hydrogen chemisorption on surface of both tubes. The very high reaction energies obtained for NT33_5cl may be due to the possibility of deformation to large extent by hydrogen chemisorption. The order of addition from the most feasible to the least feasible reaction is: $H(1,2') > H(1,2) > H(1,4) > H(1,3)$ for 5 carbon layered tubes of NT33 and NT44. The same order is

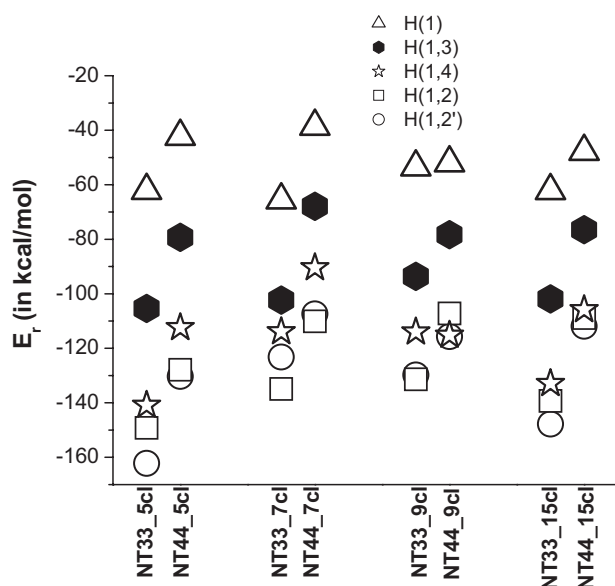


FIGURE 1. The variation of reaction energies obtained at the B3LYP/6-31G(d) level for the chemisorption of one and two hydrogen atoms on the external surface of (3,3) and (4,4) single-walled carbon nanotubes (SWNTs) of different lengths.

retained for SWNTs containing 15 carbon layers but it does not persist for 7 and 9 carbon layered tubes of both NT33 and NT44. The addition of H(1,2') is highly feasible in nanotubes where C1—C2' bond breaking occurs. The present study indicates the necessity of caution in extrapolating the results of smaller length nanotubes to longer tube lengths.

FRONTIER ORBITAL ENERGIES AND HOMO-LUMO ENERGY GAPS

Previous study suggested that hydrogenation could open up or increase the band gap of SWNTs [37]. To obtain profound understanding of the variation of HOMO, LUMO energies and band gap values (energy gap between HOMO and LUMO levels) by chemisorption of hydrogen atoms on SWNTs, we have collected those values for pristine and hydrogen chemisorbed nanotubes in Table IV. In general, the band gap values of hydrogenated nanotube and bare tube are smaller for (4,4) than (3,3) SWNT. Chemisorption of single or two hydrogen atoms on armchair SWNTs significantly changes the band gap values compared to pristine structure due to large changes in the HOMO and LUMO energy levels. Change of nanotube length affects the band gap

values of both pristine and hydrogen chemisorbed SWNTs. In all the nanotube structures considered, H(1,3) addition on the sidewalls substantially reduces the band gap of corresponding nanotubes. As mentioned earlier, H(1,3) addition is the least exothermic process among the chemisorptions involving two hydrogen atoms. Thus, the present study clearly indicates that, independent of the nanotube length, the tubes with two hydrogen atoms attached at alternate positions are kinetically as well as thermodynamically less stable than the other nanotubes with two hydrogen atoms chemisorbed.

Conclusions

We have explored chemisorptions of one and two hydrogen atoms on the external surface of small diameter (3,3) and (4,4) armchair single-walled carbon nanotubes using B3LYP/3-21G and B3LYP/6-31G(d) levels of theory. The effect of tube length on the structural and band gap changes upon hydrogen chemisorptions and the reaction energies of chemisorption processes were examined. Chemisorption of one and two hydrogen atoms alters the bond lengths in the vicinity of addition sites. Although, 3-21G basis set generally overestimates the bond distances and reaction exothermicities compared to 6-31G(d) basis set, the trend obtained using both the basis sets is similar. Therefore, the basis set of 3-21G in combination with B3LYP functional may be employed for hydrogen chemisorptions on the surface of longer and larger diameter nanotubes to obtain qualitative results. In contrast to zigzag nanotubes and graphene sheet [24], two hydrogen atoms prefer to bind at adjacent positions compared to alternate carbon sites of armchair nanotubes. Similar to the reaction exothermicity, the nanotube structures with two hydrogen atoms chemisorbed in H(1,3) type possess substantially lower band gap values compared to the corresponding bare nanotubes. Changing the length of nanotube has significant effect on the reaction energy of hydrogen chemisorption and band gap values. The present study may enhance the experimental interest on hydrogen chemisorptions with low occupancy on the sidewalls of small diameter nanotubes.

TABLE IV

HOMO, LUMO, and HOMO-LUMO energy gap values obtained at the B3LYP/6-31G(d) level for the pristine and hydrogen chemisorbed nanotubes of different lengths of (3,3) and (4,4).^a

Tube length and attachment sites	(3,3) SWNT			(4,4) SWNT		
	HOMO	LUMO	HOMO-LUMO gap	HOMO	LUMO	HOMO-LUMO gap
5 carbon layers	-4.46	-1.79	2.67	-4.61	-1.85	2.76
H(1)	-3.89 (-5.20)	-1.24 (-2.18)	2.65 (3.02)	-4.08 (-4.67)	-1.71 (-2.39)	2.37 (2.28)
H(1,2')	-4.86	-1.42	3.44	-4.86	-1.59	3.28
H(1,2)	-4.66	-1.46	3.19	-4.56	-1.78	2.78
H(1,3)	-3.94	-2.33	1.62	-3.92	-2.46	1.46
H(1,4)	-4.95	-1.14	3.81	-4.73	-1.52	3.21
7 carbon layers	-4.08	-2.48	1.60	-4.33	-2.35	1.98
H(1)	-4.06 (-4.28)	-2.04 (-2.43)	2.02 (1.86)	-4.30 (-4.27)	-2.34 (-2.73)	1.96 (1.55)
H(1,2')	-4.07	-2.37	1.70	-4.32	-2.25	2.07
H(1,2)	-3.98	-2.47	1.51	-4.20	-2.43	1.77
H(1,3)	-3.61	-2.82	0.79	-3.70	-2.97	0.73
H(1,4)	-3.89	-2.55	1.34	-4.10	-2.53	1.56
9 carbon layers	-4.36	-2.18	2.18	-4.06	-2.70	1.36
H(1)	-4.17 (-4.34)	-2.14 (-2.73)	2.04 (1.61)	-3.88 (-4.58)	-2.35 (-2.86)	1.52 (1.72)
H(1,2')	-4.39	-2.02	2.37	-4.22	-2.41	1.81
H(1,2)	-4.25	-2.30	1.95	-3.98	-2.77	1.21
H(1,3)	-3.79	-2.87	0.92	-3.76	-3.05	0.71
H(1,4)	-4.25	-2.38	1.88	-4.22	-2.62	1.60
15 carbon layers	-3.94	-2.83	1.10	-4.11	-2.91	1.20
H(1)	-4.19 (-4.10)	-2.70 (-2.93)	1.50 (1.18)	-3.94 (-4.43)	-2.66 (-3.10)	1.28 (1.33)
H(1,2')	-4.04	-2.68	1.35	-4.24	-2.70	1.54
H(1,2)	-3.98	-2.68	1.30	-4.02	-2.98	1.05
H(1,3)	-3.68	-3.07	0.61	-3.81	-3.27	0.54
H(1,4)	-4.04	-2.58	1.47	-4.07	-3.01	1.06

^a The values given in parentheses correspond to beta orbitals at UB3LYP/6-31G(d) calculations. All values are in eV.

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