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On the spectra and isomerization of azobenzene attached non-covalently to an armchair (8,8) single-walled carbon nanotube

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ABSTRACT

The structure, energies, electronic spectra and thermal *trans–cis* isomerization of azobenzene (AB) attached non-covalently to the sidewall of CNT(8,8) were calculated using the ONIOM(B3LYP/6–31 + G^*:UFF) level of theory. We found that some subtle differences existed between the structures of the attached AB and the isolated one. The combination of AB and CNT(8,8) favored in energy because of their negative interaction energies. The attached *trans*-AB (TAB) was more stable than the physisorbed *cis*-AB (CAB). The electronic spectrum calculations showed that the absorption wavelengths of the attached CAB were red-shifted for the lowest three singlet states. The *trans–cis* isomerization process of the AB attached non-covalently to the CNT(8,8) involved mainly the bending of CNN angle. The π–π interaction between AB and CNT(8,8) was found to restrain the *trans-to-cis* isomerization of AB, but had little influence on the *cis-to-trans* backward reaction.

1. Introduction

Azobenzene (AB) and its derivatives are important dyes and functional materials. AB-based photoresponsive materials have attracted interest for their potential applications in optical materials [1,2], media storage materials [3,4], light-triggered nanomachines [5,6], etc. It is well-known that two stable forms (*trans* and *cis*) can be observed in the electronic ground state of AB. Upon UV light (~365 nm) irradiation, *trans*-AB (TAB) can be converted to *cis*-AB (CAB). The *cis* → *trans* backward isomerization can readily occur at room temperature and can be promoted by visible light irradiation. The reversible *cis–trans* photoisomerization of AB is generally the basis for these AB-based photoresponsive materials.

Carbon nanotubes (CNTs), since discovered in 1991 by Iijima [7], have become a subject of intensive research because of their unique structural, electronical, and mechanical properties. CNTs functionalized with AB chromophore provide us with the ideal building block for optical nanodevices. It has been found the conduction of such functionalized CNTs can be modulated with UV light [8]. The photoisomerization of AB changes the electrical dipole moment of the chromophore and causes the local variation in the electrostatic environment of the CNTs, which is responsible for the photoresponsive property of CNTs.

There are two methods to achieve the CNTs functionalized with AB chromophore, namely covalent and non-covalent modification of nanotubes. The photoresponsive AB chromophore-modified multi-walled carbon nanotubes (MWCNTs) can be prepared by reacting acyl chloride-containing MWNTs with diaminoazobenzene [9]. Derivatization of CNTs with aryl diazonium salts is a promising way for large-scale preparation of highly functionalized nanotubes [10,11]. This strategy can also be applied to produce the CNTs functionalized covalently with AB chromophores. The procedure is based on the thermally induced reaction of CNTs with diazonium compounds that are generated by the action of isoamyl nitrite on aminoazobenzene [12]. Additionally, linking AB chromophores with CNTs by macromolecular chains is also an effective way to obtain the photoresponsive CNT-based materials. Yang et al. [13] have successfully synthesized two kinds of azobenzene-polyurethane-functionalized MWNTs (AzoPU-MWNTs). The azobenzene-appended polyurethanes were confirmed to be covalently grafted to the surface of MWNTs. The AzoPU-MWNTs exhibit reversible photoisomerization behavior. The photoisomerization rate constants of AzoPU-MWNTs can be effectively controlled by adjusting the main-chain flexibility of the polyurethane.

In contrast to covalent sidewall functionalization, non-covalent modification of CNT has its advantageous because it does not destroy the chemical structure of nanotubes and offers the ability to

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reversibly functionalize nanotubes. Some polycyclic aromatic hydrocarbons such as pyrene, naphthalene and anthracene have been shown to bind non-covalently to nanotube sidewall via π electron coupling between aromatic molecule and nanotube [14–16]. Simmons et al. [8] have presented a light-switchable nanotube-hybrid material by functionalizing single-walled carbon nanotubes (SWCNTs) with an anthracene-modified azobenzene. Upon UV illumination, the AB chromophore undergoes the *cis*–*trans* isomerization, leading to the reversible change in the conductivity of the functionalized SWCNT. This process is repeatable over long periods of time. Some azo-dyes such as Disperse Red 1 (DR1), disperse orange 3 (DO3) and 4-(4-nitrophenyl)azophenol (NPAP), which are modified by 1-pyrenebutyric acid, have also been applied to non-covalently functionalize the SWCNT [17]. These functionalized SWCNTs can convert the photo-induced isomerizations of nearby AB chromophores into electrical signals and serve as a sensitive nanoscale color detectors. The above studies also suggest an electronic interaction between AB chromophore and CNT.

Covalent or non-covalent modification of nanotubes with AB chromophore provides the photoresponsive properties of CNTs. Most researches focused on the photoresponsive behaviors of functionalized CNTs. Until recently, however, little attention has been paid to another important question, whether the isomerization mechanism of AB chromophore is modified by the interaction between AB and CNT. It is well-known that the *cis*–*trans* isomerization of AB are affected by various factors, such as polarity of solvent, viscosity, temperature, pressure, and free volume distribution of the local environment around the chromophores, etc. [18–20]. How the CNT affects the isomerization pathways of AB is not clear. In the previous works [21–24], we have studied in detail the thermal and photoisomerization mechanism of azobenzene and its derivatives. Very recently, we found that the relative thermal stability of the isomers of AB could be influenced by their encapsulation inside an armchair single-walled CNT(8,8) [25]. By analyzing the potential energy surfaces, we found that the isomerization from TAB to CAB was restrained as the AB was confined inside CNT(8,8). However, the confinement in CNT(8,8) had little influence on the *cis*-to-*trans* backward reaction.

In this study, we further investigated the complex, labeled as AB/CNT(8,8), which is formed by AB attached non-covalently to the sidewall of CNT(8,8). The molecular structure, relative energy of the isomers, interaction energy between AB and CNT(8,8), and the potential energy surfaces of the thermal isomerization were discussed in detail. We hope that this study will broaden the understanding of AB–CNT interaction and provide the theoretical guide for the design of CNT-based functional materials.

2. Computational details

Considering the compromise of accuracy and computational cost, we applied a two-layer ONIOM method to calculate the

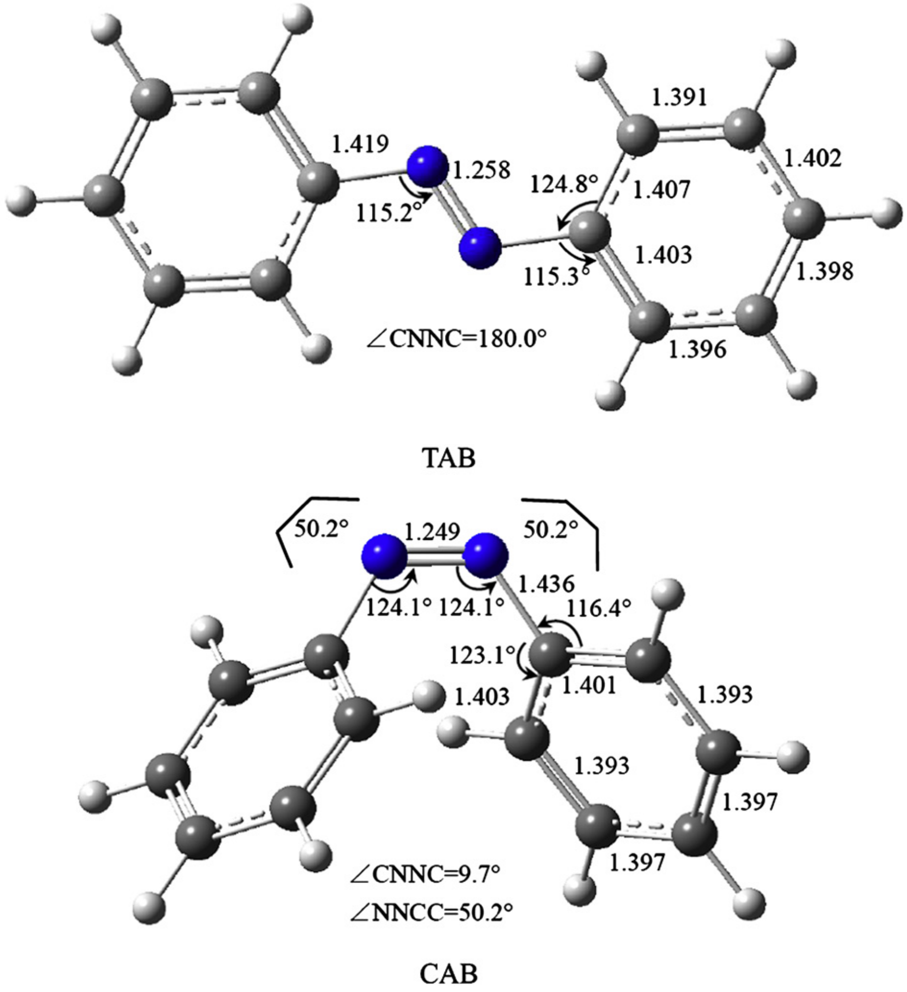

Fig. 1. Molecular structures of TAB and CAB obtained at B3LYP/6–31 + G^* level of theory. All bond lengths are in angstroms, and bond angles and dihedral angles are in degree.

structure and energy of the complex AB/CNT(8,8). The ONIOM method has been proved to be a very effective and indispensable tool to achieve insight in physical and chemical properties of CNTs. In general, the system is divided into two or three layers which are treated with different level of theories. Here, we divided the model system into two parts, in which the AB is chosen as the high layer and described with the hybrid B3LYP [26] approach in conjunction with the $6-31+G^*$ basis set. The CNT is placed into the low layer and treated by the universal force field (UFF) [27].

The combination of density functional theory (DFT) with UFF molecular mechanics has been successfully applied to model the non-covalent interactions between organic small molecules and the SWCNT [28–30]. Additionally, it has been proved that the B3LYP/$6-31+G^*$ level of theory can give reasonable descriptions of the molecular structure and isomerization pathway of AB [31]. Therefore, the ONIOM(B3LYP/$6-31+G^*$:UFF) method was chosen to model the complex AB/CNT(8,8).

As for the single-walled armchair CNT(8,8), the hydrogen atoms were added at the open ends of the tube to avoid dangling bonds. The nanotubes with the diameters in the range of 0.8–1.5 nm are significantly more stable, and hence are more abundant. CNT(8,8) was chosen as a model tube since it has the diameter of about 1.1 nm, being in the middle range of size scale. The AB being placed on the outside wall (middle portion) of CNT(8,8) was used as the initial structural model to optimize the stable complex. Harmonic vibrational frequencies were calculated to confirm the stable configurations. The potential energy surfaces (PESs) of thermal isomerization were calculated by scanning the CNN bond angle and the CNNC dihedral of AB, respectively, at the ONIOM(B3LYP/$6-31+G^*$:UFF) level of theory. For comparison, the structure and the isomerization PESs of the isolated AB molecule were also calculated at the B3LYP/$6-31+G^*$ level of theory. All the calculations were performed using a Gaussian 03 program package [32].

3. Results and discussion

3.1. Molecular geometry

The optimized geometrical parameters of TAB and CAB are given in Fig. 1. It can be seen that the TAB and CAB have the configurations with C_{2h} and C_2 symmetry, respectively. The theoretical calculations of AB have indicated that the structural parameters obtained at the B3LYP/$6-31+G^*$ level are comparable to the experimental data [31], thus it is reasonable to compute the structure of AB attached non-covalently to the sidewall of CNT(8,8) with the same theoretical method and basis set.

On the basis of the ONIOM(B3LYP/$6-31+G^*$:UFF) calculations, the structure of AB physisorbed onto the sidewall of CNT(8,8) was obtained and the corresponding two isomers are presented in Figs. 2 and 3, respectively. As compared with the isolated TAB, it can be found that the TAB in the complex shows the similar structural parameters. The bond lengths and bond angles of TAB are not evidently affected by the existence of CNT(8,8). Only the phenyl rings of TAB in the complex rotate slightly, which leads to a nonplanar configuration of TAB. The nonplanar structure of TAB should result from the π–π interaction between the TAB and the

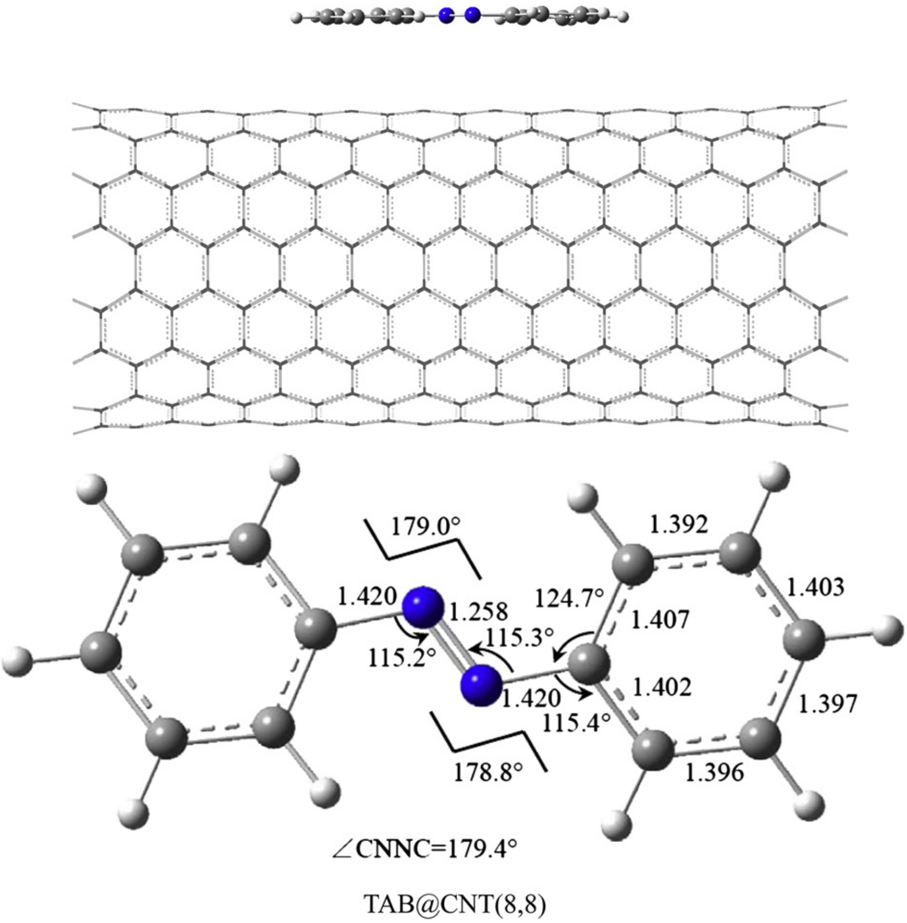

Fig. 2. Molecular structure of TAB attached non-covalently to the sidewall of CNT(8,8), optimized at the ONIOM(B3LYP/$6-31+G^*$:UFF) level of theory. Bond lengths, bond angles and dihedrals are illuminated as in Fig. 1.

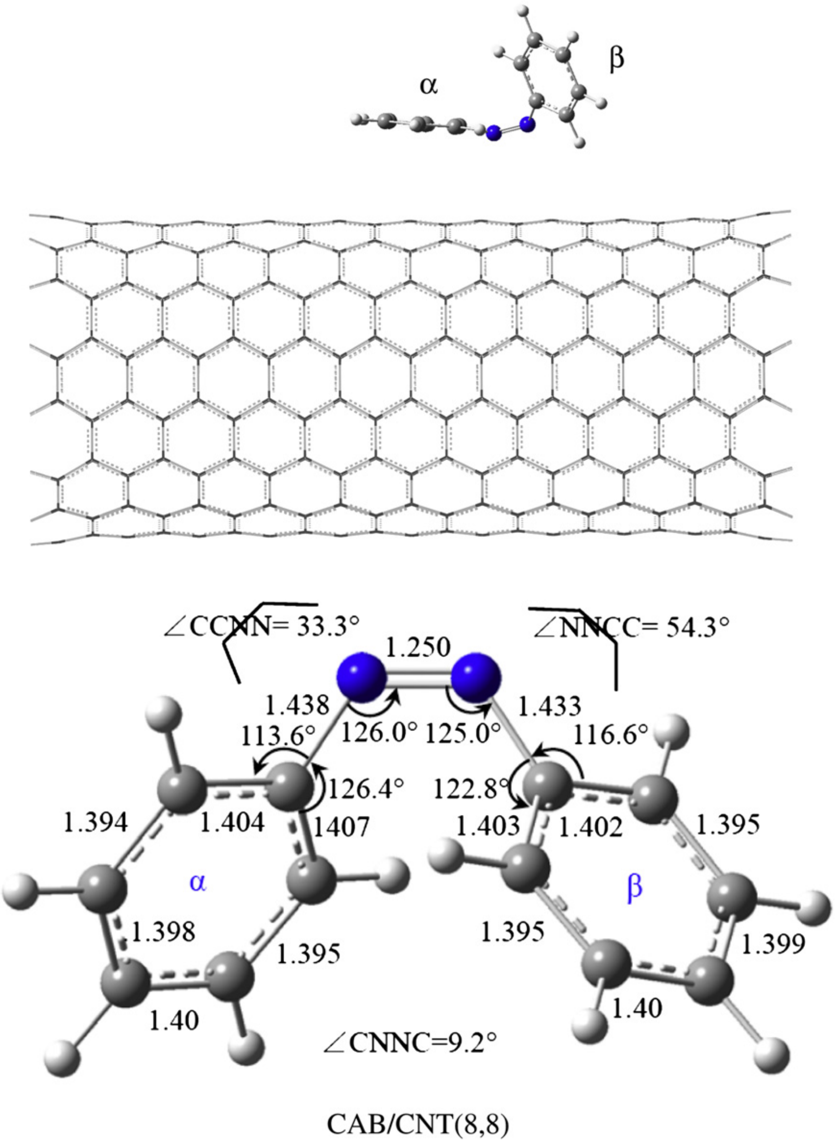

Fig. 3. Molecular structure of CAB attached non-covalently to the sidewall of CNT(8,8), optimized at the ONIOM(B3LYP/6–31 + G^*:UFF) level of theory. Bond lengths, bond angles and dihedrals are illuminated as in Fig. 1.

sidewall of nanotube. In a study on the π–π interaction between benzene and carbon nanotube [33], it has been found that the equilibrium distance between the benzene molecule and nanotube is calculated to be 3.2–3.3 Å. Interestingly, we found that the distance between the phenyl ring of TAB and the sidewall of CNT (8,8) is about 3.4 Å, which is very close to that between the benzene molecule and nanotube. Therefore, it is expected that the interaction between carbon nanotube and these aromatic molecules (e.g. benzenene, azobenzene, etc.) belongs to the π–π interaction.

As for the CAB in the complex and the isolated one, it can be seen that some structural parameters are very similar to each other, especially for the N=N bond length, CNN angles and the geometrical parameters of phenyl rings. However, there still exist some differences in the rotation of phenyl ring and C–N bond lengths. The isolated CAB with C_2 symmetry shows the C–N bonds of 1.436 Å and the NNCC dihedrals of 50.2°. The CAB in the complex shows obvious asymmetry. For the convenience to illustrate the structure of CAB, the phenyl ring neighboring the nanotube sidewall is labeled as α-Ph and the other one far away from the sidewall is labeled as β-Ph, as shown in Fig. 3. It can be seen that the α-Ph is rotated around the C–N bond by 33.3° and the β-Ph is rotated by 54.3°. Additionally, the two C–N bonds are 1.438 and 1.433 Å, respectively. The difference in the two C–N bonds and the degree of rotation of phenyl rings should be attributed to the π–π interaction between the α-Ph of CAB and the sidewall of CNT(8,8). We found that the distance between the α-Ph and the sidewall of CNT(8,8) is about 3.3 Å, which is also excessively similar to that between the benzene molecule and nanotube. Evidently, it can expect that this distance is controlled by the π–π interaction between the aromatic ring and the sidewall of nanotube.

3.2. Relative energy, interaction energy and UV–Vis spectrum

Table 1 gives the relative energies of the isomers and the interaction energies between AB and CNT(8,8). As for the isolated AB, the relative energy of CAB with respect to TAB is calculated to be 15.8 kcal/mol at the B3LYP/6–31 + G^* level of theory, which is very similar to the value reported in literatures [34,35].

Table 1
Energies of *trans*- and *cis*-isomers for azobenzene(AB) and AB/CNT(8,8).

	Total energy (a.u.)	ZPE (kcal mol^{-1})	Relative energy (kcal mol^{-1})	Interaction energy (kcal mol^{-1})
CNT(8,8)[a]	3.57826	1878.2	–	–
TAB[b]	−572.78431	119.7	0	–
CAB[b]	−572.75907	119.4	15.8[d]	–
TAB/CNT(8,8)[c]	−569.24519	1998.6	0	−23.9[f]
CAB/CNT(8,8)[c]	−569.20852	1998.3	22.8[e]	−16.7[f]

[a] Energies calculated at the UFF force field.
[b] Energy calculated at the B3LYP/6–31 + G^* level of theory.
[c] Energies calculated at the ONIOM(B3LYP/6–31 + G^*:UFF) level of theory.
[d] Relative to the energy of TAB with the ZPE corrections.
[e] Relative to the energy of TAB/CNT(8,8) with the ZPE corrections.
[f] Interaction energy = $E_{AB/CNT}$ + $ZPE_{AB/CNT}$ − (E_{AB} + ZPE_{AB} + E_{CNT} + ZPE_{CNT}).

Table 2
UV–Vis spectra of *trans*- and *cis*-isomers for AB and AB/CNT(8,8), calculated at the ONIOM(TD-B3LYP/6–31 + G^*:UFF) level of theory.

	S_1 (n,π^*) (nm)	S_2 (π,π^*) (nm)	S_3 (nm)
TAB	481.7 (0.0)	338.3 (0.8)	307.5 (0.06)
CAB	483.3 (0.04)	306.2 (0.06)	298.9 (0.01)
TAB/CNT(8,8)	482.2 (0.0)	337.7 (0.8)	307.2 (0.06)
CAB/CNT(8,8)	504.5 (0.04)	312.9 (0.06)	300.4 (0.02)

The oscillator strength is reported in brackets.

For the AB/CNT(8,8) complex, the energy of CAB/CNT(8,8) is 22.8 kcal/mol higher than that of TAB/CNT(8,8) by the ONIOM (B3LYP/6–31 + G^*:UFF) calculations, suggesting that the TAB/CNT (8,8) is more stable than CAB/CNT(8.8). To our best knowledge, there is no direct experimental data on the relative stability of the isomers of AB attached non-covalently to nanotubes. However, an experimental phenomenon in Ref. [8] can indirectly reveal the relative stability of the isomers. Simmons et al. [8] prepared the nanotube-hybrid material by non-covalently functionalizing single-walled carbon nanotubes (SWCNTs) with the azobenzene dye (DR1). They found that, after the *trans-to-cis* isomerization has saturated under the low intensity UV lamp, the current in the hybrid sample containing nanotube and DR1 decreases under continued 365 nm illumination. This indicates a relaxation of some *cis* configuration of AB chromophores to the *trans* state and suggests that the *trans*-isomer is more stable than *cis*-isomer, which is consistent with our calculation result.

Additionally, it can be found that the relative energy between CAB/CNT(8,8) and TAB/CNT(8,8) is about 7.0 kcal/mol higher than that between the isolated CAB and TAB, suggesting that the TAB is more stable than CAB when they are bound non-covalently to the sidewall of CNT(8,8). Evidently, the relative stability of *trans*- and *cis*-isomers of AB can be modified by the interaction between AB and CNT(8,8).

Furthermore, we calculated the interaction energy between the isomers of AB and CNT(8,8). The interaction energy (E_{IE}) is calculated as $E_{IE} = E_{AB/CNT} + ZPE_{AB/CNT} - (E_{AB} + ZPE_{AB} + E_{CNT} + ZPE_{CNT})$. We found that these interaction energies are about −23.9 kcal/mol and −16.7 kcal/mol for the TAB/CNT(8,8) and CAB/CNT(8,8), respectively. In view of the negative E_{IE}, it should be able to expect that the non-covalent association of AB with the CNT(8,8) is an exothermic process and favors in energy, although these calculated E_{IE} are only qualitative because of the limit of calculation accuracy. The interaction energy between TAB and CNT(8,8) is lower of 7.2 kcal/mol than that between CAB and CNT(8,8). This can be explained by the difference in the strength of π–π interaction between the aromatic ring of AB and the sidewall of CNT(8,8). For the TAB/CNT(8,8), two phenyl rings of TAB are involved in the π–π interaction. For the CAB/CNT(8,8), however, one phenyl ring of CAB is mainly involved due to the twist configuration of CAB.

The spectral property of AB chromophores is one of issues that are always addressed [36–39]. Table 2 gives the electronic absorption spectra which correspond to the excitation energies of the three lowest singlet states of AB and AB/CNT(8,8). It can be found that TAB in the complex and in the isolated state show the very similar excitation energies. However, this is not the case for the CAB. Compared with the spectra of the isolated CAB, the electronic absorption wavelengths of the CAB in the complex are red-shifted by 21.2, 6.7, and 1.5 nm for the S_1, S_2, and S_3 states, respectively.

3.3. Potential energy surfaces of thermal isomerization

Generally, two mechanisms are considered to be responsible for the thermal *tans–cis* isomerization of AB: one is concerned with the rotation of CNNC dihedral angle and the other with the inversion of CNN angle. It has been found that the substituent of azobenzene and experimental conditions (such as temperature, pressure, and polarity of solvent, etc.) have evident influence on the isomerization mechanism and process [31,40,41]. To explore the effect of nanotube on the isomerization of the physisorbed azobenzene, the potential energy surfaces (PESs) for the rotation and inversion pathways of AB attached non-covalently to CNT(8,8) were obtained by scanning the CNNC dihedral angle or CNN bending angle, while optimizing the other structural parameters at the same time. These two PESs calculated at the ONIOM(B3LYP/6–31 + G^*:UFF) are shown in Figs. 4 and 5, respectively. For comparison, the isomerization PESs of the isolated AB are also provided.

As for the thermal isomerization of AB in the isolated state, some studies have proven that the energy barrier of inversion pathway is lower than that of the rotation pathway [35,42]. Here, our calculations also confirmed this result by comparing the inversion and rotation PESs showed in Figs. 4 and 5. Therefore, the inversion mechanism should be mainly responsible for the thermal *trans–cis* isomerization of AB in the isolated state. As for the AB/CNT(8,8) complex, it is still found that the energy barrier of isomerization along the CNN inversion pathway is lower than that along the CNNC rotation pathway. This indicates that the inversion mechanism is also mainly involved in the thermal isomerization of the AB attached non-covalently to CNT(8,8). However, the comparison of PESs in Figs. 4 and 5 shows that the *tans-to-cis* isomerization energy barriers of the attached AB are higher than those of the isolated

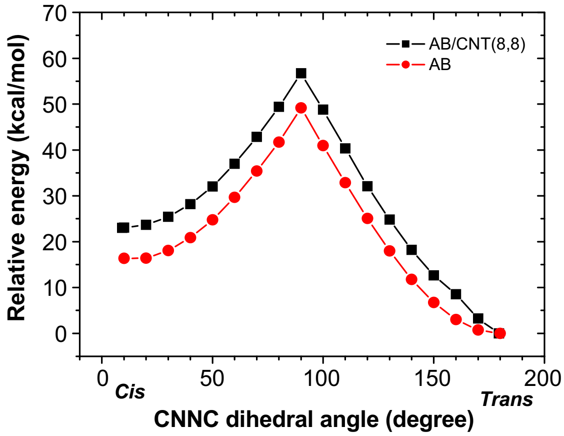

Fig. 4. Potential energy surfaces of AB and AB/CNT(8,8) along the CNNC dihedral.

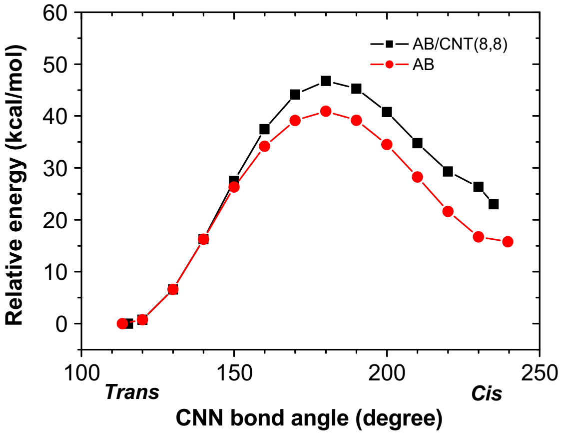

Fig. 5. Potential energy surfaces of AB and AB/CNT(8,8) along the CNN bond angle.

AB, whether for the rotation pathway or inversion pathway. An activation energy increase of about 8 kcal/mol can be found, suggesting that the *tans-to-cis* isomerization of AB can be restrained once the AB is bound non-covalently on the sidewall of CNT(8,8). On the other hand, the energy barriers of the *cis-to-trans* isomerization for the isolated AB and the attached one are close to each other. In view of the similar activation barrier, it can be expected that, via inversion pathway or rotation pathway, the *cis*-to-*trans* backward process of AB can not be evidently affected by the CNT(8,8).

As mentioned before, the reversible *cis–trans* photoisomerization of AB determines the photoresponsive properties of AB-based materials, including the AB-modified carbon nanotube. Therefore, how the carbon nanotube affects the photoisomerization process of AB should be more practical. What is more, it is well-known that the characteristics of CNTs are significantly dependent on the tube diameters and chirality. It is still unclear that how the isomerization PES of AB is controlled by the size and chirality of CNT. Therefore, more rigorous theoretical studies are still needed to shed light on these complex effects. Such relevant investigations are underway.

4. Conclusions

The molecular structure, relative energy, UV–Vis spectra and thermal *trans–cis* isomerization of azobezene physiabsorbed onto the sidewall of CNT(8,8) have been studied by means of an ONIOM approach. We found that the geometrical parameters of AB in the complex were not affected evidently by the existence of CNT(8,8) in comparison with those of the isolated AB. Only the rotation of the phenyl rings was found to occur around the CN bond to some extent for both the *trans*- and *cis*-AB due to the π–π interaction between the phenyl ring of AB and the sidewall of nanotube. The interaction energies between the isomers of AB and CNT(8,8) are calculated to be about −23.9 kcal/mol and −16.7 kcal/mol for the TAB/CNT(8,8) and CAB/CNT(8,8), respectively. With respect to the relative energy between CAB and TAB, the relative energy between the TAB/CNT (8,8) and CAB/CNT(8,8) had an increase of about 7.0 kcal/mol. The UV–Vis spectrum calculations showed that the lowest three singlet excitation energies of the attached TAB were very close to these of the isolated TAB, but the electronic absorption wavelengths of the CAB in the complex were red-shifted by 21.2, 6.7, and 1.5 nm for the S_1, S_2, and S_3 states, respectively. Compared with the case of the isolated AB, the *tans-to-cis* energy barriers of physisorbed AB are increased by about 8 kcal/mol and the *cis-to-trans* backward isomerization barriers are not evidently modified for both the rotation and inversion pathways. The interaction between AB and CNT(8,8) could restrain the *trans-to-cis* isomerization of AB, but had little influence on the *cis-to-trans* backward reaction. The *trans–cis* isomerization process of the AB attached non-covalently to the CNT (8,8) involves mainly the bending of CNN bond angle.

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