

Molecular modeling of dissociative and non-dissociative chemisorption of nitrosamine on close-ended and open-ended pristine and Stone-Wales defective (5,5) armchair single-walled carbon nanotubes

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Abstract The nitrosamine adsorbed on close-ended and open-ended pristine and Stone-Wales defective (5,5) armchair single-walled carbon nanotubes (SWCNTs) was studied using the B3LYP/6-31G(d) method. Structure optimization of all possible adsorption configurations based on the combination of two nitrosamine (amino- and imino-) isomers and four types of nanotubes was carried out. The most stable configuration for the nitrosamine adsorbed on the (5,5) armchair SWCNTs was found to be dissociative chemisorption. The adsorption energies of the most stable structures of the adsorption complexes of close-ended and open-ended pristine SWCNTs with the imino isomer of nitrosamine were -127.15 and -137.14 kcal mol⁻¹, respectively.

Keywords Carbon nanotubes · Single-walled carbon nanotube · Chemisorption · Nitrosamine · Pristine · Stone-Wales defective · Density functional theory

Introduction

N-Nitrosamines are potent carcinogens that can induce tumors in humans and animals. The International Agency for Research on Cancer (IARC) classified a number of

N-nitrosamines with respect to their cancer risk for humans [1]. The IARC considers *N*-nitrosodimethylamine and *N*-nitrosodiethylamine as belonging to the group probably carcinogenic to human, and *N*-nitrosodibutylamine, *N*-nitrosopiperidine and *N*-nitrosopyrrolidine to the group possibly carcinogenic to human [2, 3]. N-Nitrosamines occur as contaminants in different food categories and beverages [4–14]. The reaction of NH₂ and NO to yield H₂ and N₂O has been studied at several high levels of ab initio molecular orbital theory, and it was found that the reaction pathway involves initial formation without a barrier of a twisted non-planar H₂N-NO nitrosamine intermediate [15]. The rotational barrier about the N–N bond of nitrosamine is a significant factor in determining the conformations of related compounds. It is also important for understanding the mechanism of their detoxification and bioactivity [16]. The mechanisms of chemical carcinogenesis by N-nitrosamines were investigated by ab initio methods [17]. The possible Lewis structures for nine isomers of nitrosamines have been found using quantum-chemical calculations [18]. As volatile nitrosamines exist in several isomers, the existing gas-phase monomer isomers of nitrosamine, H₂NNO [19] and their dimer isomers (H₂NNO)₂ [20], and their behavior in gas phase, including thermodynamic properties, rate constants and equilibrium constants of transformations of their isomers were investigated theoretically. Since the quantum chemical-computer codes developed for computations of the large molecular structure are available, the adsorption of small gases onto large adsorbents such as nanotubes and zeolites has been the subject of many studies.

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Chemical functionalization of single-walled carbon nanotubes (SWCNTs) with Stone-Wales (SW) defects by carboxyl groups was investigated [21] and the reactivity of SW defects was compared to that of pristine sidewalls of (5,5) and (10,0) SWCNTs using density functional theory (DFT) calculations [22]. The formation energy of a single SW defect with two possible different orientations in (5,5) SWCNTs was investigated using various quantum chemical methods [23]. The adsorption mechanisms of O₃ on the sidewalls of C(5,5), C(8,8), and C(10,0) SWCNTs, also having SW defects with different orientations, were investigated using DFT [24]. The adsorptions of one and two hydrogen atoms on the external surface of (3,3), (4,4), (5,5), and (6,6) armchair SWCNTs were studied at the B3LYP/6-31G(d) level of theory [25]. Effect of tube length on the adsorptions of one and two hydrogen atoms on the sidewalls of (3,3) and (4,4) SWNTs were studied using DFT [26]. In a previous work, we studied sidewall additions of diazomethane to (*n*, *n*), *n*=3–10 armchair SWCNT on two different orientations of C–C bonds [27]. In earlier studies, we studied the chemisorption of proton, hydroxide [28] and C1–C3 alkoxides [29] on various close-ended and open-ended armchair (5,5) SWCNTs theoretically using the ONIOM method.

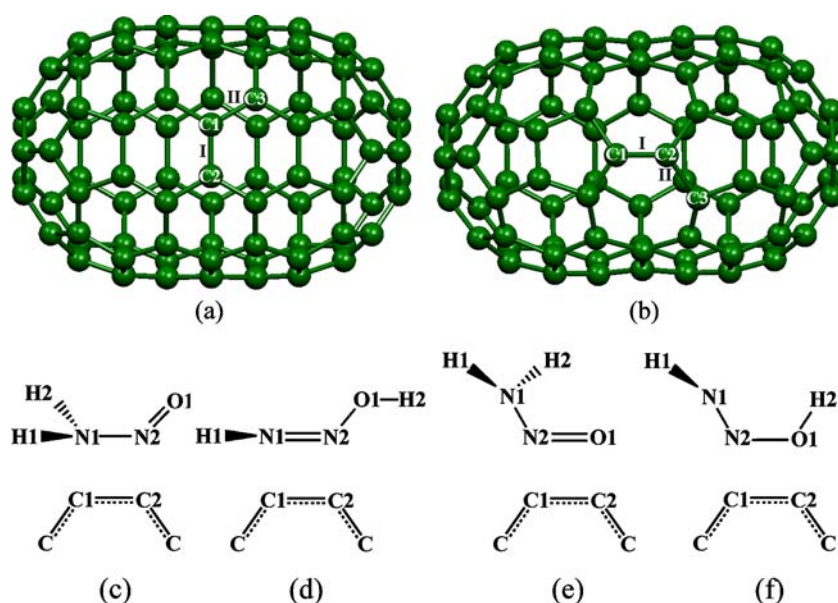
The removal of *N*-nitrosamines from food and bodies is a most interesting topic with great health and environmental relevance. The adsorption of the nitrosamine compounds, *N*-nitrosamine (NA), *N*-methyl-*N*-nitrosamine (NMA), *N*-ethyl-*N*-nitrosamine (NEA), *N,N*-dimethyl-*N*-nitrosamine (NDMA), *N*-ethyl-*N*-methyl-*N*-nitrosamine (NEMA) and *N,N*-diethyl-*N*-nitrosamine (NDEA) to H-ZSM-5 zeolite

[30], and the decomposition of *N*-nitrosamines over zeolites [31] to effect removal of *N*-nitrosamine pollution for environmental protection were studied. In the present work, chemisorption of nitrosamine isomers on close-ended and open-ended types of pristine and Stone-Wales defective armchair (5,5) SWCNTs was studied using C₉₀ and C₉₀H₂₀ models, respectively. The DFT method at the B3LYP/6-31G(d) level of theory was employed throughout the calculations. The adsorption configurations of nitrosamine isomers adsorbed on C–C bonds of different types of armchair (5,5) SWCNTs were investigated.

Computational details

Structures of close-ended and open-ended types of pristine and Stone-Wales (SW) defective (5,5) SWCNTs were modeled as C₉₀ and C₉₀H₂₀ clusters, respectively. Structures of all SWCNTs and their complexes with nitrosamine isomers were fully optimized using DFT methods [32], at the B3LYP/6-31G(d) level of theory [33]. Adsorption energies of nitrosamine isomers on pristine and SW defective (5,5) SWCNT for C₉₀ and C₉₀H₂₀ models at different types of C–C bonds were computed. The SW defective composed of a 5-7-7-5 (C16) cluster is defined as the defect model in this study. In this study, binding sites are taken as C–C bond types of all studied SWCNTs. The C1–C2 and C1–C3 bonds of pristine SWCNTs have been defined as types I and II, respectively, whereas the C1–C2 and C2–C3 bonds of SW defective SWCNTs are defined as types I and II, respectively, as shown in Fig. 1. All

Fig. 1 Definition of bond types I and II for pristine (a) and SW defective (b) single-walled carbon nanotubes (SWCNT). c–f Four possible initial adsorption configurations of amino and imino isomers of nitrosamine adsorbed on SWCNTs by positioning the chemical bonds of the nitrosamine isomer parallel to the C–C bond of the SWCNTs: c N1–N2 (type 1), d N1=N2 (type 2), e N2=O1 (type 3), f N2–O1 (type 4). Atomic numbering for the selected atoms of nitrosamine fragment and SWCNT is defined



calculations were performed with the GAUSSIAN 03 program package [34].

The adsorption energy (ΔE_{ads}) of adsorbate on the SWCNT and the strain energy (ΔE_{st}) of the adsorption

structure of the SWCNT are defined by Eqs. 1 and 2, respectively.

$$\Delta E_{\text{ads}} = E_{\text{SWCNT/adsorbate}} - [E_{\text{adsorbate}} + E_{\text{SWCNT(complex form)}}] \quad (1)$$

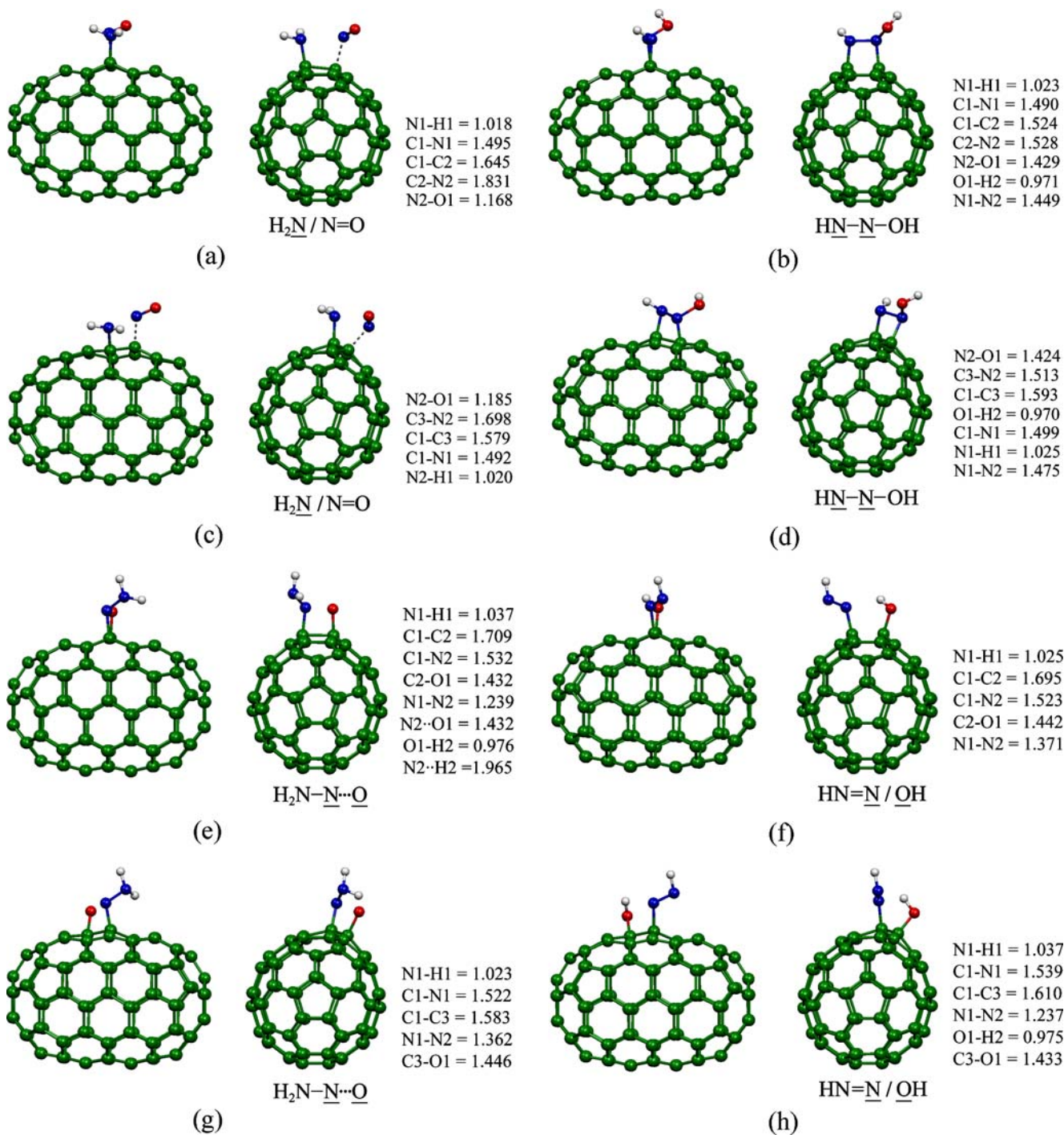


Fig. 2 B3LYP/6-31G(d)-optimized structures of multiple adsorption configurations on close-ended pristine (5,5) SWCNTs (C_{90} cluster) of nitrosamine as **a** amino isomer (configuration type 1 on bond type **I**), **b** imino isomer (configuration type 2 on bond type **I**), **c** amino isomer (configuration type 1 on bond type **II**), **d** imino isomer (configuration

type 2 on bond type **II**), **e** amino isomer (configuration type 3 on bond type **I**), **f** imino isomer (configuration type 4 on bond type **I**), **g** amino isomer (configuration type 3 on bond type **II**) and **h** imino isomer (configuration type 4 on bond type **II**). Bond distances are in Å

$$\Delta E_{st}^{SWCNT} = E_{SWCNT(\text{complex form})} - E_{SWCNT(\text{isolated form})} \quad (2)$$

The deformation energy (ΔE_{deform}) of the adsorbate, defined as an energy change of any form of adsorbate

related to its isolated form, is shown in Eq. 3. The sum of the deformation energy of adsorbate and the strain energy of SWCNT, defined as the total strain energy of adsorption ($\Delta E_{\text{ads_st}}^{\text{total}}$) is shown in Eq. 4.

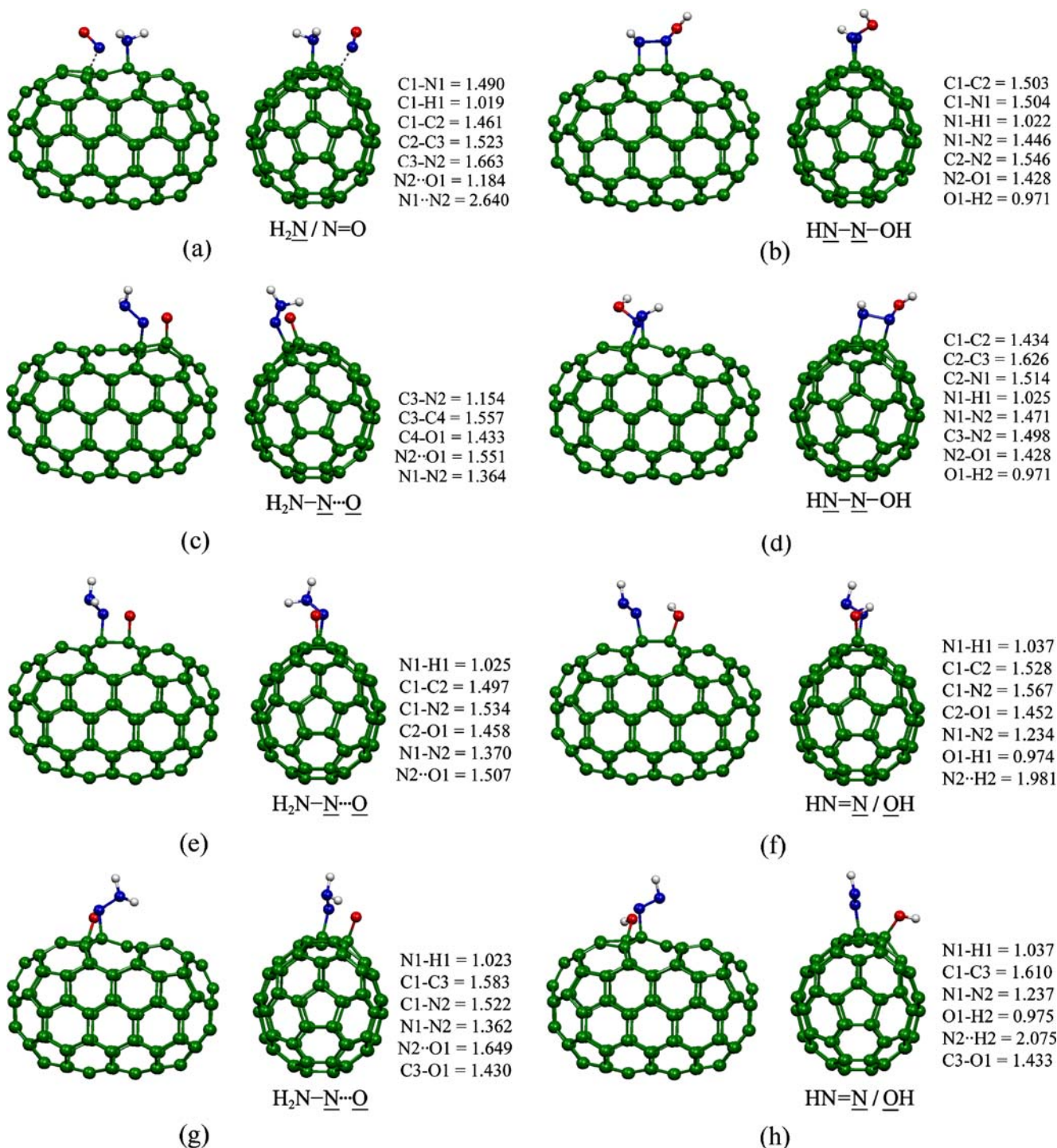


Fig. 3 B3LYP/6-31G(d)-optimized structures of multiple adsorption configurations on close-ended SW defective (5,5) SWCNTs (C_{90} cluster) of nitrosamine as **a** amino isomer (configuration type 1 on bond type I), **b** imino isomer (configuration type 2 on bond type I), **c** amino isomer (configuration type 1 on bond type II), **d** imino isomer

(configuration type 2 on bond type II), **e** amino isomer (configuration type 3 on bond type I), **f** imino isomer (configuration type 4 on bond type I) and **h** imino isomer (configuration type 4 on bond type II). Bond distances are in Å

$$\Delta E_{\text{deform}}^{\text{adsorbate}} = E_{\text{adsorbate (complex form)}} - E_{\text{adsorbate (isolated form)}} \quad (3)$$

$$\Delta E_{\text{ads_st}}^{\text{total}} = \Delta E_{\text{deform}}^{\text{adsorbate}} + \Delta E_{\text{st}}^{\text{SWCNT}} \quad (4)$$

Based on the two most stable isomers of nitrosamine (amino and imino isomers denoted as “a” and “i”, respectively), four possible initiative adsorption configurations of nitrosamine isomer and SWCNT were therefore obtained (see Fig. 1). Four

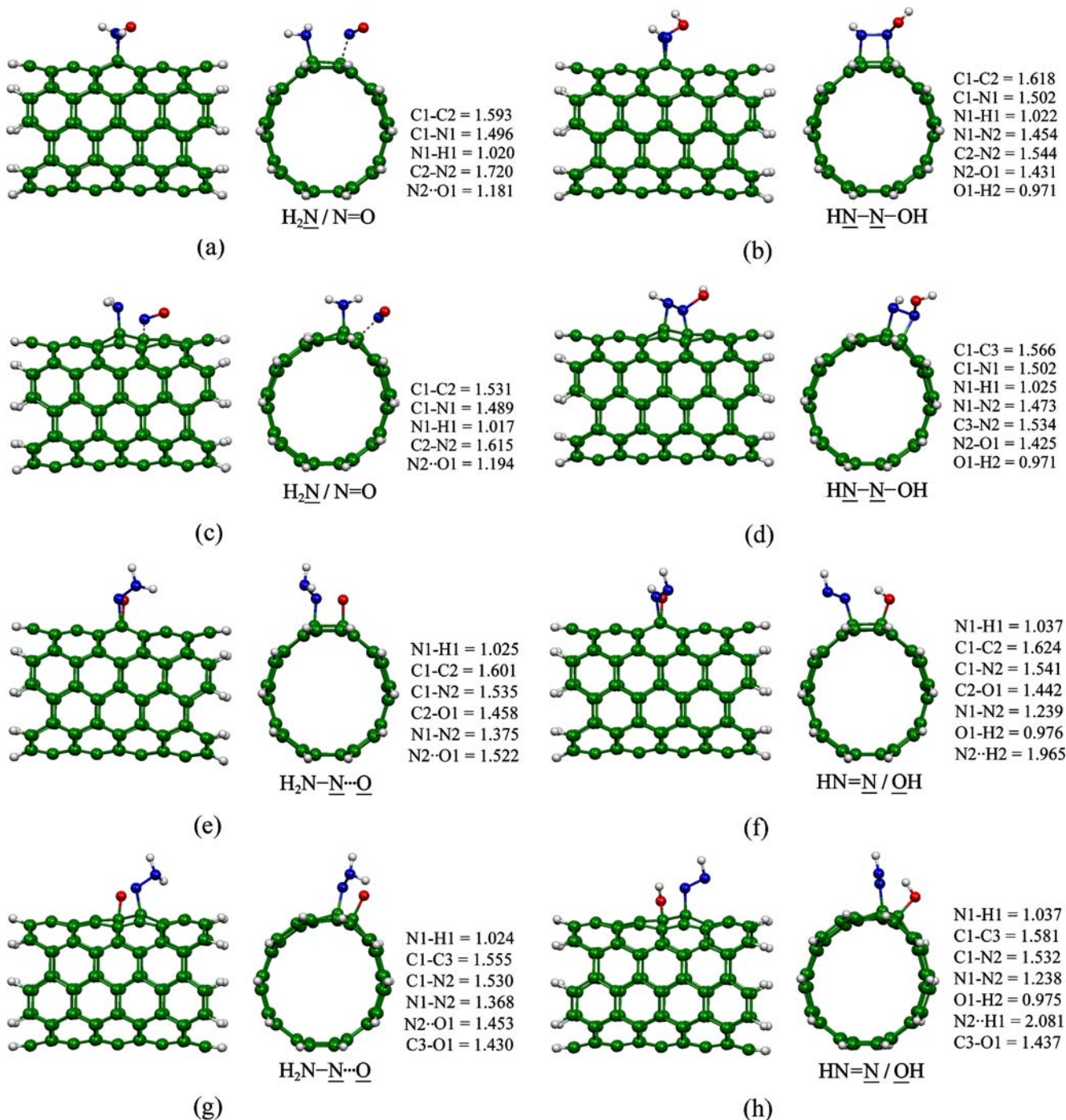


Fig. 4 B3LYP/6-31G(d)-optimized structures of multiple adsorption configurations on open-ended pristine (5,5) SWCNTs ($\text{C}_{90}\text{H}_{20}$ cluster) of nitrosamine as **a** amino isomer (configuration type 1 on bond type I), **b** imino isomer (configuration type 2 on bond type I), **c** amino isomer (configuration type 1 on bond type II), **d** imino isomer (configuration

type 2 on bond type II), **e** amino isomer (configuration type 3 on bond type I), **f** imino isomer (configuration type 4 on bond type I), **g** amino isomer (configuration type 3 on bond type II) and **h** imino isomer (configuration type 4 on bond type II). Bond distances are in Å

adsorption configurations were introduced as the initial configuration for use in geometry optimizations, and their optimized configurations were obtained as dissociative and non-dissociative adsorption configurations. For convenient demonstration, a nomenclature for adsorption configuration

of the nitrosamine and SWCNT is accordingly defined. Four types of adsorption configurations, one non-dissociative adsorption and three dissociative adsorptions, can be written as $\text{H}_2\text{N}-\underline{\text{N}}=\text{O}$ type of configuration for non-dissociative and $\text{H}_2\text{N}-\underline{\text{N}}\cdots\text{O}$ and $\text{HN}=\underline{\text{N}}/\underline{\text{O}}\text{H}$ types of configura-

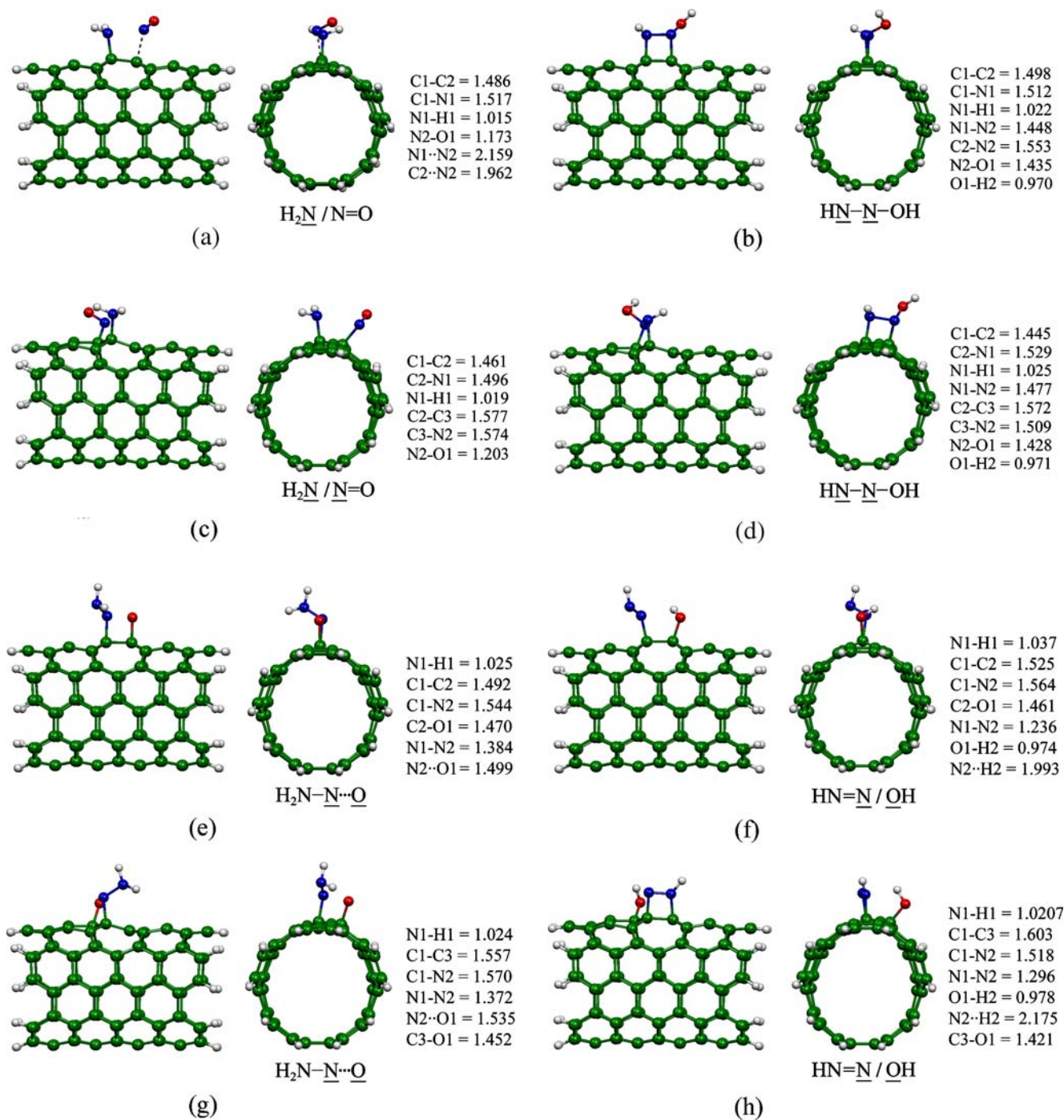


Fig. 5 B3LYP/6-31G(d)-optimized structures of multiple adsorption configurations on open-ended SW defective (5,5) SWCNTs ($\text{C}_{90}\text{H}_{20}$ cluster) of nitrosamine as **a** amino isomer (configuration type 1 on bond type I), **b** imino isomer (configuration type 2 on bond type I), **c** amino isomer (configuration type 1 on bond type II), **d** imino isomer

(configuration type 2 on bond type II), **e** amino isomer (configuration type 3 on bond type I), **f** imino isomer (configuration type 4 on bond type I), **g** amino isomer (configuration type 3 on bond type II) and **h** imino isomer (configuration type 4 on bond type II). Bond distances are in Å

tion for dissociative adsorptions. The nomenclature for types of adsorption configuration of products was defined as follows: the underlined atom of the nitrosamine indicates that it forms a chemical bond with the carbon atom on the SWCNT. Therefore, two adjacent underlined atoms describe the formation of chemical bonds with two adjacent carbon atoms on the SWCNT. In the case of the dissociative adsorption configuration, two fragments of the nitrosamine isomer are shown. If the two fragments of dissociative nitrosamine form a hydrogen bond with each other, this is denoted by a dotted line between them, as in $H_2N-\underline{N}\cdots\underline{O}$, but

if the two fragments of dissociative nitrosamine do not form a hydrogen bond, this is denoted by inserting a slash symbol between them, e.g., $HN=\underline{N}/\underline{O}H$.

Results and discussion

Adsorption configurations

The B3LYP/6-31G(d)-optimized structures for adsorption configurations of nitrosamine isomers adsorbed on the

Table 1 Total and relative energies and energy gaps of nitrosamine chemisorption complexes on four types (5,5) single-walled carbon nanotubes (SWCNTs), computed at the B3LYP/6-31G(d) level

Species/SWCNT	E_{total}^a	ΔE_{rel}^b	$\Delta E_{HOMO-LUMO}^c$
Close-ended pristine			1.98 ^d
a_ns/C ₉₀ _I	-3,615.307863	12.91	1.99
i_ns/C ₉₀ _I	-3,615.294635	21.21	1.97
a_ns/C ₉₀ _II	-3,615.293883	21.68	1.63
i_ns/C ₉₀ _II	-3,615.278964	31.04	1.65
a_ns'/C ₉₀ _I	-3,615.304178	15.22	2.00
i_ns'/C ₉₀ _I	-3,615.328435	0.00	1.98
a_ns'/C ₉₀ _II	-3,615.287928	25.42	1.65
i_ns'/C ₉₀ _II	-3,615.319674	5.50	1.62
Close-ended SW defective			1.36 ^e
a_ns/C _{90'} _I	-3,615.154572	109.10	1.95
i_ns/C _{90'} _I	-3,615.134139	121.92	1.89
a_ns/C _{90'} _II	-3,615.216818	70.04	1.97
i_ns/C _{90'} _II	-3,615.125671	127.24	0.85
a_ns'/C _{90'} _I	-3,615.155283	108.65	1.90
i_ns'/C _{90'} _I	-3,615.163313	103.62	1.89
a_ns'/C _{90'} _II	-3,615.132260	123.10	0.86
i_ns'/C _{90'} _II	-3,615.160402	105.44	0.75
Open-ended type pristine			0.58 ^f
a_ns/C ₉₀ H ₂₀ _I	-3,627.541094	22.70	1.22
i_ns/C ₉₀ H ₂₀ _I	-3,627.408261	34.28	1.23
a_ns/C ₉₀ H ₂₀ _II	-3,627.554703	14.16	1.41
i_ns/C ₉₀ H ₂₀ _II	-3,627.532220	28.27	1.42
a_ns'/C ₉₀ H ₂₀ _I	-3,627.532220	27.44	1.24
i_ns'/C ₉₀ H ₂₀ _I	-3,627.533552	9.33	1.31
a_ns'/C ₉₀ H ₂₀ _II	-3,627.562409	21.62	1.42
i_ns'/C ₉₀ H ₂₀ _II	-3,627.542820	0.00	1.44
Open-ended SW defective			1.15 ^g
a_ns/C ₉₀ H _{20'} _I	-3,627.429227	92.90	1.31
i_ns/C ₉₀ H _{20'} _I	-3,627.431403	91.53	1.51
a_ns/C ₉₀ H _{20'} _II	-3,627.449430	80.22	1.28
i_ns/C ₉₀ H _{20'} _II	-3,627.430317	92.22	1.25
a_ns'/C ₉₀ H _{20'} _I	-3,627.442301	84.70	1.51
i_ns'/C ₉₀ H _{20'} _I	-3,627.450342	79.65	1.53
a_ns'/C ₉₀ H _{20'} _II	-3,627.438992	86.77	1.25
i_ns'/C ₉₀ H _{20'} _II	-3,627.421156	97.96	0.71

^a In Hartree

^b Energies (in kcal mol⁻¹) are related to the most stable configuration; i_ns'/C₉₀_I for the close-ended SWCNT and i_ns'/C₉₀H₂₀_II for the open-ended SWCNT, respectively

^c In eV

^d Energy gap of bare tube of the close-ended pristine (5,5) SWCNT

^e Energy gap of bare tube of the close-ended SW defective (5,5) SWCNT

^f Energy gap of bare tube of the open-ended pristine (5,5) SWCNT

^g Energy gap of bare tube of the open-ended SW defective (5,5) SWCNT

close-ended type of pristine and SW defective (5,5) SWCNTs are shown in Figs. 2 and 3, respectively. The adsorption configurations of nitrosamine isomers adsorbed on the open-ended type of pristine and SW defective (5,5) SWCNTs are shown in Figs. 4 and 5, respectively. The relative energies of the B3LYP/6-31G(d)-optimized structures of adsorption complexes between nitrosamine isomers and the close-ended (C_{90} cluster) and open-ended ($C_{90}H_{20}$

cluster) types of (5,5) armchair SWCNTs are shown in Table 1. Relative reactivities of clean SWCNTs are, in order, open-ended pristine > open-ended SW defective > close-ended SW defective > close-ended pristine; this order is the inverse order of their energy gaps: open-ended pristine ($\Delta E_{\text{HOMO-LUMO}}=0.58$ eV) < open-ended SW defective ($\Delta E_{\text{HOMO-LUMO}}=1.15$ eV) < close-ended SW defective ($\Delta E_{\text{HOMO-LUMO}}=1.36$ eV) < close-ended pristine

Table 2 Adsorption energies of nitrosamine isomers adsorbed on various types of C–C bonds of close-ended (C_{90} cluster) and open-ended ($C_{90}H_{20}$ cluster) types of pristine and SW defective SWCNTs, computed at the B3LYP/6-31G(d) level

Chemisorption/SWCNTs	ΔE_{ads} ^a	Adsorbate state	Configuration type ^b , interatomic distance
Close-ended pristine			
a_ns+C ₉₀ _I → a_ns/C ₉₀ _I	-74.18	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.83 Å
i_ns+C ₉₀ _I → i_ns/C ₉₀ _I	-71.00	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ _II → a_ns/C ₉₀ _II	-76.59	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.70 Å
i_ns+C ₉₀ _II → i_ns/C ₉₀ _II	-74.66	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ _I → a_ns'/C ₉₀ _I	-67.49	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.52 Å
i_ns+C ₉₀ _I → i_ns'/C ₉₀ _I	-127.15	Dissociative	HN= <u>N</u> / <u>OH</u>
a_ns+C ₉₀ _II → a_ns'/C ₉₀ _II	-64.96	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.55 Å
i_ns+C ₉₀ _II → i_ns'/C ₉₀ _II	-122.81	Dissociative	HN= <u>N</u> / <u>OH</u>
Close-ended SW defective			
a_ns+C _{90'} _I → a_ns/C _{90'} _I	-88.64	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.66 Å
i_ns+C _{90'} _I → i_ns/C _{90'} _I	-60.38	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C _{90'} _II → a_ns/C _{90'} _II	-93.37	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.55 Å
i_ns+C _{90'} _II → i_ns/C _{90'} _II	-60.04	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C _{90'} _I → a_ns'/C _{90'} _I	-64.18	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.51 Å
i_ns+C _{90'} _I → i_ns'/C _{90'} _I	-125.21	Dissociative	HN= <u>N</u> / <u>OH</u>
a_ns+C _{90'} _II → a_ns'/C _{90'} _II	-51.01	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.56 Å
i_ns+C _{90'} _II → i_ns'/C _{90'} _II	-108.21	Dissociative	HN= <u>N</u> / <u>OH</u>
Open-ended pristine			
a_ns+C ₉₀ H ₂₀ _I → a_ns/C ₉₀ H ₂₀ _I	-90.09	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.72 Å
i_ns+C ₉₀ H ₂₀ _I → i_ns/C ₉₀ H ₂₀ _I	-68.34	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ H ₂₀ _II → a_ns/C ₉₀ H ₂₀ _II	-108.62	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.62 Å
i_ns+C ₉₀ H ₂₀ _II → i_ns/C ₉₀ H ₂₀ _II	-80.96	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ H ₂₀ _I → a_ns'/C ₉₀ H ₂₀ _I	-67.36	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.52 Å
i_ns+C ₉₀ H ₂₀ _I → i_ns'/C ₉₀ H ₂₀ _I	-133.14	Dissociative	HN= <u>N</u> / <u>OH</u>
a_ns+C ₉₀ H ₂₀ _II → a_ns'/C ₉₀ H ₂₀ _II	-73.25	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.54 Å
i_ns+C ₉₀ H ₂₀ _II → i_ns'/C ₉₀ H ₂₀ _II	-137.14	Dissociative	HN= <u>N</u> / <u>OH</u>
Open-ended SW defective			
a_ns+C ₉₀ H _{20'} _I → a_ns/C ₉₀ H _{20'} _I	-56.09	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.96 Å
i_ns+C ₉₀ H _{20'} _I → i_ns/C ₉₀ H _{20'} _I	-70.42	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ H _{20'} _II → a_ns/C ₉₀ H _{20'} _II	-113.67	Dissociative	H ₂ <u>N</u> /N=O, C...N=1.57 Å
i_ns+C ₉₀ H _{20'} _II → i_ns/C ₉₀ H _{20'} _II	-91.83	Non-dissociative	<u>HN</u> - <u>N</u> -OH
a_ns+C ₉₀ H _{20'} _I → a_ns'/C ₉₀ H _{20'} _I	-71.03	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.50 Å
i_ns+C ₉₀ H _{20'} _I → i_ns'/C ₉₀ H _{20'} _I	-131.19	Dissociative	HN= <u>N</u> / <u>OH</u>
a_ns+C ₉₀ H _{20'} _II → a_ns'/C ₉₀ H _{20'} _II	-73.64	Dissociative	H ₂ N- <u>N</u> ... <u>O</u> , N...O=1.54 Å
i_ns+C ₉₀ H _{20'} _II → i_ns'/C ₉₀ H _{20'} _II	-124.02	Dissociative	HN= <u>N</u> / <u>OH</u>

^a In kcal mol⁻¹

^b Nomenclature is defined in [Computational details](#)

($\Delta E_{\text{HOMO-LUMO}}=1.98$ eV). Due to the energy gaps, the clean close-ended SWCNT was found to be more stable than the open-ended SWCNT.

The relative stabilities of the adsorption complexes due to the close-ended (5,5) SWCNTs, modeled as C_{90} clusters, are (in order): $i_{\text{ns}}/C_{90_I} > i_{\text{ns}}/C_{90_II} > a_{\text{ns}}/C_{90_I} > a_{\text{ns}}/C_{90_II} > i_{\text{ns}}/C_{90_I} > a_{\text{ns}}/C_{90_II} > a_{\text{ns}}/C_{90_II} > i_{\text{ns}}/C_{90_II}$ and $a_{\text{ns}}/C_{90_II} > i_{\text{ns}}/C_{90_I} > i_{\text{ns}}/C_{90_II} > a_{\text{ns}}/C_{90_I} > a_{\text{ns}}/C_{90_II} > i_{\text{ns}}/C_{90_I} > a_{\text{ns}}/C_{90_II} > i_{\text{ns}}/C_{90_II}$ for the pristine and SW defective types, respectively.

For the open-ended (5,5) SWCNTs modeled as a $C_{90}H_{20}$ cluster, the relative stabilities of the adsorption complexes are (in order): $i_{\text{ns}}/C_{90}H_{20_II} > i_{\text{ns}}/C_{90}H_{20_I} > a_{\text{ns}}/C_{90}H_{20_II} > a_{\text{ns}}/C_{90}H_{20_I} > a_{\text{ns}}/C_{90}H_{20_I} > i_{\text{ns}}/C_{90}H_{20_II} > i_{\text{ns}}/C_{90}H_{20_I}$ and $i_{\text{ns}}/C_{90}H_{20_I} > a_{\text{ns}}/C_{90}H_{20_II} > a_{\text{ns}}/C_{90}H_{20_I} > a_{\text{ns}}/C_{90}H_{20_II} > i_{\text{ns}}/C_{90}H_{20_I} > i_{\text{ns}}/C_{90}H_{20_II} > a_{\text{ns}}/C_{90}H_{20_I} > i_{\text{ns}}/C_{90}H_{20_II}$, for the pristine and SW defective types, respectively. As can be seen in Table 1, i_{ns}/C_{90_I} and $i_{\text{ns}}/C_{90}H_{20_II}$ are the most stable adsorption complexes for close-ended and open-ended types, respectively. It can be concluded that either the close-ended or open-ended type of the pristine SWCNT prefers to adsorb nitrosamine as the dissociative form of the imino isomer.

Considering the energy gaps of all the (5,5) SWCNTs and their complexes with nitrosamine as listed in Table 1, the relative reactivities of the bare tubes are higher than their adsorption complexes in all cases. The adsorption energies of the addition of nitrosamine isomers to the C1–C2 and C2–C3 bonds of pristine and SW defective SWCNTs for the C_{90} and $C_{90}H_{20}$ cluster models are listed in Table 2. The results show that chemisorption of nitrosamine amino-isomer on bond type I of either the close-ended or open-ended SW defective (5,5) SWCNT is the metastable species. This result seem to support that either the close-ended or open-ended SW defective (5,5) SWCNT is a catalyst for the reaction involving nitrosamine. On the other hand, pristine (5,5) SWCNT is a good adsorbent for storage of toxic nitrosamine gas and for its removal.

Table 2 shows that there are four types of configuration of adsorption products for nitrosamine isomers adsorbed on the SWCNT, namely $H_2\text{N}/N = O$, $H_2\text{N}-\text{N}\cdots\text{O}$, $\text{HN}-\text{N}-\text{OH}$ and $\text{HN} = \text{N}/\text{OH}$. Only one configuration, $\text{HN}-\text{N}-\text{OH}$ type, represents non-dissociative chemisorption, while there are three chemisorption configurations of types $H_2\text{N}/N = O$, $H_2\text{N}-\text{N}\cdots\text{O}$ and $\text{HN} = \text{N}/\text{OH}$. Only the $H_2\text{N}/N = O$ configuration type is composed of a metastable species that contains nitric oxide, and is known as the $\cdot\text{N} = \text{O}$ radical. The hydrogen bond distance between nitrogen on nitric oxide and carbon on SWCNT lies within the range 1.57–1.83 Å.

Table 2 shows that adsorption configurations on different types of SWCNTs (close-ended pristine, close-ended SW defective, open-ended pristine and open-ended SW defective) follow the same sequential pattern of chemisorption types, i.e., $H_2\text{N}/N = O$, $\text{HN}-\text{N}-\text{OH}$, $H_2\text{N}/N = O$, $\text{HN}-\text{N}-\text{OH}$, $H_2\text{N}-\text{N}\cdots\text{O}$, $\text{HN} = \text{N}/\text{OH}$, $H_2\text{N}-\text{N}\cdots\text{O}$, and $\text{HN} = \text{N}/\text{OH}$, except for the adsorption configurations on the close-ended SW defective SWCNT, of which the third configuration (a_{ns}/C_{90_II}) is the $H_2\text{N}-\text{N}\cdots\text{O}$ type instead of $H_2\text{N}/N = O$ and is the most stable adsorption configuration on the close-ended SW defective SWCNT. The N \cdots O bond distances are within the narrow range of 1.50–1.56 Å, which is too long to form a chemical bond. The $H_2\text{N}-\text{N}\cdots\text{O}$ type may be written in $H_2\text{N}-\text{N}-\text{O}$ notation if an N–O bond is formed. Nevertheless, it may be written in $H_2\text{N}-\text{N}^+\text{O}^-$ notation, which represents the interaction between two opposite charges. The i_{ns}/C_{90_I} for the system of close-ended pristine is the most stable configuration, i.e., the $\text{HN} = \text{N}/\text{OH}$ type configuration.

Energetics of chemisorption of nitrosamine on the SWCNT

The B3LYP/6-31G(d) total energies and relative energies of nitrosamine isomers adsorbed on various types of C–C bond of close-ended pristine SWCNT (C_{90} cluster), open-ended pristine SWCNT ($C_{90}H_{20}$ cluster), close-ended SW

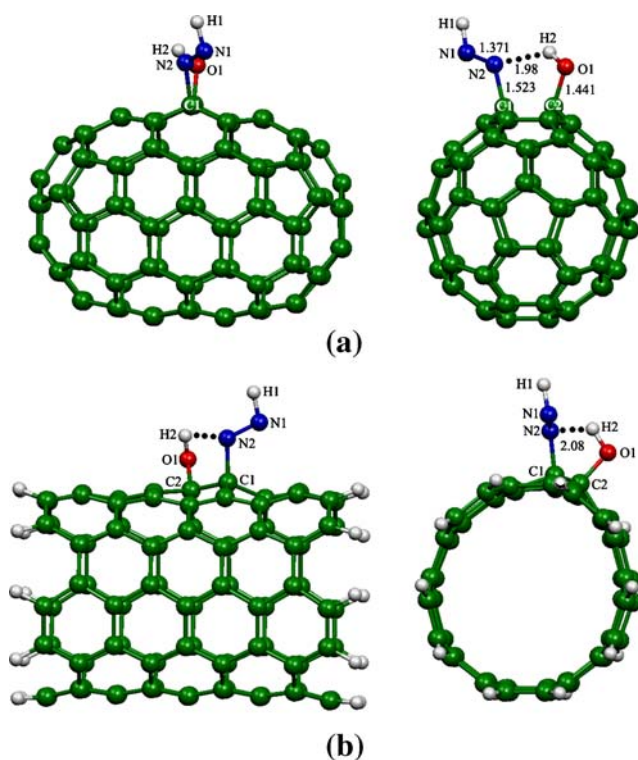


Fig. 6 The most stable structures of adsorption complexes with the imino-isomer of nitrosamine. **a** Close-ended pristine SWCNT (C_{90} cluster). **b** Open-ended pristine SWCNT ($C_{90}H_{20}$ cluster). Bond distances are in Å

defective SWCNT (C_{90} cluster) and open-ended SW defective SWCNT ($C_{90}H_{20}$ cluster) are shown in Table 1, and their adsorption energies are shown in Table 2. Table 2 shows that the adsorption energies of nitrosamine isomers on the close-ended pristine SWCNTs are within the range of -64.96 to -127.15 kcal mol $^{-1}$, and those of the SW-defective SWCNT are within -51.01 to -125.21 kcal mol $^{-1}$. On the open-ended SWCNTs, the adsorption energies of nitrosamine isomers adsorbed on pristine and SW-defective types are within the ranges of -67.36 to -137.14 kcal mol $^{-1}$ and -56.09 to -131.19 kcal mol $^{-1}$, respectively. The most stable structures of adsorption complexes of the close-ended

and open-ended pristine SWCNTs with the imino isomer of nitrosamine are shown in Fig. 6; their adsorption energies are -127.15 and -137.14 kcal mol $^{-1}$, respectively.

The adsorption energies of most stable structures of adsorption complexes of the close-ended pristine SWCNT and the open-ended pristine SWCNT with the imino isomer of nitrosamine are -127.15 and -137.14 kcal mol $^{-1}$, respectively. It can be concluded that all non-dissociative chemisorptions on all types of (5,5) SWCNT are weak, with binding energies within the range of -60.04 to -93.37 kcal mol $^{-1}$. Binding energies of dissociative chemisorptions on (5,5) SWCNT vary widely within the range of -51.01 to -137.14 kcal mol $^{-1}$.

Table 3 Strain energies of SWCNTs, deformation energies of the nitrosamine adsorbate and total strain energies of their complexes, computed at the B3LYP/6-31G(d) level

Chemisorption complex	$\Delta E_{\text{deform}}^{\text{adsorbate a, b}}$	$\Delta E_{\text{st}}^{\text{SWCNT a, c}}$	$\Delta E_{\text{ads_st}}^{\text{total a}}$
Close-ended pristine			
a_ns/ C_{90_I}	69.61	40.19	109.80
i_ns/ C_{90_I}	70.99	41.26	112.25
a_ns/ C_{90_II}	75.64	45.35	120.99
i_ns/ C_{90_II}	84.59	41.15	125.75
a_ns'/ C_{90_I}	64.16	41.27	105.42
i_ns'/ C_{90_I}	96.95	50.23	147.19
a_ns'/ C_{90_II}	69.26	43.83	113.09
i_ns'/ C_{90_II}	95.63	52.72	148.35
Close-ended SW defective			
a_ns/ $C_{90'_I}$	79.58	53.48	133.07
i_ns/ $C_{90'_I}$	67.16	47.80	114.95
a_ns/ $C_{90'_II}$	70.94	27.79	98.73
i_ns/ $C_{90'_II}$	84.45	35.48	119.93
a_ns'/ $C_{90'_I}$	60.96	47.19	108.16
i_ns'/ $C_{90'_I}$	89.80	71.68	161.48
a_ns'/ $C_{90'_II}$	70.78	38.65	109.43
i_ns'/ $C_{90'_II}$	93.98	52.31	146.30
Open-ended pristine			
a_ns/ $C_{90}H_{20_I}$	79.95	46.59	126.54
i_ns/ $C_{90}H_{20_I}$	68.47	45.23	113.70
a_ns/ $C_{90}H_{20_II}$	89.30	47.24	136.54
i_ns/ $C_{90}H_{20_II}$	83.75	36.56	120.31
a_ns'/ $C_{90}H_{20_I}$	64.76	44.39	109.15
i_ns'/ $C_{90}H_{20_I}$	97.10	56.59	153.69
a_ns'/ $C_{90}H_{20_II}$	68.55	39.36	107.90
i_ns'/ $C_{90}H_{20_II}$	95.63	52.59	148.22
Open-ended SW defective			
a_ns/ $C_{90}H_{20'_I}$	53.70	46.41	100.11
i_ns/ $C_{90}H_{20'_I}$	61.51	48.89	110.40
a_ns/ $C_{90}H_{20'_II}$	85.96	59.05	145.01
i_ns/ $C_{90}H_{20'_II}$	83.71	48.79	132.50
a_ns'/ $C_{90}H_{20'_I}$	59.17	47.67	106.85
i_ns'/ $C_{90}H_{20'_I}$	89.25	70.03	159.28
a_ns'/ $C_{90}H_{20'_II}$	65.86	45.68	111.53
i_ns'/ $C_{90}H_{20'_II}$	100.24	70.19	170.43

^a In kcal mol $^{-1}$

^b Related to the total energies of the isolated amino-isomers and imino-isomers of nitrosamine, which are -185.8436556 and -185.8393943 Hartree, respectively

^c Related to the total energies of the isolated molecules of the close-ended pristine, SW defective SWCNT (C_{90} cluster), the open-ended pristine and SW defective SWCNT ($C_{90}H_{20}$ cluster), which are $-3,429.52097643$, $-3,429.38171010$, $-3,441.75552970$ and $-3,441.65572049$ Hartree, respectively

The different relative energies between the amino and imino isomers of nitrosamine—the amino isomer being more stable than the imino isomer by $2.07 \text{ kcal mol}^{-1}$ [19]—are very small compared to the strain energies of their chemisorption on (5,5) SWCNT. Nevertheless, it can be concluded that the chemisorption strength of nitrosamine on (5,5) SWCNT depends on the strain of nitrosamine and the (5,5) SWCNT. The most preferred adsorption configuration on the close-ended pristine and close-ended SW defective is dissociative chemisorption as two fragments in the $\text{HN} = \underline{\text{N/OH}}$ and $\text{H}_2\text{N}-\underline{\text{N}\cdots\text{O}}$ types of configuration, respectively. The most stable chemisorption configuration of the nitrosamine adsorbed on the open-ended pristine and open-ended SW defective is the dissociative yield of the $\underline{\text{OH}}$ fragment.

Strain energies of all the studied SWCNTs, and the deformation energies of nitrosamine isomers that are adsorbed on their C–C bonds, are within the ranges of 27.79 to 71.68 and 53.70 to $100.24 \text{ kcal mol}^{-1}$, respectively, as shown in Table 3. The total strain energies of all adsorption complexes of nitrosamine isomers adsorbed on the (5,5) SWCNTs are within the range of 98.73 to $170.43 \text{ kcal mol}^{-1}$. Nevertheless, all various (5,5) SWCNTs are defective or distorted from ideal models of either the pristine or the SW defective type, and they are able to adsorb nitrosamine isomers with different configurations.

Conclusions

Chemisorption of nitrosamine species on the close-ended (C_{90} cluster) and open-ended ($\text{C}_{90}\text{H}_{20}$ cluster) types of pristine and SW defective armchair (5,5) SWCNTs were studied using the B3LYP/6-31G(d) method. Dissociative and non-dissociative chemisorptions of amino- and imino-isomers of nitrosamine were found. The dissociative chemisorption of nitrosamine on the C–C bond type **I** of the close-ended pristine and type **II** of the open-ended pristine SWCNTs are the most stable configuration, with adsorption energies of -127.15 and $-137.14 \text{ kcal mol}^{-1}$, respectively. The nitrosamine imino-isomer adsorbed on the close-ended pristine SWCNT is found to be the strongest adsorption-complex. Non-dissociative chemisorption of the nitrosamine imino-isomer can occur on either the C–C bond type **I** or type **II** of either the pristine or SW defective SWCNT. The most preferred adsorption configuration on the close-ended pristine and close-ended SW defective is dissociative chemisorption with two fragments in the $\text{HN} = \underline{\text{N/OH}}$ and $\text{H}_2\text{N}-\underline{\text{N}\cdots\text{O}}$ types of configuration, respectively. The most stable adsorption configuration of nitrosamine adsorbed on open-ended pristine and open-ended SW defective SWCNTs is the dissociative yield of the $\underline{\text{OH}}$ fragment.

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References

- IARC (1978) Some N-nitroso compounds. IARC monographs on the evaluation of carcinogenic risk of chemicals to humans, vol 17. International Agency for Research on Cancer, Lyon
- Gadbois DF, Ravasi EM, Lundstrom RC, Maney RS (1975) *J Agric Food Chem* 23:665–668
- Sen NP, Tessier L, Seaman SW, Baddoo PA (1985) *J Agric Food Chem* 33:264–268
- Biaudet H, Mavelle T, Debry G (1994) *Food Chem Toxicol* 32:417–421
- Sen NP, Seaman S (1981) *J Assoc Off Anal Chem* 64:1238–1242
- Sen NP, Seaman S (1981) *J Agric Food Chem* 29:787–789
- Fiddler W, Pensabene JW, Kimoto WI (1981) *J Food Sci* 46:603–605
- Hedler L, Schurr C, Marquardt P (1979) *J Am Oil Chem Soc* 56:681–684
- Dellisanti A, Cerutti G, Airoidi L (1996) *Bull Environ Contam Toxicol* 57:16–21
- Sen NP, Seaman SW, Begeson C, Brousseau R (1996) *J Agric Food Chem* 44:1498–1501
- Yurchenko S, Mölder U (2005) *Food Chem* 89:455–463
- Fazio T, Damico JN, Howard JW, White RH, Watts JO (1971) *J Agric Food Chem* 19:250–253
- Sen NP, Schwinghamer LA, Donaldson BA, Miles WF (1972) *J Agric Food Chem* 20:1280–1281
- Yurchenko S, Mölder U (2006) *Food Chem* 96:325–333
- Baker LA, Su S (1998) *Chem Phys* 228:9–16
- Miura M, Sakamoto S, Yamagushi K, Ohwada T (2000) *Tetrahedron Lett* 41:3637–3641
- Reynolds C, Thomson C (1984) *Int J Quantum Chem Quantum Biol Symp* 11:167–181
- Crawford M-J, Klapötke TM, Liebman JF (2000) *J Fluor Chem* 102:119–124
- Wanno B, Ruangpornvisuti V (2006) *J Mol Struct (Theochem)* 766:159–164
- Wanno B, Ruangpornvisuti V (2006) *J Mol Struct (Theochem)* 775:113–120
- Wang C, Zhou G, Liu H, Wu J, Qiu Y, Gu BL, Duan W (2006) *J Phys Chem B* 110:10266–10271
- Bettinger HF (2005) *J Phys Chem B* 109:6922–6924
- Dinadayalane TC, Leszczynski J (2007) *Chem Phys Lett* 434:86–91
- Akdim B, Kar T, Duan X, Pachter R (2007) *Chem Phys Lett* 445:281–287
- Dinadayalane TC, Kaczmarek A, Łukaszewicz J, Leszczynski J (2007) *J Phys Chem C* 111:7376–7383
- Kaczmarek A, Dinadayalane TC, Łukaszewicz J, Leszczynski J (2007) *Int J Quantum Chem* 107:2211–2219
- Wanno B, Du AJ, Ruangpornvisuti V, Smith SC (2007) *Chem Phys Lett* 436:218–223
- Wanbayor R, Ruangpornvisuti V (2008) *Chem Phys Lett* 441:127–131
- Wanbayor R, Ruangpornvisuti V (2008) *Carbon* 46:12–18
- Pinisakul A, Kritayakornpong C, Ruangpornvisuti V (2008) *J Mol Model* 14:1035–1041

31. Shen B, Ma LL, Zhu JH, Xu Q-H (2000) *Chem Lett* 29:380–381
32. Becke D (1988) *Phys Rev A* 38:3098–3100
33. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
34. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2006) *Gaussian 03*, Revision D.02. Gaussian Inc, Wallingford