

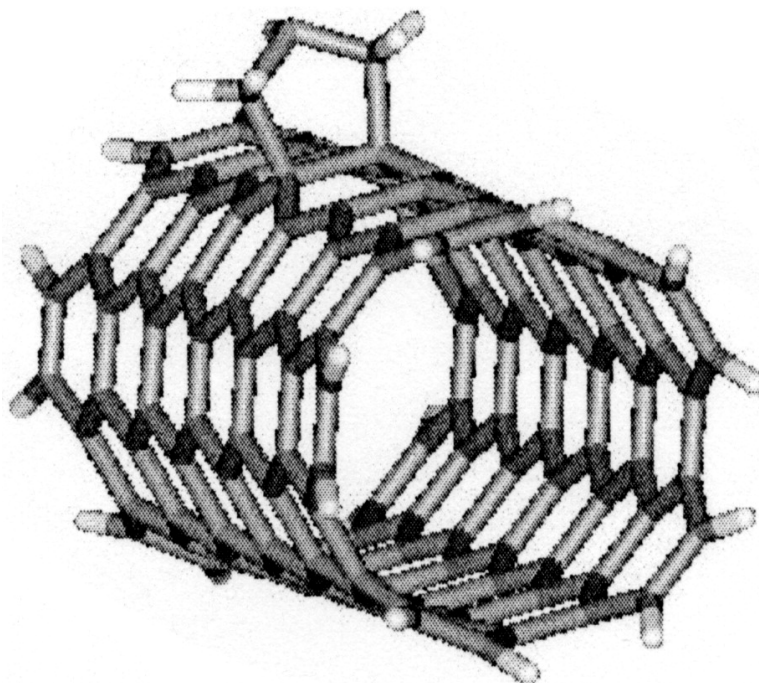
Article

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A Theoretical Exploration of the 1,3-Dipolar Cycloadditions onto the Sidewalls of (*n,n*) Armchair Single-Wall Carbon Nanotubes

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Abstract: The viability of 1,3-dipolar cycloadditions of a series of 1,3-dipolar molecules (azomethine ylide, ozone, nitron, nitrile imine, nitrile ylide, nitrile oxide, diazomethane, and methyl azide) onto the sidewalls of carbon nanotubes has been assessed theoretically by means of a two-layered ONIOM approach. The theoretical calculations predict the following: (i) other than the 18-valence-electron azomethine ylide and ozone, the 16-valence-electron nitrile ylide and nitrile imine are the best candidates for experimentalists to try; (ii) upon 1,3-dipolar cycloaddition, a 1,3-dipole molecule is di- σ -bonded to a pair of carbon atoms on the sidewall of SWNT, forming a five-membered ring surface species; (iii) the as-formed 1,3-dipole-SWNT bonding is much weaker than that in the products of the molecular 1,3-DC reactions and can be plausibly broken by heating at elevated temperatures; (iv) the sidewalls of the armchair (*n,n*) SWNTs ($n = 5-10$) are subject to the 1,3-DCs of ozone and azomethine ylides; (v) both the 1,3-DC reactivity and retro-1,3-DC reactivity are moderately dependent on the diameters of SWNTs, implying the feasibility of making use of the heterogeneous 1,3-DC chemistry to purify and separate SWNTs diameter-specifically.

Introduction

Owing to their fascinating structural, mechanical, electrical, and electromechanical properties, single-wall carbon nanotubes (SWNTs) have invoked intensive interest in the past decade.¹ However, SWNTs exhibit notorious insolubility and quite high chemical stability, which impede the separation and manipulation of SWNTs for various specific applications. Chemical modification of SWNTs that may provide a way to circumvent such a hindrance and may introduce some new physical and chemical properties for more specific applications² thus becomes highly desirable and has been the subject of recent research effort in this field.³ Yet, successful approaches so far reported for the chemical modification of SWNTs are indeed countable and can be divided into two categories, i.e., modification of the open ends of SWNTs and sidewall functionalization.³ Our interest lies in the theoretical prediction of sidewall functionalization of SWNTs.⁴⁻⁶

Despite the high chemical stability of the graphene-like sidewalls of SWNTs, some successful and significant examples in the sidewall functionalization of SWNTs have been reported recently, e.g., fluorination at elevated temperature,⁷ covalent attachment of nitrenes,⁸ electrochemical reduction of aryl diazonium salts,⁹ noncovalent attachments of a bifunctional molecule (1-pyrenebutanoic acid, succinimidyl ester)¹⁰ and tetraazaannulene macrocyclic complexes,¹¹ and solvent-free arylation.¹² Very recently, we predicted by means of quantum chemical calculations that ozone, a 1,3-dipolar molecule, can be readily attached onto the sidewall of an armchair (5,5) SWNT⁴ following the 1,3-dipolar cycloaddition (1,3-DC) mechanism.¹³ In the meantime, Prato et al. reported their experiments regarding the 1,3-DC of azomethine ylides onto the sidewalls of SWNTs.¹⁴ This latter finding is rather encouraging not only

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because it led to functionalized carbon nanotubes with unprecedentedly high solubility but also because it can be used to purify SWNTs.¹⁵ However, both O₃ and azomethine ylides were known to be the most reactive 1,3-dipoles in ordinary organic chemistry. Whether this synthetic method can be extended to other 1,3-dipoles (e.g., nitrile ylide and nitrile imine) remains uncertain. Furthermore, it is generally accepted that the chemical reactivity of the sidewalls of SWNTs, in principle, depends on the sidewall curvature or/and the diameter of SWNTs.¹⁶ Yet, in what manner the chemical reactivity of the sidewalls of SWNTs toward a given 1,3-dipolar molecule would depend on the diameters of SWNTs remains unknown. Answers to the above questions would help us have a better understanding of the heterogeneous 1,3-DC chemistry of SWNTs and, more significantly, make use of this intriguing chemistry in the chemical modification, purification, and separation of SWNTs for various practical uses.

In the present work, we will explore, by means of quantum chemical calculations, the 1,3-DC chemistry of the sidewalls of a series of (*n,n*) armchair SWNTs to see which 1,3-dipolar molecules, besides the known reactive azomethine ylide and ozone, can be plausibly added on the nanotube sidewalls and in what manner the chemical reactivity of the nanotube sidewalls toward a given 1,3-dipole would depend on the diameters of SWNTs. Dependence of the 1,3-DC reactivity of nanotube sidewalls on the chirality of SWNTs will be the subject of further theoretical effort.

Computational Details

A two-layered ONIOM approach was used.¹⁷ The semiempirical AM1 method¹⁸ and the hybrid density functional B3LYP method¹⁹ together with the standard 6-31G* basis set were employed for the low-level and high-level treatments, respectively. Geometry optimizations were performed within this two-layered ONIOM(B3LYP/6-31G*:AM1) approach using the Gaussian98 program.²⁰ As depicted in Figure 1, the armchair (5,5) SWNT was taken as an example and was represented by a C₁₃₀H₂₀ model tube (optimal diameter ~6.8 Å), in which the high-level part is a C₁₆ cluster (see the shaded atoms in Figure 1) together with 10 H atoms as boundary atoms. Such a modeling scheme was employed in our previous study of the 1,3-DC of O₃ and Diels–Alder addition of quinodimethane onto the sidewall of (5,5) SWNT.^{4,5} Similar ONIOM modeling was used in our theoretical investigation of the base-catalyzed [2+3] cycloaddition of transition

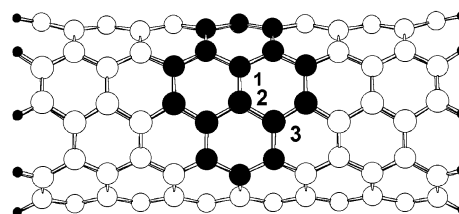


Figure 1. C₁₃₀H₂₀ model tube representing an armchair (5,5) SWNT, in which the 16 shaded atoms are used for the high-level treatment in the two-layered ONIOM(B3LYP/6-31G*:AM1) calculations.

metal oxide (OsO₄) on (5,5) SWNT⁶ and by other groups in the theoretical studies of carbon nanotube chemistry.²¹ Our previous study showed that on this nanotube the 1,2 pair site is far more dipolarophilic than the 2,3 pair site⁴ (see Figure 1). As such, we considered only the 1,2 pair site in the present study.

Apart from the (5,5) SWNT, we have considered the 1,3-DC chemistry of a series of (*n,n*) armchair SWNTs with *n* ranging from 6 to 10, for which the model tubes employed follow the formula C_{26*n*}H_{4*n*} correspondingly. The high-level parts in the ONIOM(B3LYP/6-31G*:AM1) calculations of these SWNTs are the same as that for the (5,5) SWNT, i.e., a C₁₆ cluster with 10 hydrogen atoms as boundary atoms.

Results and Discussion

A. 1,3-DCs of a Series of 1,3-Dipoles on (5,5) SWNT. We first consider the 1,3-DC of a series of 1,3-dipoles onto the sidewall of (5,5) SWNT. As listed in Table 1, a total of eight 1,3-dipoles molecules have been considered in the present study, including five 16-valence-electron (16VE) 1,3-dipoles, i.e., nitrile ylide (HCNCH₂), nitrile imine (HCNNH), nitrile oxide (HCNO), diazomethane (H₂CN₂), and methyl azide (CH₃N₃), and three 18-valence-electron (18VE) 1,3-dipoles, i.e., ozone (O₃), azomethine ylide (H₂CN(H)CH₂), and nitron (H₂CN(H)O). The predicted reaction heats and barrier heights for the 1,3-DCs of these 1,3-dipoles on the nanotube sidewall are given in Table 1.

First, our ONIOM calculations predict that the 1,3-DC of azomethine ylide on the nanotube sidewall is exothermic by 39.3 kcal/mol with a barrier height of only 3.4 kcal/mol. This demonstrates that the 1,3-DC of azomethine ylide onto the tube wall is facile, in accordance with the experimental finding by Prato et al.¹⁴ Such an agreement justifies the theoretical approach used. For the 1,3-DC of O₃, the present ONIOM calculations predict a reaction heat of −31.3 kcal/mol and a barrier height of 2.8 kcal/mol, showing the ozonization of (5,5) SWNT is feasible. It is worthy of noting that our theoretical prediction of the facile sidewall ozonization of SWNTs⁴ promoted the recently reported experiments on the rational sidewall functionalization and purification of single-wall carbon nanotubes by solution-phase ozonolysis.²²

The 1,3-DC of another 18VE 1,3-dipole, nitron, is found to be less feasible than that of azomethine ylide and O₃. The predicted barrier height and reaction heat of this reaction are 15.5 and −5.0 kcal/mol, respectively. This means the addition of nitron onto the sidewall of a (5,5) tube is plausible, but

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Table 1. Calculated Reaction Energies (E_r , in kcal/mol) and Barrier Heights (E_a , in kcal/mol) for the Cycloadditions of a Series of 1,3-Dipoles to the 1,2 Pair Site on the Sidewall of a (5,5) SWNT and to Ethylene (C_2H_4), and the Barrier Heights (E_a^{retro} , in kcal/mol) of the Retro-1,3-DC Reactions

		16VE 1,3-dipoles					18VE 1,3-dipoles		
		HCNCH ₂	HCNNH	HCNO	H ₂ CN ₂	CH ₃ N ₃	H ₂ CN(H)CH ₂	H ₂ CN(H)O	O ₃
(5,5) SWNT ^a	E_r	-38.5	-28.6	-13.2	-3.2	6.1	-39.3	-5.0	-31.3
	E_a	13.7	15.3	20.6	22.1	29.2	3.4	15.5	2.8
	E_a^{retro}	52.2	43.9	33.8	25.3	23.1	42.7	20.5	34.1
C_2H_4 ^b	E_r	-63.2	-55.2	-38.7	-30.0	-22.9	-56.0	-23.2	-56.6
	E_a	8.7	8.0	13.0	16.1	17.7	5.9	16.6	-1.8
	E_a^{retro}	71.9	63.2	51.7	46.1	40.6	61.9	39.8	56.6

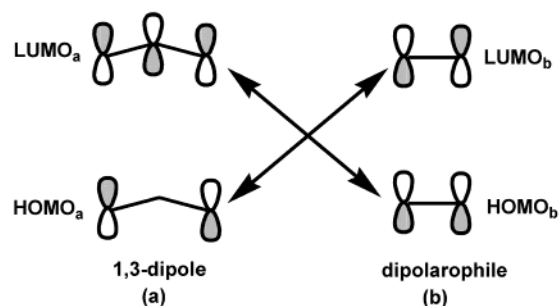
^a Data obtained by two-layered ONIOM(B3LYP/6-31G*:AM1) calculations. ^b Data obtained at the B3LYP/6-31+G* level of theory (see ref 23a).

may become implausible on SWNTs with larger diameters, as it is generally accepted that the reactivity of the sidewalls of carbon nanotubes depends on the tube wall curvature and the larger nanotubes would be less reactive.¹⁶ The retro-1,3-DC reaction for nitrene has an activation barrier of 20.5 kcal/mol, smaller than that of azomethine ylide (42.7 kcal/mol) and ozone (34.1 kcal/mol), meaning that the detachment of nitrene from the as-functionalized (5,5) tube is easier than that of azomethine ylide and ozone.

For the 1,3-DCs of those 16VE 1,3-dipoles onto the sidewall of the (5,5) tube, the predicted activation energies follow the order nitrile ylide < nitrile imine < nitrile oxide < diazomethane < methyl azide, which coincides with the trend predicted for their molecular analogues.²³ Specifically, with moderate activation energies and considerable exothermicities, the 1,3-DCs of the most reactive 16VE ones, nitrile ylide and nitrile imine, on the sidewall of (5,5) SWNT would be viable too. Except for the experimentally known reactive azomethine ylide and ozone, these two 1,3-dipoles are the best candidates for experimentalist to try. The 1,3-DC of nitrile oxide, though less feasible than that of nitrile ylide and nitrile imine, is also plausible on the sidewall of a (5,5) tube, with a predicted reaction heat of -13.2 kcal/mol and a barrier height of 20.6 kcal/mol. The 1,3-DCs of diazomethane and methyl azide require large activation energies (>22 kcal/mol) and are nearly thermoneutral or even endothermic. Hence, the 1,3-DCs of diazomethane and methyl azide would not be viable. It should be mentioned that organic azides can be thermally decomposed to give rise to quite reactive nitrenes, which may undergo [1+2] cycloaddition onto the sidewalls of SWNTs.⁸

The predicted ordering of 1,3-DC reactivity for the 18VE and 16VE 1,3-dipoles can be understood in terms of the orbital symmetry and frontier molecular orbital (FMO) theory^{24,25} or in terms of the configuration mixing model.^{23b,26} The relevant π FMOs of a 1,3-dipolar molecule and a dipolarophile (e.g., ethylene) involved in a 1,3-DC reaction are presented in Scheme 1. It is clear from Scheme 1 that the relative 1,3-DC reactivity depends on the magnitudes of the two energy gaps, i.e., $|LUMO_a - HOMO_b|$ and $|LUMO_b - HOMO_a|$. The smaller these energy

Scheme 1



gaps, the easier the 1,3-DC reaction. Furthermore, it has been recently revealed that for the 1,3-DC reactions of various 16VE 1,3-dipolar molecules with ethylene a 1,3-dipole having a smaller triplet-singlet gap or a smaller HOMO-LUMO gap is more reactive.^{23b} A similar trend should be followed in the 1,3-DCs of 18VE 1,3-dipoles, accounting for their higher reactivity than the 16VE 1,3-dipoles in the heterogeneous 1,3-DC reactions. Note that at the B3LYP/6-31G* level, the HOMO-LUMO gaps predicted for the three 18VE 1,3-dipoles, i.e., ozone, azomethine ylide, and nitrene, are 0.1506, 0.1645, and 0.2038 au, respectively, smaller than or comparable to the LUMO-HOMO gap (0.2004 au) predicted for the most reactive 16VE 1,3-dipole, nitrile ylide.

The optimized geometries of the 1,3-DC products and transition states are presented in Figures 2 and 3, respectively. From Figure 2, it can be seen that upon the 1,3-DC reactions, the 1,3-dipoles are di- σ -bonded onto the nanotube sidewall, forming five-membered ring surface species. The reacted sidewall carbon atoms thus adopt sp^3 hybridization, and the corresponding sidewall C-C bond is largely elongated with a bond length around 1.64 Å, which is even longer than the typical C-C single bond in simple alkanes (~1.56 Å). From Figure 3, it is clear that similar to their molecular analogues,²³ all these 1,3-DCs on the nanotube sidewall proceed concertedly, as indicated by the geometries of the transition states.

We then compare the above-mentioned heterogeneous 1,3-DCs with their molecular analogues, i.e., the molecular 1,3-DCs of the eight 1,3-dipoles with ethylene. The reaction heats and barrier heights for the molecular 1,3-DCs that were predicted previously at the B3LYP/6-31+G* level of theory^{23a} are also given in Table 1. It can be seen that the heterogeneous 1,3-DCs on the nanotube sidewall are far less exothermic than their molecular analogues. For the 16VE 1,3-dipoles, the exothermicity of the heterogeneous ones is by about 27 kcal/mol lower than that of the molecular ones. For the 18VE 1,3-dipoles, the difference is smaller, around 20 kcal/mol. A similar trend was

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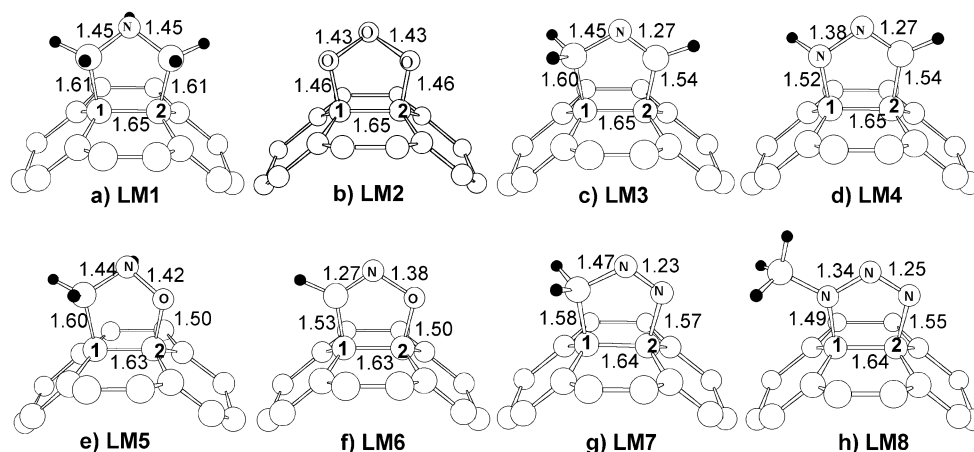


Figure 2. Optimized geometries (local views) of the 1,3-DC products: (a) **LM1** for azomethine ylide, (b) **LM2** for ozone, (c) **LM3** for nitrile ylide, (d) **LM4** for nitrile imine, (e) **LM5** for nitron, (f) **LM6** for nitrile oxide, (g) **LM7** for diazomethane, and (h) **LM8** for methyl azide, on the sidewall of (5,5) SWNT.

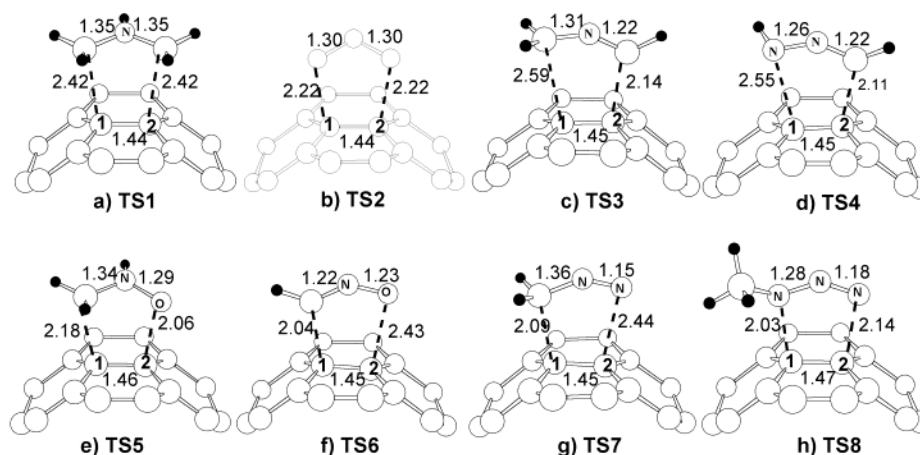


Figure 3. Optimized geometries (local views) of the 1,3-DC transition states: (a) **TS1** for azomethine ylide, (b) **TS2** for ozone, (c) **TS3** for nitrile ylide, (d) **TS4** for nitrile imine, (e) **TS5** for nitron, (f) **TS6** for nitrile oxide, (g) **TS7** for diazomethane, and (h) **TS8** for methyl azide, on the sidewall of (5,5) SWNT.

found in our previous theoretical studies concerning the Diels–Alder cycloadditions of quinodimethane⁵ and the base-catalyzed [3+2] cycloadditions of OsO₄⁶ to the sidewall of (5,5) SWNT and to ethylene, for which the molecular reactions with ethylene were predicted to be much more exothermic than the heterogeneous analogues on the nanotube sidewall.^{5,6} The much lower exothermicity of the heterogeneous reactions on the nanotube sidewall can be ascribed to the rather high π -conjugation within the nanotube sidewall. The much weaker 1,3-dipole–SWNT bonding suggests that it would be plausible to break the as-formed 1,3-dipole–SWNT bonding at elevated temperatures. In other words, it is plausible to make use of the 1,3-DC chemistry to purify SWNTs.^{15,22}

To break the as-formed 1,3-dipole–SWNT bonding, a retro-1,3-DC reaction should be invoked. A measure of the plausibility of a retro-1,3-DC reaction is its activation energy, which is related to the strength of the 1,3-dipole–SWNT bonding. As such, using different 1,3-dipoles would give rise to functionalized SWNTs with different bonding strengths between 1,3-dipoles and SWNTs. Indeed, for the eight 1,3-dipoles concerned, their retro-1,3-DC reactions have rather different activation energies (see Table 1), offering more choices and higher flexibility in making use of the 1,3-DC chemistry for the purification of SWNTs.

As the (5,5) SWNT is modeled by a C₁₃₀H₂₀ model tube, in which 20 hydrogen atoms are used to saturate the unfilled valencies at the ends of the open nanotube, one should further consider how such saturation (or substitution)²⁷ would affect the reactivity of the tubewall in the 1,3-DC reactions concerned. Theoretically, it has been shown that, for molecular 1,3-DC reactions of nitrile ylide (a 16VE 1,3-dipole) with disubstituted ethylenes, ethylenes bearing more strongly electron-withdrawing substituents can facilitate 1,3-DC reactions.^{23c} This means that the more electron-deficient a dipolarophile is, the more dipolarophilic it is. On the other hand, it has recently been revealed that the electrostatic potentials are weakly positive on the outer surface of a closed, all-carbon (5,5) carbon nanotube, whereas the electrostatic potentials are slightly negative on the outer lateral surfaces of open carbon tubes with charge-donating hydrogens at the ends.²⁷ As such, the outer surface of a closed, all-carbon (5,5) tube would be more electron-deficient and, hence, more dipolarophilic than that of the hydrogen-saturated open-end model tube concerned herein. In practice, “acid-purified” SWNTs always possess electron-withdrawing carboxylic groups located at their open ends and at wall defects.^{2,16c}

(27) Peralta-Inga, Z.; Lane, P.; Murray, J. S.; Boyd, S.; Grice, M. E.; O'Connor, C. J.; Politzer, P. *Nano Lett.* **2003**, *3*, 21.

Table 2. Relative Energies (ΔE) and Critical Geometric Parameters of 1,3-DC Products (Pro) and Transitions States (TS) of O_3 on the Sidewalls of (n,n) SWNTs Predicted by Two-Layered ONIOM(B3LYP/6-31G*:AM1) Calculations

SWNT	diameter (Å)		critical bond lengths and angles ^a				ΔE (kcal/mol)
			C–C	C–O	O–O	O–O–O	
(5,5)	6.8	Pro	1.654	1.464	1.434	101.0	−31.3
		TS	1.442	2.216	1.301	111.8	2.8
(6,6)	8.4	Pro	1.642	1.468	1.433	101.0	−26.5
		TS	1.446	2.187	1.305	111.4	4.3
(7,7)	9.8	Pro	1.635	1.472	1.432	100.9	−23.3
		TS	1.449	2.169	1.307	111.1	5.6
(8,8)	11.2	Pro	1.628	1.474	1.432	100.9	−21.2
		TS	1.450	2.158	1.308	111.0	6.2
(9,9)	12.5	Pro	1.624	1.476	1.431	100.8	−19.5
		TS	1.449	2.148	1.308	110.6	6.9
(10,10)	13.9	Pro	1.621	1.477	1.431	100.8	−18.2
		TS	1.451	2.143	1.311	110.8	7.5

^a Units in Å for bond lengths and deg for bond angles.

Thus, these oxidized SWNTs would be more dipolarophilic than the defect-free, all-carbon SWNTs.

B. 1,3-DC of O_3 on (n,n) SWNT ($n = 5–10$): Dependence of 1,3-DC Reactivity on the Diameters of (n,n) SWNTs. To explore the dependence of the 1,3-DC reactivity of the nanotube sidewalls on the diameters of SWNTs, we choose the most simple 1,3-dipolar molecule, O_3 , and consider its 1,3-DC reactions on a series of armchair (n,n) SWNTs ($n = 5–10$). The relative energies and some critical geometric parameters of the 1,3-DC products and transition states predicted by ONIOM(B3LYP/6-31G*:AM1) calculations are given in Table 2.

The predicted exothermicity of the heterogeneous 1,3-DC of O_3 ranges from -31.3 kcal/mol on the (5,5) tube (the smallest tube concerned) to -18.2 kcal/mol on the (10,10) tube (the largest tube concerned), while the activation barriers range from 2.8 kcal/mol on the (5,5) tube to 7.5 kcal/mol on the (10,10) tube (see Table 2). First, these data suggest that sidewall ozonization is viable on all considered armchair (n,n) SWNTs ($n = 5–10$). Note that azomethine ylide has been shown to be more reactive than ozone in the (5,5) tube case. It is reasonable for us to infer that the 1,3-DC of azomethine ylide on the sidewalls of this series of nanotubes is viable, too. Second, these data give a trend that follows the generally accepted rule concerning the sidewall reactivity of SWNTs; that is, the larger the diameter the SWNT has, the lower reactivity (i.e., lower exothermicity and higher reaction barrier) the nanotube sidewall displays, as schematically shown in Figures 4 and 5. It is clear from Figures 4 and 5 that the 1,3-DC reactivity of the tubewalls is moderately dependent on the diameters of SWNTs. That is, the difference in the 1,3-DC exothermicity of two neighboring SWNTs ranges from 1.3 to 4.8 kcal/mol, and the difference in the 1,3-DC barrier height of two neighboring SWNTs ranges from 0.6 to 1.5 kcal/mol. Third, the trend that the heterogeneous 1,3-DC of O_3 with lower barrier height has higher exothermicity is in agreement with the Hammond postulate.²⁸

The 1,3-DC transition states display the following structural feature: the lengths of the two forming C–O bonds are identical on a given SWNT, but decrease with the increase of the diameter of SWNTs, indicating that the heterogeneous 1,3-DC has an earlier transition state on the sidewall of a smaller SWNT. This

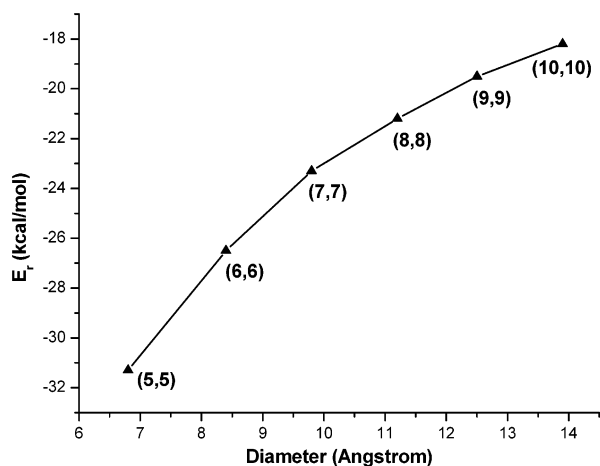


Figure 4. Exothermicity (E_r) of the 1,3-DC reaction of ozone vs diameters of (n,n) SWNTs.

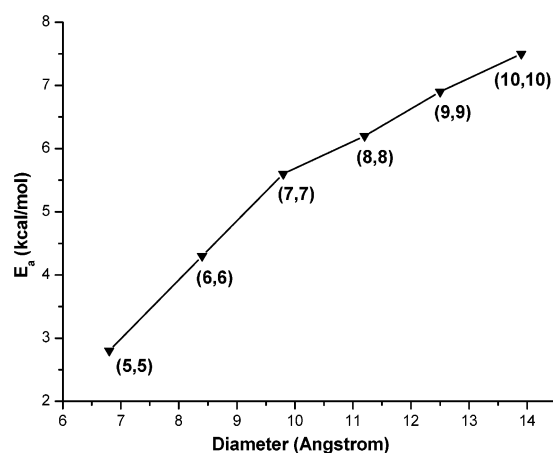


Figure 5. Reaction barrier (E_a) of the 1,3-DC reaction of ozone vs diameters of (n,n) SWNTs.

also agrees well with the Hammond postulate;²⁸ that is, the reaction with lower barrier height and higher exothermicity has an earlier transition state.

In principle, curvature-dependence (or diameter-dependence) of sidewall reactivity of SWNTs can be ascribed to the curvature-induced pyramidalization and misalignment of π -orbitals of the tubewall carbon atoms.^{16c,d} For the 1,2 pair sites in the sidewalls of (n,n) armchair SWNTs, the local strain of the π -orbitals is solely induced by pyramidalization.^{16c,d} The pyramidalization angle of a carbon atom in the sidewall of a SWNT is defined by the angle between the π -orbital and adjacent σ -bonds. The pyramidalization angles of tubewall C atoms in (n,n) SWNTs ($n = 5–10$) determined in previous π -orbital axis vector (POAV) analyses are 5.97°, 4.99°, 4.27°, 3.74°, 3.33°, and 3.00°, respectively,^{16c} decreasing with the increasing of tube diameters. Thus the diameter-dependent 1,3-DC reactivity of the (n,n) SWNTs ($n = 5–10$) shown in Figures 4 and 5 is a result of the pyramidalization of π -orbitals, corroborating the previous finding that “the reactivity of (n,n) SWNTs towards sidewall addition depends on the diameter of tubes and more precisely on the pyramidalization angle of the tube C atom where the addition takes place.”^{16d}

As the retro-1,3-DC reaction is related to the purification of SWNTs,¹⁵ it should be interesting to see how the retro-1,3-DC reactivity of as-functionalized SWNTs depends on the tube

(28) Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *77*, 334.

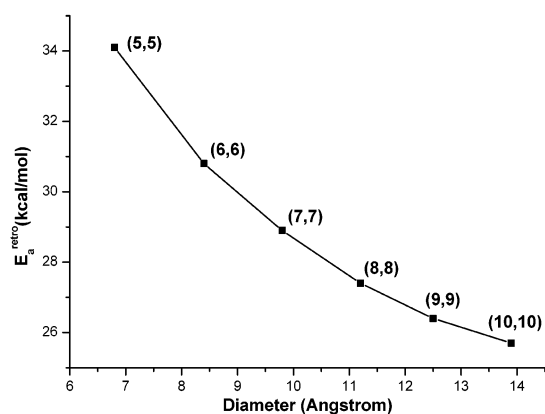


Figure 6. Reaction barrier (E_a^{retro}) of the retro-1,3-DC reaction of ozone vs diameters of (n,n) SWNTs.

diameters. If the activation barrier of the retro-1,3-DC reaction is highly dependent on the diameters of SWNTs, it would be plausible to make use of the 1,3-DC chemistry to separate SWNTs diameter-specifically by step-by-step heating the as-functionalized SWNTs at different temperatures. As shown in Figure 6, the activation barrier of the retro-1,3-DC reaction is also moderately dependent on the tube diameters, ranging from 34.1 kcal/mol for a functionalized (5,5) tube to 25.7 kcal/mol for a functionalized (10,10) tube and giving a trend that the larger diameter the tube has, the easier the retro-1,3-DC reaction is. The moderate dependence of both the 1,3-DC and retro-1,3-DC reactions on the diameters of SWNTs implies that it is possible to make use of the 1,3-DC chemistry to separate SWNTs diameter-specifically.

Conclusion

The present work examined systemically the viability of 1,3-DCs of a series of 1,3-dipoles onto the sidewall of an armchair (5,5) SWNT and predicted that, other than azomethine ylides and ozone, nitrile ylide and nitrile imine are the best candidates for experimentalists to try. The as-formed 1,3-dipole-SWNT bonding is much weaker than that in the products of the molecular 1,3-DC reactions and can be plausibly broken by heating at elevated temperatures. The dependence of both the

1,3-DC reactivity and retro-1,3-DC reactivity on the diameters of SWNTs has been investigated by considering the simplest 1,3-dipole, ozone, on a series of armchair (n,n) SWNTs ($n = 5-10$). The results showed that the sidewalls of these SWNTs are subject to the 1,3-DCs of ozone and azomethine ylides. Both the 1,3-DC reactivity and retro-1,3-DC reactivity are moderately dependent on the diameters of SWNTs. This implies the possibility to make use of the 1,3-DC chemistry to purify and to separate SWNTs diameter-specifically.

Further theoretical effort is being made to explore the 1,3-DC chemistry of other SWNTs, e.g., zigzag $(n,0)$ SWNTs and other chiral (n,m) SWNTs, which have different chirality than those considered here. Preliminary ONIOM(B3LYP/6-31G*:AM1) calculations²⁹ predicted that the exothermicity of the 1,3-DC of ozone onto the sidewall of a zigzag (9,0) SWNT is -31.7 kcal/mol, comparable to that of the 1,3-DC on the sidewall of an armchair (5,5) SWNT. Note that both tubes have similar diameters, ~ 6.8 Å for (5,5) SWNT and ~ 7.0 Å for (9,0) SWNT. This preliminary result suggests that the 1,3-DC reactivity of tubewalls is weakly dependent on the chirality of SWNTs that have similar diameters.

Finally, we believe that with the increasing powerfulness of computer and theoretical methods, theoretical simulations, e.g., those presented herein and previously,^{4-6,21} are becoming a more resource-saving and easily accessible route in the exploration of SWNT chemistry by providing much instructive information that helps waive a lot of exhausting trial-after-trial experiments in further experimental work.

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(29) In the two-layered ONIOM(B3LYP/6-31G*:AM1) calculations, the zigzag (9,0) SWNT was represented by a closed-end model tube consisting of 150 carbon atoms with D_{3d} symmetry, in which the high-level part is a C_{24} cluster with 12 H atoms as boundary atoms.^{21a}