

Organic Functionalization of the Sidewalls of Carbon Nanotubes by Diels–Alder Reactions: A Theoretical Prediction

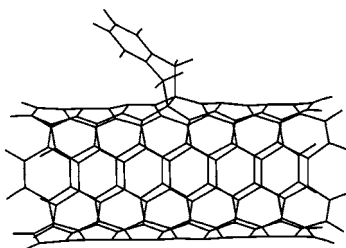
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ABSTRACT



The viability of the Diels–Alder (DA) cycloaddition of conjugated dienes onto the sidewalls of single-wall carbon nanotubes is assessed by means of a two-layered ONIOM(B3LYP/6-31G*:AM1) approach. Whereas the DA reaction of 1,3-butadiene on the sidewall of an armchair (5,5) nanotube is found to be unfavorable, the cycloaddition of quinodimethane is predicted to be viable due to the aromaticity stabilization at the corresponding transition states and products.

Single-wall carbon nanotubes (SWNTs) exhibit fascinating and unique structural, mechanical, electrical, and electro-mechanical properties and have attracted much attention in the past decade.^{1–4} Bearing a structural resemblance to graphene, they also display quite high chemical stability and insolubility, which limit their flexibility for practical applications. Accordingly, much effort has been made recently on the chemical modification of SWNTs, especially on the sidewall functionalization, as this might introduce new physical and chemical properties for specific applications.^{5–12}

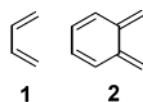
For the sidewall functionalization, some successful examples were obtained by fluorination at elevated temperature,⁷ noncovalent attachment of a bifunctional molecule (1-pyrenebutanoic acid, succinimidyl ester),⁸ electrochemical reduction of aryl diazonium salts,⁹ covalent attachment of nitrenes,¹⁰ and so on. More fascinating are the very recent experimental and theoretical findings that 1,3-dipoles such as azomethine ylides¹¹ and ozone¹² can be covalently attached onto the sidewalls of carbon nanotubes by following the

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well-known 1,3-dipolar cycloaddition (1,3-DC) mechanism.¹³ The significance of these findings lies in that they demonstrated the plausibility of functionalizing the sidewalls by means of synthetic organic chemistry. Stimulated by these findings, we have considered the viability of functionalizing the sidewalls of SWNTs by using another pericyclic reaction, Diels–Alder (DA) reaction, that is well-known to occur between a conjugated diene and a dienophile (e.g., ethylene).

It is known that in organic chemistry a dipolarophile is also dieneophilic.¹³ Accordingly, the dipolarophilic nanotube sidewalls should be dieneophilic and subject to DA reactions with conjugated dienes. Indeed, both the DA and 1,3-DC reactions have been very successfully employed in the functionalization of the highly conjugated fullerenes.¹⁴ In this communication, a theoretical assessment is made of the viability of DA reactions of conjugated dienes (1,3-butadiene **1** and quinodimethane **2**) onto the sidewalls of carbon nanotubes.



We took the armchair (5,5) SWNT (optimal diameter ≈ 6.8 Å) as an example and used a two-layered ONIOM approach¹⁵ to investigate the mechanism of the DA reactions onto the nanotube sidewall. The semiempirical AM1 method¹⁶ and the hybrid density functional B3LYP method¹⁷ were employed for the low-level and high-level treatments, respectively. The standard 6-31G* basis set was used in conjunction with the B3LYP calculations. Geometry optimizations were performed within such a ONIOM(B3LYP/6-31G*:AM1) approach using the Gaussian98 program.¹⁸ Figure 1 depicts a C₁₃₀H₂₀ tube modeling an armchair (5,5) SWNT (optimal diameter ≈ 6.8 Å), in which the high-level part is a C₁₆ cluster (see the shaded atoms in Figure 1) in together with 10 H atoms as boundary atoms. Such a modeling scheme was employed successfully in our previous

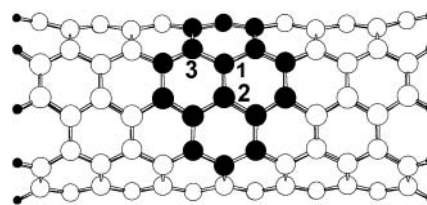


Figure 1. A fragment of (5,5) SWNT, in which the 16 shaded atoms are used for the high-level treatment in the two-layered ONIOM(B3LYP:AM1) calculations.

study of the 1,3-DCs on the (5,5) SWNT.¹² As shown in Figure 1, there are two types of inequivalent C–C pair sites, i.e., the 1,2 pair site and the 1,3 pair site, on the (5,5) SWNT. Our previous study showed that the 1,2 pair site works better as a dipolarophile than does the 1,3 pair site.¹² On account of the mechanistic resemblance in both the 1,3-DC and DA reactions, we believe the 1,2 pair site would be more dieneophilic than the 1,3 pair site and, hence, considered only the DA reactions on the 1,2 pair site.

For the DA reaction of the prototype diene, 1,3-butadiene (**1**), onto the 1,2 pair site, our ONIOM calculations predicted an exothermicity of only -1.6 kcal/mol and an activation energy of 32.4 kcal/mol, showing that this reaction is nearly thermoneutral and kinetically very unfavorable. As such, more reactive dienes are essential for a viable DA reaction onto the sidewall of the nanotube.

It is known that quinodimethanes are more reactive than 1,3-butadiene in molecular DA reactions with simple dieneophile (e.g., ethylene) due to the strong aromatic stabilization at the transition states and products.¹⁹ The reaction heats and barrier heights^{19c,d} of the DA reactions of 1,3-butadiene (**1**) and quinodimethane (**2**) with ethylene predicted at the B3LYP/6-31G* level of theory are listed in Table 1,

Table 1. Calculated Activation Energies (ΔE_a , in kcal/mol) and Reaction Energies (ΔE_r , in kcal/mol) for the DA Reactions of Dienes **1** and **2** with the Sidewall of a (5,5) SWNT and Ethylene

		1	2
SWNT(5,5) ^a	ΔE_a	32.4	17.9
	ΔE_r	-1.6	-30.1
C ₂ H ₄ ^b	ΔE_a	22.4	8.5
	ΔE_r	-43.1	-70.9

^a ONIOM(B3LYP/6-31G*:AM1) calculations. ^b Data extracted from refs 19c,d were obtained at the B3LYP/6-31G* level of theory.

which clearly shows the much higher DA reactivity of quinodimethane **2** toward ethylene. One infers that similar

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aromatic stabilization would work in the DA cycloaddition of quinodimethane onto the sidewalls of carbon nanotubes and would lead to lower activation energies for the DA reaction of **2** than that of **1**. Indeed, our ONIOM(B3LYP/6-31G*:AM1) calculations predicted that the DA cycloaddition of **2** onto the sidewall of (5,5) SWNT is exothermic by 30.1 kcal/mol with an activation energy of 17.9 kcal/mol. This clearly demonstrates the viability of the DA reaction of **2** onto the nanotube sidewall.

Figure 2 depicts the optimized geometries of the products and transition states for the DA reactions of dienes **1** and **2** onto the sidewall of the (5,5) SWNT. Noteworthy, the structures of the transition states indicate that the DA reactions of these dienes onto the nanotube sidewall proceed in a concerted pathway.

In summary, we predicted that the DA cycloaddition of quinomethane is viable onto the sidewall of a (5,5) SWNT. It is the aromatic stabilization at the DA transition state and product that facilitates the DA cycloaddition of quinodimethane onto the sidewall of SWNT. However, the reaction that requires moderate activation energy to occur on the (5,5) SWNT may become unfavorable on nanotubes with larger diameters, as it is generally accepted that the reactivity of the sidewalls of carbon nanotubes depends largely on the tube wall curvature, and the nanotubes with larger diameters would be less reactive.²⁰ Nevertheless, the present work demonstrated the plausibility of functionalizing the sidewalls of carbon nanotubes by means of synthetic organic chemistry. More detailed work is under way to show the manner in

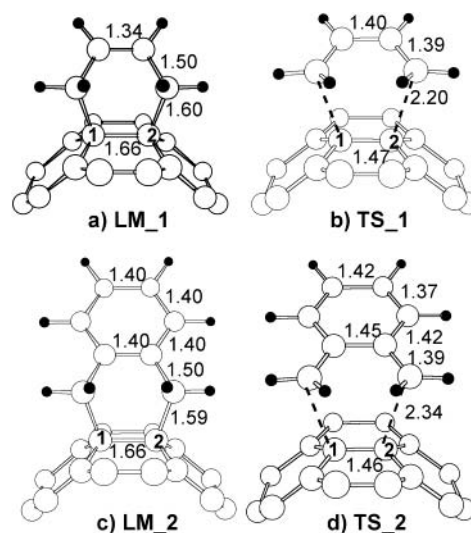


Figure 2. Optimized geometries (local views) of the DA products and transition states for dienes **1** (LM1 and TS1) and **2** (LM2 and TS2) on the sidewall of (5,5) SWNT.

which the DA reactivity of tube sidewalls would depend on the chiralities and diameters of SWNTs.

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