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The Role of Curvature on Diels-Alder Functionalization of Carbon-Based Materials †

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We have estimated theoretically the impact of curvature on the free energies of activation and reaction associated to Diels-Alder reactions on carbon-based materials. Significant reductions are calculated for both energy values with increasing curvature for core-functionalization, while the opposite trend prevails for edge-functionalization, as further supported by SEM/fluorescence measurements.

Chemical functionalization of carbon-based materials such as fullerenes, carbon nanotubes, or graphene is a promising approach to tune their properties for desired applications in the field of electronics, composites, or biology.¹⁻⁵ In particular, the Diels-Alder chemistry has been largely exploited to covalently functionalize carbon-based materials owing to its reversibility and efficiency, without the need for catalysts and the formation of byproducts. Experimental studies have demonstrated that carbon-based materials can be involved into thermo-reversible [4+2] Diels-Alder reactions due to the presence of conjugated C-C double bonds on their surface acting as diene or dienophile.^{6, 7} So far, successful Diels-Alder functionalization of fullerenes,^{8, 9} graphene,¹⁰ single and multi-walled carbon nanotubes^{6, 7} have been reported. Intuitively, the curvature of the carbon surface is expected to favor the Diels-Alder reaction by introducing a sp³ character into the carbon atoms,¹¹ i.e., a rehybridization increasing the reactivity of the curved carbon-based material, as already reported for ozonation and hydrogenation reactions on the side-wall of a nanotube.¹²⁻¹⁵ However, the *quantitative* impact of this curvature on the free energy of activation ($\Delta G^\ddagger$) and free energy of reaction (ΔG°) of Diels-Alder reactions involving inner (core) versus edge (peripheral) C-C

bonds has been scarcely explored. A few *qualitative* examples have been described by Zydziak et al.,¹⁶ though no systematic study deals with the quantification of this phenomenon, especially in the case of [4+2] Diels-Alder cycloaddition on curved carbon-based nanostructures. This has motivated the present theoretical study performed on relevant model structures by means of the widely used Density Functional Theory (DFT). All calculations rely on the M062X functional, to properly account for the dispersion effects when the two reactants are brought together, and a 6-31G(d) basis set.

In this study, we have considered as dienophile the prototypical maleimide molecule, widely used for the design of thermo-responsive materials,¹⁷ and a polycyclic aromatic hydrocarbon (PAH) made of 23 fused benzene rings as diene (see Fig. 1); calculations have also been performed for the reaction between the furan molecule (as diene) and PAH (as dienophile). The geometries of the diene and dienophile were first optimized separately at the DFT level using Gaussian 5.0.9. software. The curvature of the surface was imposed by fixing the separation between the external carbon atoms in the folding direction during the geometry optimization (see d_{C-C} in Fig. 1a and 1b). The way to obtain the characteristic d_{C-C} of a given carbon-based material is detailed below in the case of SWNTs. Assuming that SWNTs have an average diameter of 1 nm ($d = 10 \text{ \AA}$) and are completely circular, the perimeter of the tube is $\pi \cdot d$ ($P = 31.41 \text{ \AA}$). The distance d_{C-C} for our model graphenic structure used for the theoretical study is 12.27 Å. The ratio between d_{C-C}/P ($12.27/31.41 = 0.3906$) represents the fraction of the circle covered by the curved graphene structure. The angle intercepting this arc is $360^\circ \times \text{fraction of the circle}$ ($\theta = 360 \times 0.3906 = 140.6^\circ$). The length of the segment joining the extremities of the arc (d_{C-C} for the SWNT) can be calculated using the following formula:

$$d_{C-C \text{ curved}} = d * \sin\left(\frac{\theta}{2}\right)$$

where $d_{C-C \text{ curved}}$, d and θ represent the distance between the two external carbons along the folding direction for the curved

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Fig. 1. Inner [4+2] Diels-Alder reactions on a curved graphene sheet. a) top view of the reactive site highlighted in yellow, b) side view of the maleimide/graphene partners involved in the Diels-Alder reaction, c) chemical structure of maleimide, d) chemical structure of furan.

structure, the diameter of the actual nanotube and the angle intercepting the arc associated to the curved nanotube, respectively. For SWNT : $d_{C-C \text{ curved}} = 10 \cdot \sin(140.6/2) = 9.4 \text{ \AA}$. The d_{C-C} values for realistic carbon-based structures are tabulated in the Supporting Information 1. Note that this model deviates from a cylindral shape for distances below $9 \text{ \AA}$, which are not representative of realistic carbon nanotubes.

The transition-state geometry needed to estimate the activation barrier is obtained by means of the intrinsic reaction coordinate (IRC) method by approaching the four relevant carbon atoms involved in the Diels-Alder cycloaddition; Fig. 1a and 3a illustrate in yellow respectively the dienes involved on the carbon-surface for an inner attack versus an edge attack on the adapted armchair edge. The free energies of activation (i.e., between the reactant and transition state geometries) and free energies of reaction (between the reactant and product geometries) are calculated at the same level of theory for curvatures representative of various carbon-based materials (see the SI for more details).

Fig. 2 illustrates the theoretical evolutions of $\Delta G^\ddagger$ and ΔG° for different curvatures of the PAH for a Diels-Alder reaction involving inner carbon atoms of the surface and the maleimide molecule. The corresponding data are tabulated in Table S2 (see Supporting Information S2). The results provide evidence for a clear reduction of the activation barriers for more strained structures, i.e., a drop by about 20 kcal.mol^{-1} going from graphene, to multi-walled carbon nanotubes (MWNTs), double-walled carbon nanotubes (DWNTs) and single-walled carbon nanotubes (SWNTs). High values of $\Delta G^\ddagger$ and ΔG° (31.61 and $39.92 \text{ kcal.mol}^{-1}$, respectively) are calculated for the planarized structure ($d_{C-C} = 12.32 \text{ \AA}$ in Fig. 2), thus suggesting that the core functionalization of a graphene surface by standard Diels-Alder reactions is an inefficient process. Similar results using the M062X functional have been reported for Diels-Alder reactions of graphene with dienes (2,3-dimethoxy-1,3-butadiene and 9-methylanthracene) and dienophiles (tetracyanoethylene and maleic anhydride), suggesting in all cases highly unfavored reactions.^{18, 19}

Fig. 2. DFT (M062X/6-31G(d))-calculated evolutions of the free energies of activation ($\Delta G^\ddagger$) and reaction (ΔG°) for a Diels-Alder reaction involving maleimide and inner carbon atoms of the PAH, as a function of its curvature. Note that $12.32 \text{ \AA}$ corresponds to the full length of the planar model system.

For curvatures characteristic of the external walls of MWNTs ($d_{C-C} = 11.5\text{--}12 \text{ \AA}$), the activation barriers and free energies of reaction are reduced compared to the model flat structure but remain highly positive. The corresponding values are further reduced with an increased curvature, reaching negative values for the activation barrier when $d_{C-C} < 9.32 \text{ \AA}$ (representing a realistic value for a single-walled carbon nanotube). Accordingly, we can conclude that MWNTs are less reactive than SWNTs in Diels-Alder reactions for which the reactive site is the side-wall, in agreement with previously reported experimental data in the literature.⁷ These results are consistent with those obtained by Osuna and co-workers, suggesting the same curvature effect for cycloadditions on single-walled nanotubes and fullerenes, using the ONIOM method.^{20–22} In addition, Araujo *et al.* have also reported the feasibility of Diels-Alder functionalization on nanotube structures with *ab initio* calculations in periodic conditions.²³ Interestingly, the same trend is observed for the Diels-Alder cycloaddition of furan; however, the higher values of $\Delta G^\ddagger$ and ΔG° point to an inefficient reaction for this diene on the core of carbon-based materials (see Supporting Information S3).

It is worth stressing that the fullerene (C_{60}) structure represents the extreme case of curvature for carbon-based materials and as a consequence, are highly reactive compared to nanotubes.²⁴ In [4+2] Diels-Alder reactions, fullerene acts as a dienophile due the high electron affinity of C_{60} ^{25, 26} and can be efficiently functionalized by common dienes such as anthracene, tetracene, furan or cyclopentadiene.^{8, 27–29} Osuna *et al.*²² reported ONIOM(M062X/6-31G(d))-calculated values of $\Delta G^\ddagger$ and ΔG° to be 6.8 and $-24.2 \text{ kcal.mol}^{-1}$ for the Diels-Alder reaction of cyclopentadiene on C_{60} . Such a negative ΔG° points to highly exothermic conditions for the cycloaddition on C_{60} .

The edge-functionalization of curved graphene sheet with maleimide was also investigated using the same methodology (Fig. 3). The graphene sheet was curved along the armchair edge to expose two double C-C bonds in trans at the edge in the curved structures, as highlighted in yellow in Fig. 3. The corresponding values of ΔG° and $\Delta G^\ddagger$ are presented in Fig. 4 and tabulated in Table S4 (see Supporting Information 4). Compared to the core functionalization, the trends are strikingly opposite when the edge-functionalization is considered. For graphene and MWNT like structures, Diels-Alder cycloadditions are expected to be efficient ($\Delta G^\circ = -2.19 \text{ kcal.mol}^{-1}$, $\Delta G^\ddagger = 24.58 \text{ kcal.mol}^{-1}$), which is fully consistent with previously reported theoretical and experimental works.^{18, 30, 31} Note that, besides the armchair edge of planar structures, defects such as Stones-Wales and single-vacancy have also been suggested to be efficient reaction sites in graphene for Diels-Alder reactions.¹⁹ For more curved structures, the edge-functionalization becomes highly unfavored. Based on these results, we can conclude that the Diels-Alder functionalization of *defect-free* carbon-based materials occurs primarily on the side-wall for highly curved structure such as SWNTs and mostly on the edges for more planarized structures such as graphene and MWNTs.

Fig. 3. Edge atoms [4+2] Diels-Alder reaction on curved graphene sheet. a) top view of the reactive site highlighted in yellow, b) side view of the maleimide/graphene partners involved in the Diels-Alder reaction.

In order to verify within a singly integrated work our predictions, we have used the Scanning Electron Microscopy (SEM) coupled to fluorescence microscopy techniques to assess experimentally whether MWNT and SWNT exhibit different reactivities against Diels-Alder cycloadditions involving a fluorescent maleimide derivative (Fig. 5). The experimental procedure for the functionalization of the carbon nanotubes is depicted in Fig. 5a (more details are given in the Supporting Information S5). The optical microscopy and SEM images on samples prepared by drop-casting the bi-component dispersions containing maleimide with either MWNT or SWNT in o-DCB on silica are shown in Fig. 5b-c and 5e-f, respectively. Fig. 5d displays the fluorescence image recorded on the film consisting of bundles of MWNTs where no significant emission can be detected. Conversely, strong emission was monitored in the case of the films composed of bundles of functionalized SWNTs (Fig. 5g). These results support our theoretical finding indicating a minor functionalization of MWNTs localized at the edges in well-adapted armchair configurations compared to a major covalent attachment of the maleimides on the SWNT sides-walls.

Fig. 4. DFT(M062X/6-31G(d))-calculated evolutions of the free energies of activation ($\Delta G^\ddagger$) and reaction (ΔG°) for a Diels-Alder reaction involving maleimide and edge carbon atoms of the PAH, as a function of its curvature.

Fig. 5. a) Scheme of the Diels-Alder functionalization of carbon nanotubes via fluorescent maleimides. MWNT images (same area) recorded by b) optical microscopy, c) SEM, d) fluorescence microscopy. SWNT images (same area) recorded by e) optical microscopy, f) SEM, g) fluorescence microscopy (more details in Supporting Information s6.a).

In conclusion, DFT calculations have demonstrated that the free energies enthalpies of activation and reaction for the

inner Diels-Alder functionalization of carbon-based materials are strongly reduced when the curvature of the surface is increased. This makes the functionalization of flat or weakly curved surfaces (such as graphene or MWNTs) inefficient for standard dienophiles, whereas this reaction is favored for higher curvatures (such as in SWNTs or fullerenes). Moreover, the opposite trend is calculated when the edge-functionalization is considered. These theoretical findings are supported by a combination of scanning electron microscopy and fluorescence microscopy applied to functionalized SWNTs and MWNTs. Our study opens the way to the investigation of other attractive diene/dienophile couples and motivates further work aiming at a deeper analysis of the Diels-Alder reactivity in presence of realistic defects.

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