Research paper

Diels-Alder reactions onto fluorinated and hydrogenated graphene

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ABSTRACT

We studied Diels-Alder (DA) reactions onto functionalized graphene. When fluorine, hydrogen or oxygen functional groups are present on one side of the sheet, the DA cycloadditions become significantly more exergonic when performed on the opposite side. Hydrogen is more effective than fluorine and oxygen to promote these cycloadditions. In contrast with the results obtained for perfect graphene, the functionalization with H, F or O turns the DA reactions exergonic, with $\Delta G°_{298}$ = −127.2 kcal/mol. The reaction barriers are expected to be considerably lowered with respect to perfect graphene because the functional groups significantly reduce the distortion energy.

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1. Introduction

Organic reactions constitute a useful approach to attain the covalent functionalization of graphene. For example, the addition of aryl diazonium salts [1–3] is one the preferred approaches to functionalize graphene. The alkylation of graphene has been studied [4–6], as well as 1,3 dipolar cycloadditons [7–12], [2+2] cycloadditions [13–16], [2+1] cycloadditions[17–19], Friedl-Crafts acylation [20], and recently the alkylation and arylation were performed via the Grignard reaction with fluorographene [21]. A particular case of organic reactions of graphene are the Diels-Alder processes [21–33]. Graphene can be either diene or dienophile, even though our theoretical calculations showed that the dienophile character is slightly stronger [21]. The first report of successful Diels-Alder reactions with graphene is that by Sarkar et al. [23] published as early as 2011. They altered the semimetallic character of graphene by the addition of dienophiles such as tetracyanoethylene (TCNE) and maleic anhydride (MA). The dienes employed where 2,3-dimethoxy-1,3 butadiene (DMBD) and 9-methylanthracene (9MA). In the case of tetracyanoethylene, the retro-Diels-Alder reaction was observed that at 100° C, and graphene was obtained again. Considering the latter results, it is not surprising that force-accelerated Diels-Alder reactions were used to add cyclopentadienes onto graphene [23]. Recent density functional theory studies performed by us [21] and Cao et al. [25], suggested that perfect graphene, is unreactive against TCNE, MA, 9MA and DMBD. For example, the free energy change at 298 K for the addition of DMBD is close to +50 kcal/mol. For this reason, defects [21,25], edges [21,25], curvature [26], heating [23], force accelerated processes [24], or the presence of hydroxyl groups [29] are

required to achieve a successful Diels-Alder reaction onto graphene. However, a recent investigation by Daukiya et al. [30] reported that for some specific fluorinated maleimide molecules the Diels-Alder reaction can be performed without pre-existing defects. T-matrix approximation calculations were used to conclude that a (1,2) or (1,4) cycloaddition was performed [30]. Our most recent study on this area [31], showed that the introduction of heteroatoms on the graphene framework is likely to be the best approach to facilitate Diels Alder reactions onto graphene, and also to determine the desired reaction product: [4+2] or [2+2]. In effect, we found that a benzyne group can be added to Si-doped graphene with bond energy of −112.5 kcal/mol, while a [2+2] cycloaddition of benzynes has bond energy of −93.9 and −84.4 kcal/mol onto B and N-doped graphene, respectively. The latter values represent a dramatic increase with respect to the bond energies calculated for perfect graphene: −12.8 and −9.6 kcal/mol, for [2+2] and [4+2] cycloadditions, respectively. Finally, Tang et al. showed that the oxygen functional groups present in graphene oxide increase the dienophile character of graphene improving Diels-Alder reactions [32].

Motivated by the encouraging results obtained for heteroatom doped graphene we considered that the presence of functional groups in the graphene plane should be another approach to facilitate Diels-Alder reactions onto graphene. By means of first principle periodic calculations we found that for fluorinated and hydrogenated graphene there is a remarkable increase the exothermicity of Diels-Alder reactions onto graphene. In effect, for some particular cases we observed that a benzyne group can be attached to hydrogenated graphene with reaction energy of −190 kcal/mol. Also, we demonstrate that the sites selected to fluorinate or hydrogenate one side of graphene determine the cycloaddition product obtained in the other side of the sheet.

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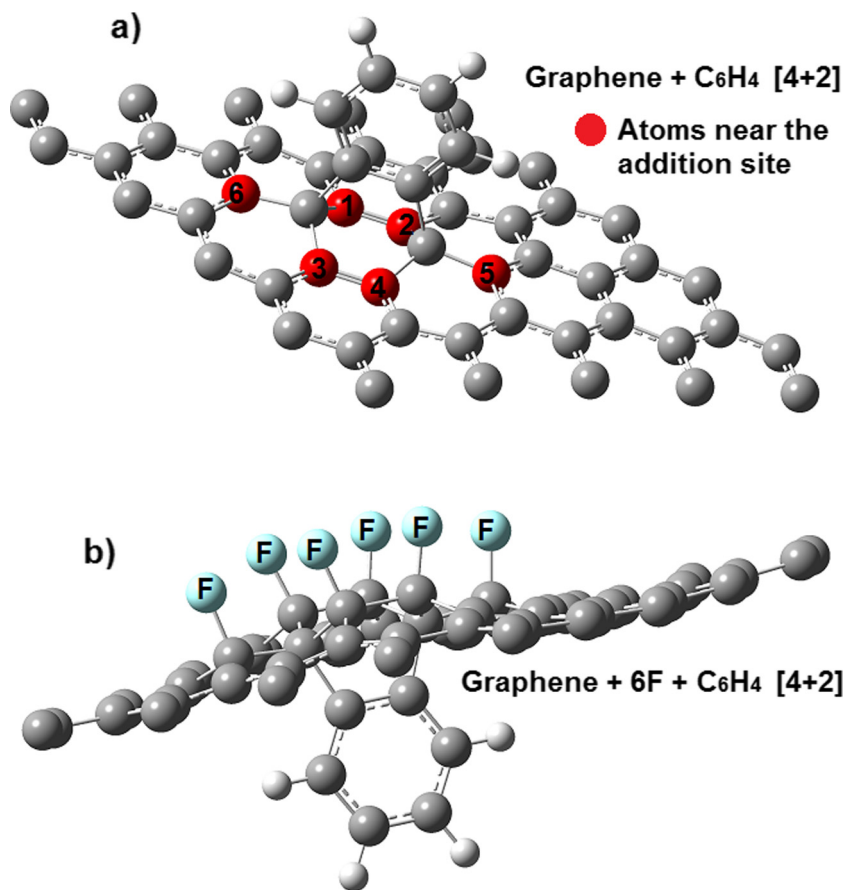
Fig. 1. (a) Graphene 5 × 5 unit cell functionalized with a benzyne group following the [4+2] path. The colored atoms represent the atoms near the addition site, which were used to functionalize the graphene sheet. The numbers indicated the functionalization sequence adopted. (b) Optimized graphene 5 × 5 unit cell functionalized six fluorine atoms and a benzyne group. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Methods

Truhlar's M06-L [34,35] functional was selected to perform for periodic density functional calculations over a 5 × 5 unit cell. This size of lattice parameters prevents any lateral interactions between the functional groups attached. For comparative purposes we also performed calculations using a circumcoronene model, which we shown below that it is large enough to mimic graphene. The basis set selected was Pople's 6-31G∗ [36]. 1000 k-points were used to sample the unit cell and the ultrafine grid was employed. The M06-L calculations were performed with Gaussian 09 [37]. This methodology is the same that we used to investigate Diels-Alder reactions onto perfect [22], defective [22], and doped graphene [31]. It is important to note that the conclusions reached in our previous work [22] were supported the results obtained by Cao et al. [25].

3. Results and discussion

3.1. [4+2] cycloadditions

In first place we considered the addition of one benzyne group via the [4+2] reaction path to fluorinated graphene. When C_6H_4 is attached to graphene, two C—C single bonds are formed. Therefore, the electron density of the carbon atoms of graphene which are bonded to the C_6H_4 group must be altered in order to increase the reactivity. As described in the introduction, the addition of functional groups to the nearby three C atoms is expected to be a

suitable approach. These atoms are shown in Fig. 1. A total of six covalent additions can be performed, one group of three for each C atom. The reaction energies are presented in Table 1. There is a significant increase of the absolute value of reaction energies as the number of fluorine atoms is increased. Starting from the reaction energy of −9.6 kcal/mol determined for pristine graphene, it is

Table 1
Reaction energies (kcal/mol) determined for the [2+2] and [4+2] cycloadditions of benzyne onto functionalized graphene[f].

	[2+2]	[4+2]		[4+2]
F	−40.7[b]	−33.8[a]	H	−35.0[d]
2F	−61.2[b]	−75.7[a]	2 H	−72.4[d]
3F	−79.9[b]	−88.0[a]	3 H	−88.6[d]
4F	−91.8[b]	−137.0[a]	4 H	−139.7[d]
4F-1,4	−44.6[c]	−43.7[c]		
5F-1		−151.6[a]	5 H	−155.4[d]
5F-2		−119.0[a]		
6F		−183.4[a]	6 H	−190.2[d]
1 epoxy		−50.4[e]		
2 epoxy		−83.2[e]		
4 epoxy		−128.5[e]		
6 epoxy		−148.4[e]		

[a] Fluorination sequence shown in Fig. 1.
[b] Fluorination sequence shown in Fig. 5.
[c] Fluorination sequence shown in Fig. 6.
[d] Hydrogenation sequence shown in Fig. 1, it is similar to the one used for fluorine.
[e] Oxidation sequence shown in Fig. 4.
[f] The reactions energies for the addition of C_6H_4 onto perfect graphene are −12.8 and −9.6 kcal/mol for the [2+2] and [4+2] paths, respectively.