Research Article

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The influence of the grafted aryl groups on the solvation properties of the graphyne and graphdiyne - a MD study

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Abstract: The mechanism of the adsorption and grafting of diazonium cations onto the surface of graphyne and graphdiyne was investigated using Density Functional Theory (DFT). The adsorption energy (both in vacuum and water as solvent) of the phenyl diazonium cation was evaluated at three different positions of the graphyne and graphdiyne surface. Moreover, the lowest energy adsorption sites were used to calculate and plot Non-covalent Interactions (NCI). The Bond Dissociation Energy (BDE) results (up to 66 kcal/mol) for the scission of the phenyl group support the remarkable stability of the grafted layer. As both of these materials are non-dispersible in aqueous solution, in this work through the use of Molecular Mechanics (MM) and Molecular Dynamics (MD) we explored also the effect of the grafted substituted aryl groups derived from aryldiazonium salts onto the solvation properties of these materials.

Keywords: Graphyne; Graphdiyne; Grafting; Molecular Dynamics; Solvation; Aryldiazonium Salts; adsorption; bond dissociation energy; non-covalent interactions.

1 Introduction

It is now well established that the aryl diazonium cations are the most promising candidates for the surface modification of materials. The use of such molecules for the surface modification dates in the 90's from the ground-breaking work of Prof. Pinson [1]. In comparison to other molecules used for this purpose (thiols, silanes, phosphonic acids) [2] aryl diazonium salts are easy to

synthesize and can be applied in a variety of materials (oxides, insulator, powders, polymers, metals, etc) a feature that is absent in the case of other molecules [3,4].

The surface modification reaction in the case of the diazonium salts is based on the attack of the very reactive aryl radical that is created upon scission of nitrogen moiety from the parent aryldiazonium cations. The formed interface (by spontaneous [5-7], electrochemical [1, 4, 10-12], sono-chemical [13], thermal [13,14] or light-driven de-diazonation [15] reactions) has been analyzed using immense number of analytical characterization methods (AFM, Tof-SIMS, XPS, RBS, IRRAS, TGA) [3,16]. The existence of the covalent binding between the grafted moiety and the material is supported both by experimental evidence [3], [16] and also using DFT calculations [9,17,18]. Up to now, to our knowledge, no existing study is focused toward the surface modification of graphyne and graphdiyne by aryl radicals derived from de-diazonation reactions of the aryldiazonium cations. In contrast, there are numerous studies where the aryldiazonium chemistry is applied for the modification of other carbon like nanomaterials [19-25]. Such study is of immense interest as graphyne and graphdiyne represent the two newest members of the very large family of nanocarbon allotropic materials that possess a lot of potential for use in the materials science. Both of these structures are one-atomic thick materials composed of sp² and sp atoms, in which the adjacent benzene rings are linked in a huge network by one (in graphyne) or two acetylenic groups (in case of graphdiyne). Graphyne and graphdiyne are both members of the very large family of nanocarbon allotropic materials [0D (fullerenes, quantum dots, graphene dots, carbon dots, onion-like carbon, nano-diamonds), 1D (single-walled and multi-walled nanotubes, nanohorns), 2D (graphene, multilayered graphitic sheets, graphene oxide) and 3D (graphite), their surface modification using aryldiazonium salts is supposed to proceed in a similar way as with other carbon-rich nanomaterials [19, 20, 22, 24]. They are promising materials for a number of

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applications (gas separation, lithium storage, as a possible replacement material for silicon transistor technology etc.) since they pose a number of remarkable properties (extreme hardness, very high electric conductivity, high thermal resistance, etc.). In order to gain mechanistic details, interface stability of the grafted layers derived from aryl diazonium salts and their practical utility oriented toward the tuning of solvation properties of the grafted structures DFT [26, 27], molecular mechanics [28], and molecular dynamic calculations were employed. This represents the first study that addresses the impact of surface modification and the influence of the grafted aryl groups on the solvation properties of the graphyne and graphdiyne.

2 Computational details

2.1 DFT

DFT calculations were performed using the DMol³ software (BIOVIA). The graphyne and graphdiyne models used to compute the Bond Dissociation Energy and the solvation properties are presented in Figure 1. The models consist of a central phenyl ring (in green) linked to six other groups via -C≡C- (graphyne) or -C≡C-C≡C- (graphdiyne) linkages. All electron calculations are employed for geometry optimization with the double numerical plus polarization basis set (DNP) [29]. The exchange-correlation energy is described by the Perdew–Burke–Ernzerhof functional within the generalized gradient approximation (GGA–PBE) [9,30,31].

All energy minima were characterized by performing a vibrational analysis to ensure the lack of imaginary frequencies [9],[18].

The adsorption energy ($E_{\text{ads.}}$) [9],[32] was calculated as:

$$E_{\text{(ads.)}} = - (E_{\text{Graphyne or Graphdiyne /aryldiazonium cation}} + E_{\text{aryldiazonium cation}} - E_{\text{Graphyne or Graphdiyne}})$$

where: $E_{\text{Graphyne or Graphdiyne /aryldiazonium cation}}$ is the total energy of the adsorption system. $E_{\text{Graphyne or Graphdiyne}}$ and $E_{\text{aryldiazonium cation}}$ are the energies of the isolated Graphyne or Graphdiyne and aryldiazonium cations, respectively. The transition state (in water, using COSMO solvation model [33]) is computed using the combination of Linear Synchronous Transit (LST) and Quadratic Synchronous Transit (QST) [34]. The NCI (Non-Covalent interaction) were computed using Multiwfn software [35] from the DFT calculations

Figure 1: A. Graphyne and B. Graphdiyne structure used for DFT calculations.

[B3LYP/6-311++g (d,p)]. The same was applied also to calculate the homolytic bond dissociation energy of the phenyldiazonium cation (using the bond scan). The NCI surface is plotted using VMD (Visual Molecular Dynamics) software [36].

2.2 Molecular Mechanics / Molecular Dynamics

Model systems for bare and modified graphyne and graphdiyne structures were constructed as amorphous three-dimensional periodic boxes using the Amorphous Cell Tool in Materials Studio. The simulation cells enclosed 200 solvent molecules (either water or hexane). The steps used to compute solvation energies are presented in the Figure 2. The calculation was performed using the COMPASS II force field [37].

The total solvation free energy is calculated as the sum of three contributions: Ideal, van der Waals, and Electrostatic. The partition-coefficient Log P, was calculated using the equation:

$$\log P = 0.434 (A[\text{water}] - A[\text{hexane}]) / RT$$

where 0.434 corresponds to $10 \log e$, R is the gas constant (1.987×10^{-3} kcal/mol/K), T the temperature in the simulation (298 K), and $A[\text{water or hexane}]$ is the solvation free energy in water or hexane.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

From the Figure 3, the adsorption energies for the phenyl diazonium cation (PhN_2^+) onto the graphyne surface in

Figure 2: Step used to calculate the solvation energy for graphyne.

Figure 3: Adsorption energy of phenyldiazonium cation (in water and vacuum) at 3 different adsorption sites onto A. Graphyne and B. Graphdiyne.

a vacuum are in the range from -28.72 to -24.61 kcal/mol depending on the adsorption site. In the presence of water as the solvent, the maximum adsorption energy is found for the adsorption position 3 (where the phenyldiazonium cation is flat onto the central phenyl ring of graphyne with the diazonium group oriented above the alkyne bond) with the value of -14.85 kcal/mol. The similar trend

in adsorption energy is also observed for the graphdiyne structure, in this case again the maximum adsorption energy (in water) is found for the third adsorption position with the energy value of -14.62 kcal/mol.

In order to understand the adsorption details, the NCI 2D and 3D plots for the interaction of PhN_2^+ with both surfaces were computed (Figure 3) [35],[38]. The

Figure 4: Non-covalent interaction surfaces and the plot of Reduced Density Gradient (RDG) vs. $\text{sign}(\lambda)p$ for the interaction of A. Graphyne/Ph-N₂⁺ and Graphdiyne/Ph-N₂⁺.

result shows that the adsorption is done through the van der Waals interactions. This interaction is considerably stronger than a simple π - π stacking (for which a gas phase value for such interaction is in the range of 2-3 kcal/mol) [39]. Understanding the adsorption of the aryl diazonium cations is of great interest to gain insights regarding the grafting of phenyl radicals that are the product of aryl diazonium cation induced or spontaneous de-diazonation reactions [4]. It is believed, that prior to the grafting reaction the adsorption of the diazonium cations takes place [4], this claim is supported by the obtained results (Figure 3 and 4).

The grafting reactions are essential for surface tuning of materials and add many interesting properties to them. For the practical applications, the grafted layers need to own certain stability. An indirect measure to assess such stability is the Bond Dissociation Energy (BDE) between

the bonded aryl radical and the grafted moiety (in this case Graphene). For the BDE calculation, three different grafting positions were explored (Figure 5). The highest BDE values are obtained for the grafting position 2 with the BDE energy value of -66 kcal/mol. This value is much higher than the values obtained for the gold surface (up to -38 kcal/mol) reflecting much stronger interface stability. The BDE has similar value as in the case of grafted graphene oxide surface (when the phenyl moiety is attached directly on aromatic carbon), even though in comparison to this surface, the adsorption energy for the graphyne and graphdiyne is smaller [40].

In Figure 6 is presented the bond scission diagram for the homolytic de-diazonation of the phenyldiazonium cation:

Figure 5: BDEs computed in: vacuum and water (COSMO) for the bonding of phenyl- radicals on 3 distinctive grafting position onto Graphyne surface.

Figure 6: Homolytic BDE of phenyl diazonium cations.

Figure 7: BDEs computed in: vacuum and water (COSMO) for the bonding of phenyl- radicals on 3 distinctive grafting position onto Graphyne surface.

Figure 8: A. The solvation energy differences for the grafted graphyne structure (with two phenyl groups) in water and hexane. B. Calculated Log P values.

The BDE, in this case, is 32.45 kcal/mol. From experimental studies on bulk carbon and other nanoscopic carbon, materials are known that the grafting takes place also spontaneously [6,7].

Thus, such reaction could be initiated through the instability of phenyldiazonium cation and further sustained (Figure 7) through the energy gain due to the difference between the reaction energy (-38.48 kcal/mol) and the energy barrier for the grafting reaction (34.17 kcal/mol) to take place.

The attached moieties derived from aryldiazonium cations (as calculated by Molecular Dynamics) have a certain impact on the solvation properties of graphyne (Figure 8). In this case, we took the solvation energy value of bare graphyne as zero in order to see only the effects of the grafted moieties on the solvation energy. The most pronounced effect is shown by the grafted Ph-COOH layers.

4 Conclusions

The adsorption of the phenyldiazonium cation and its subsequent grafting onto graphyne and graphdiyne surface was investigated using theoretical calculations for the first time. The computed NCI surfaces point out that the adsorption takes place by van der Waals interaction. The grafted phenyl group forms a quite stable interface with the BDE in the range of 66 kcal/mol pointing out to a covalent type of bonding. Taking into account the transition state calculations for the grafting of phenyl moiety onto the graphyne structure and the BDE from the formation of the phenyl radical from the corresponding aryldiazonium cation, the spontaneous surface modification is possible to take place. The Molecular Dynamics calculation, from which solvation properties and Log P can be computed clearly evidence the possibility to tune the solvation/dispersion properties of these structures by using aryldiazonium cations that bear polar or non-polar substituents. The present study not only provides a prospect to understand the grafting of aryl radicals onto graphyne and graphdiyne surface but also shows the benefits of the attached groups for tuning dispersibility of such structures.

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