Synthetic Amination of Graphene: Molecular Dynamics and Thermodynamics

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ABSTRACT: Functionalization of graphene using organic moieties constitutes an affordable way to modulate its physical and chemical properties. Finding an exact structural formula of functionalized graphene using experimental approaches is challenging. We studied in detail the thermal stability and thermodynamics of amino- and ethylamino-graphene and found a surprising synergistic effect: more amino groups stabilize functionalized graphene favoring further amination, whereas a small concentration of amino groups is unstable in many cases. The functional groups can be attached either on the same side or simultaneously on different sides of the graphene sheet. Deformation of functionalized graphene is proportional to the number of amino groups. Complete amination leading to formation of the ultimate product, C_3(NH_2)_x, is hindered sterically. Our study assists in the determination of the structure of chemically modified graphene and makes specific predictions that can be tested and validated experimentally.

Graphene (GRA) exhibits many unusual and valuable properties, stimulating active investigation by chemists and physicists.1−33 GRA functionalization is of crucial importance for efficient solubilization and for tuning numerous chemical and physical characteristics.3,9,13−17 Certain physical properties of GRA can be improved further if the grafted atoms or groups weaken the impact of existing structural defects. Functionalization facilitates binding of GRA and organic molecules.3,11,13,15,19,23,27,35−37 It also makes GRA an ideal platform for anchoring metallic nanoparticles.3,15 Functionalized graphene (FG) can be obtained by both covalent and noncovalent modification. The first class of techniques usually delivers stronger changes in GRA properties. For instance, electrical conductivity of FG is much smaller than that of pristine GRA; surface area decreases because of oxidation, chemical reduction, and sonication; and chemical reactivity of graphene oxide (GO) appears much different than that of pure GRA or graphite.3 FG can be further processed by solvent-assisted techniques, such as drop-casting, layer-by-layer assembly, spraying, filtration, and spin-coating. Sheets of FG do not agglomerate in solution, thus maintaining the properties of graphene as an isolated two-dimensional layer of carbon with a honeycomb structure.12,13

The most widely spread functionalization of GRA involves some kind of oxidation with a formation of multiple carboxyl, carboxyl, hydroxyl, epoxide, and diol groups at the surface.3,16,30 Oxidation is actively employed for exfoliation directly from graphite. Alternative recipes to obtain FG rely on nucleophilic substitution, electrophilic addition, condensation, and other addition reactions.3,16,30 Nucleophilic substitution mainly takes place via the epoxy groups of GO. The amino group, −NH₂, bearing a lone pair of electrons attacks the epoxy group readily at room conditions in the aqueous medium. Aliphatic and aromatic amines, amino acids, room-temperature ionic liquids, and amine-terminated biomolecules were proven to efficiently functionalize GRA and GO.1 This method exhibits a potential to be used for industrial scale applications. Spontaneous grafting of the aryl diazonium salt to GRA is a straightforward example of an electrophilic substitution.14 Condensation of GRA occurs with isocyanate, disiocyanate, and amine compounds via the formation of amides and carbamate ester linkages.15 Two or more molecules combine to form a larger molecule in organic addition reactions. An important illustration of the addition reactions involving GRA is the 1,3-dipolar cycloaddition of azomethine.12

Different substituted amines were embedded into GO for energy storage applications, electrocatalytic oxygen reduction reactions, and electrochemical sensors.33−35 An improved performance was observed in certain cases. Similarly, the amin functionalization of carbon nanotubes was used to enhance the controlled covalent bonding to polymers and biological molecules.27 These wide applications inspire research efforts toward synthesis of amino-FG with a fine control over its structure and properties. Detailed knowledge about amino-FG is required for this purpose.

Navaee and Salimi proposed a simple method based on the Bucherer reaction to attach −NH₂ to GO.31 In that method, the reaction of ammonia and GO is catalyzed by sodium bisulfate. According to the surface analysis and material characterization, the authors establish the presence of multiple −NH₂ groups on the GRA surface. An improved electro-
catalytic activity of the product was recorded. Alkylamino-FG with oxygen-containing groups was reported to exhibit a good dispersion in organic solvents and a relatively strong interfacial interaction with organic polymers.39 Despite the experimental successes, the structural formula of amino-FG remains largely unknown.

A number of theoretical papers focused on FG and its properties. Tetsuka et al. used amino groups to tune optical properties of GRA quantum dots,38 while Chakraborti and Pal explored amino-GRA flakes for application as anode material in Li-ion batteries.40 Multiple papers investigated hydrogenated11−43 and fluorinated33,37,44 GRA. More complex aspects of GRA chemistry, such as oxygen reduction45 and Diels−Alder reaction,46 were studied.

In this letter, we employ ab initio gas-phase thermochemistry and long-scale finite-temperature electronic-structure-based molecular dynamics (MD) to characterize in detail the composition and structure of amino-FG. We address the following and related questions: What is the maximum theoretically stable concentration of amino groups? Can amino groups be grafted in ortho and meta positions in view of steric conditions? Can −NH2 exist both above and below the GRA plane simultaneously? How does the formation free energy depend on the number and location of −NH2 groups?

We discover, quite surprisingly, a strong synergistic effect. The presence of multiple amino groups stabilizes FG and favors further amination. At the same time, a small concentration of amino groups leads, in many cases, to unstable products. The groups can be attached on one or both sides of the graphene sheet. Steric hindrances play an important role in preventing complete GRA amination. The reported results can be verified experimentally, complementing the experimental efforts aimed at characterization of FG.

Figure 1 depicts simulated models of amino- and ethylamino-FG, whereas Table 1 provides a full list of the considered systems. We investigated a variety of structures involving different attachment and substitution positions—such as ortho (1,2); meta (1,3); para (1,4); neighboring rings (2,7); different arrangements of three, four, and six (ethyl)amino groups per single 6-membered carbon ring—using a small model sheet (graphene quantum dot). According to our previous (unpublished) benchmark studies, dependence of functionalization on the hybridization state and chemical environment is much stronger than on the size of the model.

Thermodynamic data are provided for the last stage of amination, i.e., GRA + 4NH2 ↔ GRA-NH2 or GRA-H + 5NH2 ↔ GRA-NH2 + 4H at 298.15 K and 1.0 bar. We do not consider 6NH2 liberation reactions, which depend on a particular method of synthesis, employed catalysts, and available nitrogen source. Those reactions were well-studied upon derivation of each particular method. If the last stage of amination exhibits a sufficiently positive Gibbs free energy, such a reaction is, most likely, impossible. According to Table 1, all

<table>
<thead>
<tr>
<th>no.</th>
<th>group</th>
<th>positions</th>
<th>stability</th>
<th>ΔG°M11 (kJ mol−1)</th>
<th>rmax(C−C) (nm)</th>
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<td>1</td>
<td>−NH2</td>
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</tr>
<tr>
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<td>stable</td>
<td>+67</td>
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</tr>
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<td>1,4</td>
<td>stable</td>
<td>−41</td>
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<tr>
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<td>0.152</td>
</tr>
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<td>unstable</td>
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<td>stable</td>
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<td>0.160</td>
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<td></td>
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<td>3,10 (below)</td>
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<td>−</td>
<td>−</td>
</tr>
<tr>
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<td>stable</td>
<td>+13</td>
<td>0.151</td>
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<td>1,2</td>
<td>unstable</td>
<td>−</td>
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<tr>
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<td>1,3</td>
<td>unstable</td>
<td>−</td>
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<td>13</td>
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<td>18</td>
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<td>1</td>
<td>stable</td>
<td>−3</td>
<td>0.151</td>
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</table>

*See Figure 1 for the site designation. Stability indicates integrity of the FG during the 200 ps long PM7-MD simulations at 500 K, as described in the Computational Methods section. The length of the longest carbon−carbon (C−C) bond neighboring the grafted (ethyl)amino group. The longest bond is provided, because it directly reflects FG stability of FG. The C−C bond is 0.141 nm long in pristine GRA.
amination reactions bring modest changes in the free energy. In comparison, formation of most covalent bonds brings ca. 1000 kJ mol\(^{-1}\). Many of the considered amination positions appear thermodynamically forbidden, e.g., the ortho and meta positions, the edge position, etc. However, the para position is allowed, irrespective of the substituent. Grafting the ethylamino groups is generally more energetically favorable. For instance, attachment of the lone amino group to a central atom of GRA costs 13 kJ mol\(^{-1}\), whereas attachment of the lone ethylamino group at the same position brings 3 kJ mol\(^{-1}\). All presented values (Tables 1 and 2) were normalized per mole of \(-\text{NH}_3\). Substitution of \(^1\text{H}\) by \(^1\text{NH}_3\) or \(^1\text{C}_2\text{H}_5\text{NH}_2\) at the rim carbon atom without a catalyst is forbidden in line with the known amination of arenes.

Table 2. Standard Enthalpic Contribution (\(\Delta H\)), Entropic Contribution (\(-T\Delta S\)), and Entropy (\(\Delta S\)) for the Investigated Amination Reactions

<table>
<thead>
<tr>
<th>positions</th>
<th>(\Delta H^{\mathrm{M11}}) (kJ mol(^{-1}))</th>
<th>(-T\Delta S^{\mathrm{M11}}) (kJ mol(^{-1}))</th>
<th>(\Delta S^{\mathrm{M11}}) (J mol(^{-1}) K(^{-1}))</th>
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<tbody>
<tr>
<td>(-\text{NH}_3)</td>
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<td></td>
<td></td>
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<tr>
<td>1,2</td>
<td>-26</td>
<td>+50</td>
<td>-167</td>
</tr>
<tr>
<td>1,3</td>
<td>+18</td>
<td>+49</td>
<td>-165</td>
</tr>
<tr>
<td>1,4</td>
<td>-91</td>
<td>+50</td>
<td>-168</td>
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<tr>
<td>2,7</td>
<td>+7.0</td>
<td>+49</td>
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<td>1,2,4</td>
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</tr>
<tr>
<td>1,2,4,5,6</td>
<td>-138</td>
<td>+52</td>
<td>-176</td>
</tr>
<tr>
<td>edge</td>
<td>+14</td>
<td>+16</td>
<td>-54</td>
</tr>
<tr>
<td>‘1’</td>
<td>-34</td>
<td>+46</td>
<td>-156</td>
</tr>
<tr>
<td>(-\text{C}_2\text{H}_5\text{NH}_2)</td>
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<tr>
<td>‘1,4’</td>
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<td>+54</td>
<td>-180</td>
</tr>
<tr>
<td>‘2,7’</td>
<td>-19</td>
<td>+55</td>
<td>-185</td>
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<tr>
<td>‘1,4,2,5’</td>
<td>-120</td>
<td>+56</td>
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<tr>
<td>‘1’</td>
<td>-56</td>
<td>+53</td>
<td>-178</td>
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</table>

A clear synergistic effect is seen upon amination. While lone amino groups at the surface of GRA are unstable, addition of more \(-\text{NH}_3\) stabilizes the product. Two, three, and four groups lead to systematically more favorable FG. Six amino groups per ring, four above the GRA plane and two below the GRA plane, constitute an unexpectedly favorable FG sample, \(-85\) kJ mol\(^{-1}\). Note that the free energy is given per number of \(-\text{NH}_3\). A natural supposition is that the synergistic stabilization occurs because of Coulombic attraction between \(-\text{NH}_3\) and an electronically polarized GRA surface. This hypothesis is supported by several facts. First, amino-FG is more favorable than ethylamino-FG, \(-85\) versus \(-64\) kJ mol\(^{-1}\). Second, formation of the ‘2,7’ amino-FG and ethylamino-FG systems is unfavorable because the distance between these positions is significant, weakening the stabilizing Coulombic attraction. Many other interesting correlations can be derived from Tables 1 and 2.

Table 2 decomposes Gibbs free energies of the corresponding reactions into the enthalpic (\(\Delta H\)) and entropic (\(-T\Delta S\)) components. Entropy of the GRA amination is unfavorable in all cases. The entropic component, 298.15 K \(\times\) \(\Delta S^{\mathrm{M11}}\), of the reaction at the rim carbon atom amounts to 16 (amino-FG) and 18 kJ mol\(^{-1}\) (ethylamino-FG). Compare this value to that for amination of benzene, 18 kJ mol\(^{-1}\), obtained using the same level of theory. Similarity of the entropic components confirms our earlier supposition that enthalpy (including Coulombic attraction) ultimately determines the direction of the amination process in the considered cases. Note, however, that the absolute value of the entropy change plays an extremely important role for this reaction at room conditions, constituting more than half of the reaction free energy in many cases.

Thermal stability was investigated using PM7-MD simulations. The geometries of the constructed systems were optimized using PM7 and gradually heated from 0 to 500 K. Trajectories that were 200 ps long were used to derive distance distributions (Figures 2 and 3) and dihedral distributions (Figure 4). Note that we study thermal stabilities of the FG samples in vacuum. If any aggressive solvent is present, the reported stabilities may alter drastically. The reported trends are expected to hold in inert solvents.

It was found that the ‘1,2,3’ amino-FG is unstable. This occurs for steric reasons: amino groups do not have enough space on the same side of the GRA plane. An average C–C–N angle, with both carbon atoms belonging to GRA, is 110° in the ortho-FG, 107° in the meta-FG, and 106° in the para-FG. The C–C–N angle is 106° also in the ‘2,7’ amino-FG system. Geometry analysis also explains the thermodynamic observations (Tables 1 and 2). Note that the ‘1,2’ amino-FG system is perfectly stable over the entire MD run, even though its formation out of pristine GRA is not thermodynamically allowed. A more sophisticated synthetic approach should be used.

Steric problems undermine thermal stabilities of the ‘1,2’, ‘1,3’, and ‘1,3,5’ ethylamino-FG systems as well. We anticipate that longer alkylamino chains deliver new spatial restrictions, because a natural shape of the hydrocarbon chain has to
accommodate to the available space. Calculations involving other groups can be readily performed applying our currently established methodology.

The length of the carbon−nitrogen bond in aminobenzene is 0.144 nm. The corresponding distances in FG are different and slightly dependent on the position (Figure 2). When −NH₂ gets linked at the “edge” position, the bond length is 0.139 nm. If the attachment occurs at any other position (Table 1), the bond length is ca. 0.150 nm. The ‘1,4’ (para) position allows for C−N bonds that are somewhat shorter than the meta and ortho positions. Compare these lengths to the lengths of the C−C bonds in the 6-membered rings (Table 1) for different positions of −NH₂.

Figure 3 characterizes the C−C and C−N distances in the case of ethylamino-FG. Note that the C−N distances correspond to the nitrogen atoms of −NH₂ and the closest carbon atom of GRA. That is, these distances are not covalent bond lengths, unlike the C−C distances, which were calculated between the GRA plane and the closest ethylene group of the linked −C₆H₄NH₂ moiety. The ethylamino groups are very mobile at 500 K, sampling 0.30−0.45 nm C−N distances to the GRA plane. A larger number of the −C₆H₄NH₂ moieties makes each of them stiffer (Figure 3, right panel).

The grafted −NH₂ perturbs planarity of the GRA sheet considerably. The effect in the case of amino-FG is stronger than in the case of ethylamino-FG (Figure 4), because the nitrogen−carbon groups are polar. In turn, the carbon−carbon bonds in ethylamino-FG are nearly nonpolar. Importantly, a clear dependence is observed between the number of −NH₂ groups and nonplanarity of the corresponding 6-membered ring. An improper dihedral of the pristine GRA was also plotted for comparison (Figure 4). On the average, pristine GRA and GRA with a single −NH₂ at the edge are planar. Thermal fluctuations are significant; deviations of ±9° are seen in the pristine system at 500 K. The analogous deviations are somewhat larger in the edge-amino-FG. Although the ring deforms very significantly because of functionalization, the structure is maintained. The distribution of improper dihedrals in the ‘1,2,4,5&3,6’ system is quite narrow, suggesting nearly harmonic fluctuations from planarity during MD. One can expect that long-range interactions present between polar groups in large graphene sheets will average out geometry fluctuations, reducing somewhat the nonplanarity observed with the current systems.

Figure 5 depicts an interesting product of amination, which was obtained during the PM7-MD simulations during the first 5 ps. The starting configuration was 1,2-diethylaminegraphene.
This molecule readily cleaves two hydrogen molecules, formed out of two amino groups, whereas unsaturated nitrogen atoms create a double bond, thereby closing the ring. The 1,2-diethylamino-FG is, therefore, unstable but gives immediate rise to another stable compound.

Following the practice of Adeli and co-workers working with carbon nanotubes,7 we investigated hydrogen bonds between the nitrogen atom of the amino group and the hydrogen atom(s) of the neighboring amino groups. It was found that a single hydrogen bond, 2.0−2.2 Å long, was formed when the amino groups were attached to the same carbon ring. The hydrogen bond in the ortho and para positions is longer, ca. 2.2 Å, than in the meta position, ca. 2.0 Å. The ortho position is less favorable for hydrogen bonding because of a nitrogen−nitrogen electron−core repulsion, with the equilibrium distance of 2.6 Å. In turn, the meta position allows the nitrogen−nitrogen distance to be 2.9 Å, i.e., this distance is closer to the van der Waals diameter of the nitrogen atom. Hydrogen bonding between the grafted groups makes the free energy of the respective configuration more favorable.

Figure 6 compares the accuracy of PM7-MD to the accuracy of the M11 hybrid density functional theory48 (HDFT) Born−Oppenheimer molecular dynamics (BOMD) for the 1,2,4,5-tetraaminographene using PM7-MD and M11-HDFT BOMD.

Oppenheimer molecular dynamics (BOMD) for the 1,2,4,5 system, i.e., one of the most complicated amino-FG. The derived pair correlation functions for the carbon−carbon, carbon−nitrogen, and nitrogen−nitrogen atom pairs suggest minimal discrepancies between these methods, while all relevant peaks are reproduced perfectly.

To recapitulate, we used the M11 HDFT electronic-structure calculations and PM7-MD simulations to unravel regularities and peculiarities of structure and thermodynamic properties of amino- and ethylamino-FG. We discovered an unusual, synergistic amination of GRA and characterized the products in detail. A large number of amino-groups stabilize functionalized graphene favoring further amination. In contrast, a small number of amino-groups typically leads to unstable products. The functional groups can be attached on the same side or on different sides of the GRA plane. Steric hindrances play an important role in preventing complete amination and formation of the ultimate FG, C₈(NH₂)₈. The amination reactions bring modest changes in the Gibbs free energy. Many amination positions are thermodynamically forbidden, including ortho, meta, and edge positions. The para position is allowed, irrespective of the substituent. Grafting a single ethylamino group is more energetically favorable compared to a single amino group. Deformation of functionalized GRA is proportional to the number of attached groups. Testable experimentally, the presented results are particularly useful for structure determination experiments and assist in new organic syntheses.

**COMPUTATIONAL METHODS**

Thermodynamic potentials for the selected reactions were derived using molecular partition functions. The wave functions were calculated at the M11/6-311+G** level (hybrid density functional theory),48 followed by calculation of force constants and resulting vibrational frequencies. The self-consistent field convergence criterion was set to 10⁻⁸ hartree. Prior to frequency analysis, all molecular geometries were thoroughly optimized following evolution of energy gradients. The reported enthalpy, entropy, and Gibbs free energy correspond to the gas-phase approximation. According to the developers, M11 provides an improved structure and electronic and thermochemical properties, as compared to earlier functionals.48

The thermal stabilities of amino- and alkylamino-functionalized graphene were investigated using the PM7-MD simulations49−53 at 500 K. After an initial geometry optimization, every system was gradually heated from 0 to 500 K with a pace of 0.025 K/fs. Production runs that were 200 ps long were used to investigate the dependence of FG structure and stability on −NH₂ positions. The equations of motion were propagated with a 0.5 fs time-step using the velocity Verlet algorithm. The system temperature was maintained by means of the Andersen thermostat.54 PM7-MD was successfully applied to a set of problems in chemistry including ion-molecular systems,51 competitive solvation,52 nanoparticles,50 gas capture,53 etc. The present computations were parallelized using 4 processor cores with a speed-up factor of 2.4.

The M11 HDFT-BOMD simulation48 was used to record a 3.000 ps molecular trajectory. The 6-31G* atom-centered split-valence double-ζ polarized Pople basis set was used. The constant temperature, 500 K, was maintained via a simple velocity rescaling every 50 integration steps to obtain the target temperature. The trajectory was propagated with a 0.5 fs time-step.

The PM7-MD simulations were performed using an in-house code (developed by V.V.C). Thermochemistry and HDFT-BOMD were calculated by the GAMESS quantum chemistry program suite. Visualization of the PDB files was performed by VMD 1.955 and Gabedit 2.4.56

**AUTHOR INFORMATION**

Notes
The authors declare no competing financial interest.

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