Computational analysis of hydrogenated graphyne folding

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A B S T R A C T
This letter employs molecular mechanics simulations to analyze the geometric changes of foreign-atom-doped graphyne. Simulation results show that higher the density of dopant and the greater the area covered by the dopant correlates to a greater folding angle of the graphyne sheet. Compared to graphene, graphyne folding could prove to be more effective for various nanodevices based on its unique band gap, especially when doped, and its tunable interactions with and absorption of foreign molecules. Therefore, our findings may offer unique perspectives into the development of novel graphyne-based nanodevices and stimulate the community’s research interest in graphene-related origami.

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1. Introduction

In the past decade, there has been an explosive growth in the development and utilization of novel nanostructured materials. Accordingly, interest in two-dimensional materials such as graphene has raised many folds. It has been shown that this single-atom thick, carbon-based material possesses intriguing and promising properties especially useful for the fields of electronics and material science [1–8]. Because of its unique two-dimensional geometry, this material has a tremendous surface area to volume ratio. Despite its size and two-dimensional geometry, graphene endows surprisingly robust mechanical properties including high values of elastic modulus, ultimate stress, and strength. Graphene’s great conductivity and unique electronic structures have also been exhibited [9–11]. This distinctive set of properties holds enormous potential in the design of future nanotechnologies, such as electronics, filters, biomedical devices, and many other technologies.

Recently, there has been a wealth of literature focused on the properties and functionalities of graphene folding [6,7,12–14]. However, far less is known about its potentially similarly useful allotropes, including graphyne. Graphyne is also a single-atom thick material made of carbon, like graphene, but differs in its bonding. Unlike the bonding in graphene, cyclohexanes are bonded to each other indirectly via a set of acetylenic linkages (−C≡C−) [9,10,15–17]. These single and triple bonds lead to potentially unlimited lattice structures, endowing graphynes with a variety of mechanical [15,18–22], electrical [23–28], and chemical properties [29–31]. There are different forms of graphyne based on the number of acetylene linkages between benzene-like rings and the patterns of the bonds. For example, α-, β-, γ-graphynes have all been defined and vary in their respective bonding patterns [32]. γ-Graphyne is a lattice of benzene-like rings attached to one another by any number of alternating single and triple bonds; as it is the only form of graphyne covered in this work, it shall henceforth be referred to as “graphyne”. Graphyne-n describes the specific type of graphyne where n is an integer describing the number of triple bonds between neighboring benzene rings. For example, graphyne-3 has three triple bonds in a line between two benzenes. For convenience, graphyne-0 is just graphene. These are shown in Fig. 1a and d.

Previously, much of the research into graphynes has focused on the properties of the pure substance [9,15,17,18,32–34]. For example, numerical results from both molecular dynamics (MD) simulations [2,4,7,19,20,35–37] and first-principle calculations [9,24,28,38] showed that the in-plane stiffness of graphyne-n is substantially lower than that of graphene and the band gap of the graphene family is found to be modified by applying strain through various approaches. In this letter, we study dopant-influenced graphyne folding. Using molecular mechanics simulations, we compare how the number of acetylene linkages, doping patterns, and choice of dopant affect the ways in which graphene self-folds. Specifically, we focus on γ-graphynes with n = 1, 2, and 3. Graphyne-1, graphyne-2, and graphyne-3 are shown in Fig. 1b–d to illustrate the different number of linkages. Recent research on graphene has proven that this two-dimensional material can be utilized in DNA sequencing, filtration devices, and other biomedical devices [39,40]. Similarly, we expect that our results can be employed in designing new nanomaterials and hopefully inspire further research into the folding processes and functionalization possibilities of graphyne. Folded graphyne shows potential to be tailored for drug delivery systems, electrical devices, and...
other nanotechnologies. Folded two-dimensional carbon sheets have the capability to encapsulate drugs, respond to magnetic fields, and filter liquids [36–38,41]. All of these properties can be used in the biomedical field. Doping and applying strains to graphynes alters the magnetic and electronic properties of the material [10,11,22,42–48]. This programmability will be useful in the electronic development fields.

2. Computational models and methods

All of the experimentation and production of models are performed using molecular mechanics simulation. All models are created using the same process. First, a repeating unit cell of each type of graphyne is constructed based on similar dimensions from many previous works [9,16,18]. Using these crystals, a sheet is created for each graphyne with 1000–1300 carbon atoms and a width to length ratio of approximately 2:1. These parameters were decided upon instead of a common sheet size because of the variances in lengths of the acetylene linkages for each value of n. The simulation box the sheet is placed in is larger than the sheet itself. Therefore, any out-of-plane behavior and any motion of the sheet that occurs during the minimization process will not be influenced by the boundary conditions. Essentially, these reactions are carried out with aperiodic boundary conditions.

After a sheet is created, dopants are added in some specified patterns by bonding the dopants to the carbon atoms and adjusting the hybridizations of the doped carbons. For example, when a carbon comprising the benzene-like ring is doped, a single bond to a dopant atom is created, and the partial double bonds from the doped carbon to the surrounding carbons in the benzene-like ring are changed to single bonds. The doping patterns are chosen so that there is a sufficient width of graphyne on each side to respond to the dispersive forces of the dopant. Also, doping in the lengthwise direction allows for sheets with shorter lengths to expedite the simulation process. A series of different doping patterns are chosen in order to illustrate the effects of different doing patterns, densities, and areas. These specific doping patterns are used to find local deformations of graphynes for the purpose of providing details for the creation two- or three-dimensional structures in future research. Keeping the dopants in a line, but varying the densities and areas of the dopants, allows for a controlled study of graphyne’s reactions, which can prove to be useful for functionalization studies. Once a sheet is doped and the bonding is altered appropriately, simulations are run.

The same process is carried out for each molecular mechanics simulation. Energy minimization simulations are completed using condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field, an ab initio force field. It has been shown to produce accurate results for simulations with all of the bonding interactions present in carbon-based system. Energy minimizations are set to calculate both van der Waals interactions and Coulomb forces existing within the crystal containing the model. The summation method is atom based. The Fletcher–Reeves and Newton method, based on Broyden–Fletcher–Goldfarb–Shano (BFGS), is used in the minimization process. The cutoff, spline width, and buffer width for both van der Waals and Coulomb forces were set to 12.5, 3, and 1 Å, respectively. The NVT ensemble is used with a constant temperature of 298 K. The type of summation for the long-range electrostatic interaction is Ewald, and conjugate gradient (Fletcher-Reeves) method is used to minimize the energy of the system. Energy minimization is run for 250,000 iterations to ensure no unexpected changes in energy are missed. It is concluded that after a certain amount of steps, the energy minimization has converged for each sample. In this work, the x–y plane is that of the undeformed sheet, while the z direction is perpendicular to the undeformed sheet.

In order to ensure that our results are accurate when graphyne is doped, we first examine how graphyne minimizes its energy under normal conditions, before it is doped. When each type of pristine graphyne is allowed to relax, we have the results displayed in Fig. 2. Our results indicate that increasing n, and thereby increasing the number of acetylene groups, increases planarity of the sheet. The wave-like pattern displayed by graphyne-1 can be explained by previous works. As shown by Liu et al., graphene, or graphene-0, displays “intrinsic ripples” [49]. Cranford and Buehler [15] display how pristine graphyne-1 exhibits ripples as well. This
trend can be explicated by the increased distance between benzene rings. Graphynes with more acetylenic linkages are less dense than graphynes-0 and -1. Since the carbon atoms are spread farther apart, they sustain weaker repulsive van der Waals interactions that would force the sheets out of plane. As a result, the sheets remain more planar.

3. Results and discussions

3.1. Folding angle vs. linkages

Using the afore-mentioned sheets, three hydrogen doping patterns are used to compare the dopant-induced folding angles of graphene-1, -2, and -3. Hydrogen is chosen because of its ease of use and to allow for comparisons to the many former studies on doping graphite with hydrogen [6,7,49,50]. The three patterns vary in aperture angle and density, but all of the doping patterns are in the reclined-chair direction. It is ensured that only the sp² carbons of the benzene rings are doped; this alters the hybridization of the doped carbons to sp³ and changes the aromaticity of the ring. It has been shown that doping the sp² carbon atoms in the graphene rings results in the greatest stability [11,48]. The bonding of hydrogen atoms results in a strong attraction to their respective carbon atoms. The hydrogenated carbon atoms must transition from a planar sp² hybridization to a tetrahedral sp³ hybridization to adjust for the extra bonding [6]. Also, each of the surrounding carbon atoms experiences a repulsive force. Driven by van der Waals interactions and the change in molecular geometry, there is a local deformation of the graphene sheet as the surrounding carbons are pushed away from the hydrogens [6,7,48], resulting in designed deformations of the sheet.

It has been shown that the degree of bending induced in the graphene sheets is related to the number of acetylenic linkages (n) in the graphene. This is a result of the varying hardness and bending stiffness associated with the sheets. Also, the distances between neighboring carbon atoms and the dopants affect the angle. Recent studies by Cranford [15] and Becton [41] indicate that the mechanical properties, including bending stiffness and hardness of graphene, are very similar to those of graphene-1. Since there is a single acetylenic linker between benzene-like rings in graphene-1, and triple bonds are harder to rotate than single bonds, graphene-1 is almost as stiff as graphene. However, once n exceeds one, the hardness and bending stiffness decrease drastically. The presence of the easily-rotated single bonds on the longer sets of linkers between benzylic rings allows these sheets to bend more readily and gives them a more elastic property. Hou [35] also pointed out that the effective bond density decreases as n increases. No matter how densely the graphene sheet is doped, there are fewer carbons close enough to experience any repulsive force of the dopant. Although graphynes with higher values of n are less resistant to bending, more dopants are needed over a wider area to induce smaller bending angles.

Three doping patterns are studied to compare graphene-1, -2, and -3. Doping Pattern #1 is characterized by a narrow line of hydrogens that are densely packed. Doping Pattern #2 has a large doping area, but it is less densely doped. Doping Pattern #3 has a high density of hydrogen doping, and the doping area is wider. Each of these patterns is shown in Fig. 3, subfigures a, e and i. The greater the density of dopant, the stronger the bending forces. With a wider doping area comes a higher chance for multiple bends. Multiple bends in a sheet result in multiple angles. These angles can either have a large impact on the overall geometry of the sheet or have a miniscule one. When two angles are formed, the initial angle between lines of dopants is formed first during the minimization process, and it has little effect on the final geometry of the graphene sheet. To measure the bending at local carbons in the bending regions, angles are measured from the center to the edges of the doping width, as shown in Fig. S1 (in Supplementary Materials). The second angle to form in during the energy minimization is the β bending angle. This is the angle that truly defines the overall bending, and therefore is referred to as the effective bending angle. The effective bending angle (β) is defined to be the angle produced between the halves of the sheet outside of initial angle within doped lines. The effective bending angle in Fig. 4 is the angle denoted as β in Fig. 3. The angle is formed outside of the width of all dopants, from the outer lines to the edges of the sheet. By measuring the angle from one far end of the graphene sheet to the outside line of dopants, denoted as angle μ, we can approximate that the opposite angle is identical since both sides of the sheet are of equal length, making an isosceles triangle. Knowing angle μ allows us to calculate the bending angle, β as shown in Fig. S2. Angle β can be found using this approximation and simple geometry. The reported angles are averages of all angles measured from equilateral points along the lengths of the sheets as shown in Fig. S3.

Doping Pattern #1 has only one bending angle because of the narrow doping pattern used. Therefore, the β bending angle is the only angle formed, as illustrated in the figure. Doping Patterns #2 and #3 have multiple lines of benzene rings that are doped. This produces multiple angles. Fig. 4 summarizes the results of the energy minimizations for all cases. The higher values of n correspond to a steeper change in angle as a result of initial doping. This is most likely a result of the relative stiffness of each graphene. As n increases, the number of weaker C-C single bonds increases, and the modulus of elasticity for the sheet decreases [17,18,41]. The softer graphynes react more quickly to the doping by bending more easily. However, once a very large amount of area is doped very densely, graphene-1 produces the greatest change in bending angle. The increasing area of dopant and increasing density of dopant have an overall effect of decreasing the effective bending angle, and increasing the change in angle.

Analysis of the energy minimization potential and non-bonding energies reveals that when two angles are formed, two separate dips in energy occur. These two dips are illustrated in Fig. 5. The energy minimization step-by-step process displayed in Fig. 6 is graphene-1 when doped with Pattern #3. Initially, the doped carbons rise slightly and push the distal end of the sheet downward (Fig. 6a). This quickly forces the sheet the curve, but planarity of the ends is quickly regained as a result of van der Waals forces (Fig. 6b). The sheet curves and returns to planar halves during the almost level portion of the energy graph (Fig. 6c). The angle between lines of dopants is the first to form, and the energy graph displays a second drop when the β angle forms (Fig. 6d). Once the medial portion of the sheet has formed the effective bending angle, the distal half of the sheet must follow (Fig. 6e and f). This is a result of the localized dispersive forces applied by the hydrogen. Then, once again,
Fig. 3. Results of Doping Patterns #1, #2, and #3. (a, e, i) the Doping Patterns #1, #2, and #3; (b–d) the results of energy minimization of graphyne-1, -2, and -3, respectively; (f–h) the energy minimization results of graphyne-1, -2, and -3, respectively; (j–l) the energy minimization results of graphyne-1, -2, and -3, respectively.

Fig. 4. Comparison of the effective bending angles versus number of linkers.

Fig. 5. Energy minimization graph for the formation of two angles.
van der Waals forces allow the ends of the sheet to complete the β angle and become planar once again (Fig. 6g). The bending angle used for comparisons was the angle that resulted after the structure was completely relaxed. The structure was deemed to have finished the minimization process after at least one extra minimization simulation was run till the structure did not change any more and the energy in the system remained constant. Extra simulations were run to ensure the structure was relaxed even in the case that a local minimum was found. After the appropriate graphyne has been selected for specific designs of novel nanotechnologies, these results can be tailored for the geometrical designs.

Another simulation was run to analyze the folding when graphyne is doped on both sides. The doping pattern used has the lowest density and area compared to the other patterns used. If adatoms are placed directly oppositely, the van der Waals pressure exerted by the electron orbitals cancel out, and folding does not occur. However, if the dopants are placed on opposite sides but not directly oppositely, then folding occurs similar to the way it does when a single side is doped. When the length of the sheet is kept as the same used for the single-side doping patterns, the dual-sided doping pattern results in an angle decrease of about 20° as shown in Fig. S4 (a) of the supplementary material. However, in an attempt to make keep the distance from dopant to sheet edge consistent with single-sided doping trials, there is an angle increase of about 7° as shown in Fig. S4 (b).

3.2. Doping patterns vs. folding patterns

In order to study the different folding effects of hydrogen patterning, we restrict our models to only include graphyne-1. We use the same original sample sheet that was used for graphyne-1 in the previous section. In the first trials, only benzene rings are doped, as hydrogenated graphynes are more stable in this way. The doping patterns for benzene doping are shown in Fig. 7. These patterns include the patterns used previously and an additional three patterns. The added doping patterns allow for a more gradual transition from a low doping density and low doping area to a high doping density and high doing area. The resulting β angles are displayed below the corresponding doping patterns. As a general trend, the more densely packed the hydrogens are, and the more area covered by the hydrogens, producing multiple bends, the smaller the resulting angle. The more hydrogen bonded within a small area the larger the bending force. As the electron clouds of the atoms are forced closer together, they require more room, meaning that the surrounding carbon atoms must move farther away to minimize the strain energies. When two bends are produced by a wider hydrogen distribution, the angles of each of these are effectively added together to form the β bending angle. The multiple angles result in a larger overall angle than the angle produced by a narrow line of dopants. Fig. 8 shows the graphical representation of the comparison of these effective bending angles. As described before, the change from graphyne’s planar, 180° sheet, increases as the doping density and area of doping increases.

Although doping only the benzenes in graphyne results in greater stability, hydrogens preferentially bind to sp² carbons on the acetylenic linkages under normal conditions [48]. When doping along the linkages, the bonding between carbons is altered. All of the triple bonds along the doping line are changed to double bonds as the π electrons are used to bond the hydrogens, and the hybridization of these carbons changes to sp². Once again, only graphyne-1 is considered in these trials, and the sheet used initially has the same dimensions as the previous trials for graphyne-1. As shown in Fig. 9a, the first sheet is doped along the reclined-chair direction, resulting in a straight line of hydrogens separated by benzene rings. Also, graphyne is doped along its shorter length. Interestingly, instead of producing a distinct angle along the dopant line, this patterning resulted in a curvature in the direction perpendicular to the expected bending. Fig. 9b and c show the structure that forms in response to the energy minimization. This is a result of the major forces being applied to neighboring hydrogens, instead of to neighboring carbons. The reason for the different bending may be attributed to the relative distances of neighboring atoms. The closest carbons that will experience the bulk of the van der Waals forces are the neighboring, doped carbons and the neighboring benzylic
Fig. 7. Doping patterns and corresponding effective bending angles produced after minimization. (a–c, g–i) The doping patterns from 1 to 6; (d–f, j–l) the resulting structure and bending angles after minimization.

carbons. From Fig. S5, we can see that these are 1.6 and 1.2 Å away from the nearest doped carbon. The next closest carbons are 2.75 and 3.57 Å away. The undoped carbons may be so far away from the dopants’ van der Waals that they are hardly affected at all by their electron clouds. Fig. 9c shows a slight indentation along the doping line, indicating that the local, undoped carbons are affected by these forces; but, they do not experience the bulk of the forces. The added distance from dopant to undoped carbons results in the curvature exhibited.

In the following trial of acetylene doping, we use a similarly sized sheet, but this time it is oriented so that the reclined-chair direction runs the width of the sheet instead of along the length. Its dimensions are shown in Fig. 10a. Fig. 10 is very similar to Fig. 9. However, the graphyne sheet has dimensions opposite to those from Fig. 9. The doping pattern is in the same direction in both figures, but the length is much longer, and the width is much shorter. This means that the line of dopants is much longer, based on the direction and size of the sheets. The added length of dopants gave the sheet more room to curl into a tubular pattern. Other than the size difference and the amount of dopant that was used, every other variable was held constant from Fig. 9 to Fig. 10.

By altering the lengths of the sheets we found that a nanoscroll can be formed in some cases, but not in others. With additional simulations, varying the length of the graphyne sheets results in the two patterns shown in Fig. S6, a nanoscroll and a broad, circular shape. At very short sheet lengths and at very long sheet lengths, a curvature is formed. However, at an intermediate length,
like in the trial at 95 Å in Fig. S6 (b), a nanoscroll will be formed. In the study of nanotubes, transport, or other fields, these results may provide promising and intriguing design strategies. A cylindrical graphyne sheet with such an engineered radius may be able to transport or encapsulate proteins, cells, or drugs to be used in the fields of biomedical nanotechnologies and drug delivery systems.

3.3. Alternative dopants

Previous studies, like those analyzing carbon nanoscrolls [49], have suggested that alternating dopants can better control the desired curvature and angle of graphynes. Here, we analyze how the folding angle of graphyne-1 changes when the dopant is changed. We use the same doping patterns and sheet dimensions already used previously to allow for accurate comparisons. In the first trials, we change the dopant to fluorine. Results of the minimization are illustrated in Fig. 11. The main effect fluorine has, other than the torsional effects on Doping Pattern #3, is a smaller bending angle for lower densities and areas of dopant. Once the doping area and density are high enough, as seen in Doping Patterns #5 and #6, hydrogen produces a smaller bending angle. This may be a result of fluorine’s higher electronegativity. The larger electron clouds of fluorine may contribute to the difference in bending angle and the torsion (shown in Fig. 11c). In the very narrow and densely doped pattern, the large van der Waals radii of fluorine may force the neighboring fluorine atoms and doped carbons to bend out of plane as was seen when the acetylenic linkages were doped. The additional strong forces displayed by fluorine are most likely the cause of the two-dimensional bending. Other than the previously-mentioned differences in bending, the trends of results from each dopant from pattern to pattern are similar. This may stem from between hydrogen and fluorine in terms of their small size and single-bond forming properties. To further test the effects of dopants, nitrogen, silicon, and sulfur were used, and the

![Fig. 9. (a) Doping pattern along linkages; (b) view perpendicular to the z-axis after minimization; (c) view along the z-axis after minimization.](image)

![Fig. 10. (a) Dimensions of graphyne sheet and doping pattern; (b) view perpendicular to the z-axis after minimization; (c) view along the z-axis after minimization.](image)
resulting angles are compared graphically in Fig. 12. These elements were chosen purely for theoretical study, and were used in an attempt to find a correlation between properties of dopants, such as Van der Waals radii, molecular weight, and electronegativity, and resulting bending angles in graphyne. Each change in dopant results in a change in angle. Though, they all tend to follow the same trend as their densities and areas increase. However, there does not seem to be a correlation between bending angle and either atomic radii or electronegativity, respectively.

4. Conclusions

This work has examined and compared the ways in which the number of acetylenic linkages, types of doping patterns, and varying dopants affect the minimized geometries of sheets of graphynes. We conclude that more flexible graphynes with higher values of \( n \) respond more quickly to doping, but all graphynes follow the same trend of decreasing their effective bending angles as the amount of dopant and area of dopant are increased. When multiple angles are produced, there is a great change from its original planarity. The choice of doping ring structures for stability results in a continuous bend in a graphyne sheet that is dependent on the amount and area of dopant. When linkages between the benzene-like rings are doped, energy minimization of the sheet produces a curvature in the opposite direction. Various dopants all produce the same trend in bending angles, but each provides a different degree of bending. Based on these results, this study should serve as a basis for studying the functional possibilities of graphynes, and further research should be conducted to compliment this.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2016.01.025.

References
