

Third conformer of graphane: A first-principles density functional theory studyA. Bhattacharya,^{1,*} S. Bhattacharya,^{1,†} C. Majumder,^{2,‡} and G. P. Das^{1,§}¹*Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India*²*Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

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We propose, on the basis of our first-principles density functional based calculations, an interesting isomer of graphane in which the C-H bonds of a hexagon alternate in three-up-three-down fashion on either side of the sheet. This two-dimensional puckered structure, called “stirrup,” has an intermediate stability between the previously reported chair and boat conformers of graphane. The physicochemical properties of this conformer are found to be similar to the other two conformers of graphane with an insulating direct band gap of 3.1 eV at the Γ point. Any other alternative hydrogenation of the graphene sheet disrupts its symmetrically puckered geometry and turns out to be energetically less favorable than these three conformers.

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The discovery of graphene,¹ the two-dimensional (2D) array of hexagonal units of sp^2 -bonded C atoms, has initiated considerable scientific interest in this decade with its unusual electrical and mechanical properties.² The nanoribbons and nanoflakes of graphene show high magnetic moment depending upon their edge states.³ Graphene nanosheet has been used for storage of molecular hydrogen.⁴ Recently, a fully hydrogenated graphene sheet, called graphane, which is an “extended two-dimensional covalently bonded hydrocarbon” having a formula unit CH, was predicted by Sofo *et al.*⁵ Subsequently, this compound has been synthesized in the laboratory,⁶ and various interesting properties of this two-dimensional sheet, such as reversible hydrogenation-dehydrogenation,⁶ insulating wide-band gap,^{5,7} magnetization by partial dehydrogenation of the sheet,⁸ etc., have been reported. This hydrocarbon was reported to have two possible conformers, viz. “chair” and “boat,” having a 2D puckered honeycomb like structure with one hydrogen atom bonded covalently (sp^3) to each carbon atom of the sheet.⁵ In the chair conformer, the H atoms attached to the C atoms of the sheet alternate on both sides of the sheet [one up, one down, as in Figs. 1(a) and 1(b)] while in the boat conformer, the C-bonded H atoms alternate in pairs [two up, two down, as in Figs. 1(c) and 1(d)]. It has been shown by Sofo *et al.* that these conformers of graphane have higher binding energies compared to many known members of the hydrocarbon family (methane, cyclohexane, polyethylene, acetylene, and benzene) with an insulating direct band gap at the Γ point. The objective of this Brief Report is to present our first-principles based prediction of the existence of a different conformer of graphane. We name this conformer “stirrup,”⁹ which has an intermediate stability between the chair and boat conformers of graphane. The structural and physical properties of this conformer have been compared with the other two conformers of graphane and are discussed here in detail.

Our calculations have been carried out using first-principles density functional theory (DFT)^{10,11} based on total-energy calculations using VASP¹² code. We have compared our results with local density approximation (LDA) and generalized gradient approximation (GGA) using different exchange correlations. For both LDA and GGA calculations we have used projected augmented wave (PAW) potential¹³ for all

elemental constituents, viz. H and C. We have compared our results using Ceperley-Alder (CA)¹⁴ exchange correlation for LDA calculations and Perdew-Wang (PW91)¹⁵ and Perdew-Burke-Ernzerhof (PBE)¹⁵ exchange correlations for GGA calculations. An energy cutoff of 600 eV has been used. The k mesh was generated by the Monkhorst-Pack¹⁶ method and the results were tested for convergence with respect to mesh size. In all our calculations, self-consistency has been achieved with a 0.0001 eV convergence in total energy. For optimizing the ground-state geometry,^{17,18} atomic forces were converged to less than 0.001 eV/Å via conjugate gradient minimization.

In order to analyze the stability of the structure we have implemented *ab initio* molecular dynamics (MD) simulation using a Nose thermostat.¹⁹ The Mulliken population analysis²⁰ and vibrational frequency analysis have been carried out by using DMOL3 code,²¹ where the GGA calculations are performed by PW91 exchange correlation. A double- ζ numerical basis set with a polarization function (DNP) has been used.

In the stirrup⁹ structure [Figs. 1(e) and 1(f)] proposed in this Brief Report, each carbon atom is bonded to a hydrogen atom in such a way that three consecutive H atoms of each hexagon alternate on both sides of the sheet (i.e., three up, three down), in contrast to the chair or boat conformer, where the H atoms alternate singly or pairwise in either side of the C plane, respectively. Figure 1(e) shows a stirrup hexagonal unit with three H atoms pointing up and three pointing down the C plane (encircled in blue and red, respectively). The space group, lattice parameter, atomic positions, bond lengths, and the physical properties of all three conformers are listed in Table I. In the stirrup conformer, the angles that each H-C bond makes with the three adjoining C atoms of the sheet (\angle HCC) are about 107.3°, which is close to the \angle HCC bond angle in the chair conformer (107.4°). The boat conformer has the lowest \angle HCC bond angle of 107.1°. Therefore, the \angle HCC bond angles in all three conformers suggest a tendency towards sp^3 hybridization ($\Phi_{sp^3} = 109^\circ$). The stirrup conformer has two different \angle CCC bond angles, which are close to \angle CCC bond angles in the chair conformer (Table I). All the C-H bond lengths in the chair conformer are 1.10 Å while the C-H bond lengths in boat and stirrup conformers are equal and higher than those in the chair conformer (1.11 Å). The chair and stirrup conformers have a constant value of C-C bond lengths throughout the

TABLE I. Comparison of input structural parameters and optimized ground-state properties of the three conformers of graphane.

Properties			Chair	Boat	Stirrup
Space group			$P\bar{3}M1$ (164)	$PMMN$ (59)	$PMNA$ (53)
Lattice Parameter(Å)	a		2.46	2.46	2.46
	b		2.46	4.26	10.00
	c		10.00	10.00	4.26
Atomic positions	H	X	0.666 667	1.000 000	1.000 000
		Y	0.333 333	1.259 391	0.651 931
		Z	0.352 310	0.638 576	0.470 709
	C	X	0.666 667	1.000 000	1.000 000
		Y	0.333 333	1.182 504	0.551 700
		Z	0.456 925	0.533 077	0.358 844
Bond lengths (Å)	C-C		1.53	1.53, 1.57	1.54
	C-H		1.11	1.10	1.10
Bond angles	HCC		107.4	107.16	107.3
	CCC		111.5	110.7, 112.3	111.2, 112.4
Band gap (eV)			3.1	3.3	3.14
Vibrational freq. of highest freq. mode (cm^{-1})			3080	3233	3167
Mulliken population Analysis (electrons)	C		-0.09	-0.12	-0.10
	H		0.09	0.12	0.10

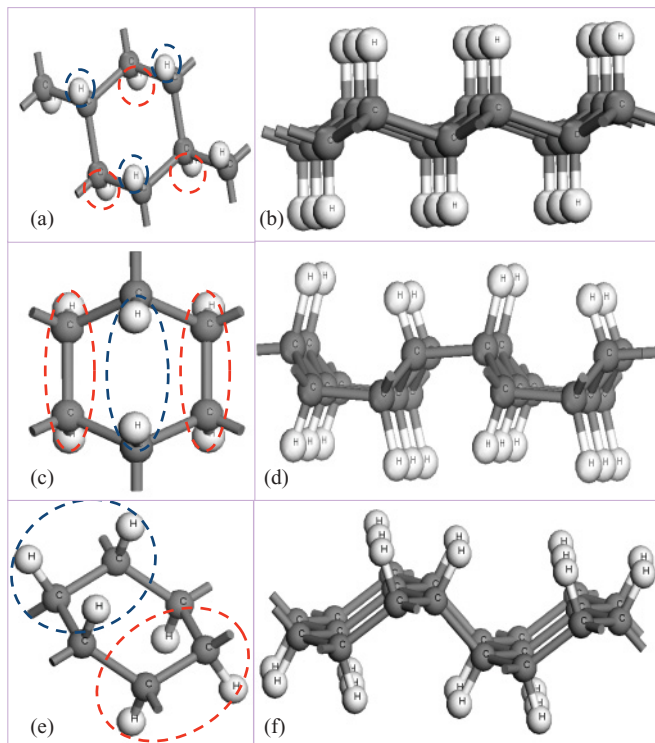


FIG. 1. (Color online) Ball-and-stick model of the chair, boat, and stirrup conformers, with black balls representing the carbon atoms and white balls representing the hydrogen atoms. The H atoms pointing up and down the C plane are encircled in blue and red, respectively. (a), (c), and (e) show hexagonal unit of chair, boat, and stirrup conformers, respectively. (b), (d), and (f) show the lateral view of chair, boat, and stirrup layers, respectively.

chair (1.53 Å) and stirrup conformers (1.54 Å) while the boat conformer of graphane has two different C-C bond lengths [Figs. 1(c) and 1(d)], due to the repulsive interaction between H atoms lying on the same side of the plane. The binding energy (BE) of the specific conformer having n number of C and n number of H atoms in one unit cell is calculated by the formula

$$BE = \frac{E_{\text{tot}}(\text{conformer}) - n \times E_{\text{tot}}(\text{C}) - n \times E_{\text{tot}}(\text{H})}{2n}.$$

We have implemented three different exchange correlations to compare our results. These results are enlisted in Table II. Our GGA based calculation under PW91 and the PBE exchange correlation show exactly equal BEs for all three conformers. We find that the chair conformer has a BE of 5.19 eV/atom, which is followed by the stirrup and boat conformers with a BE of 5.17 and 5.14 eV/atom, respectively. Comparing with Table I of Ref. 5, we find that our estimated BE values are consistently lower than those of Sofo *et al.*, although the relative trend in magnitude remains unchanged. In order to establish our results, we have performed LDA

TABLE II. Comparison of the ground-state stabilities of the three conformers as obtained by varying the exchange correlations.

Conformers	BE (eV/atom)		
	PBE (GGA)	PW91 (GGA)	CA (LDA)
Chair	5.19	5.19	5.83
Boat	5.14	5.14	5.78
Stirrup	5.17	5.17	5.81

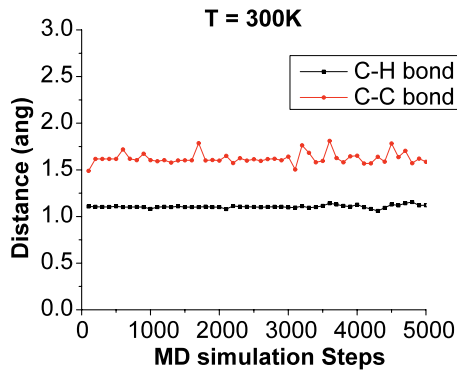


FIG. 2. (Color online) Molecular dynamics simulation showing the average relaxation of C-H and C-C bonds at 300 K with 5-ps time period and 1-fs time step.

calculations under CA exchange correlation, which yields a higher magnitude of BE values but a similar relative trend, as shown in Table II.

The interlayer bonding between two stirrup layers is found to be negligible, which is similar to that of the other conformers of graphane. This is a consequence of the saturated bonding between the C and H atoms in the sheet. In order to verify the stability of the structure, we have performed a 5-ps *ab initio* molecular dynamics simulation using the Nose algorithm²⁰ with a 1-fs time step and a 5000 self-consistent-field run. Our detailed MD simulation suggests that the stirrup structure is quite stable at high temperature (~ 1000 K). In Fig. 2 we have plotted the average relaxation of the C-C and C-H bonds with the increase in time step as estimated at room temperature ($T = 300$ K). The average bond distances do not vary considerably throughout the MD run, which does suggest that it is possible to realize the stirrup structure at room temperature (300 K).

The salient features of the electronic structures of the stirrup conformer can be seen from the band structure in the $\Gamma \rightarrow M \rightarrow K$ plane and the site-projected densities of states (*p*-DOS), as shown in Fig. 3. As is well known, a pure graphene sheet, the dehydrogenated counterpart of graphane, is a semimetal with its valence band and conduction band merging to a Dirac cone at the Fermi level. However, the hydrogenation of the graphene sheet leads to opening of the band gap, with a concomitant increase in the inherent stability of the single sheet 2D material. The stirrup structure is found to have a band gap of 3.14 eV which is nearly the same as that of the chair (3.1 eV), while the boat conformer has the highest value (3.3 eV) among the three conformers. This is

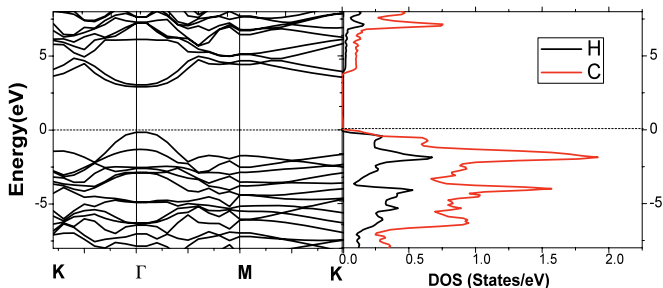


FIG. 3. (Color online) Band structure and density of state (site projected) plots of a stirrup conformer.

in conformity with the results of Sofo *et al.* who had also predicted the boat conformer to have higher band gap than the chair. All three conformers have a direct band gap at the Γ point (Fig. 3). From the *p*-DOS plot, hybridization between the H and C atoms of the sheet can be seen in both the occupied and the unoccupied parts of the DOS (Fig. 3). We have also carried out a spin polarized calculation of the sheet and found the spin-up and spin-down DOS to be identical, thus ruling out any signature of ferromagnetism in the system.

In order to calculate the charge distribution between the C and H atoms of the stirrup conformer, we have deployed the Mulliken population analysis scheme. The stirrup structure shows an electronic charge state of 0.10 electrons for the H atoms while the C atoms have a charge state of -0.10 (Table I). The corresponding Mulliken charge for H atoms in chair (0.09) and boat (0.12) conformers are shown in Table I. It is to be noted that the Mulliken population analysis of a benzene ring also shows an electronic charge state similar to the chair conformer of graphane. However, the boat conformer undergoes larger charge transfer (from the C to H atoms), as compared to the chair and stirrup configurations, thereby leading to the weakening of the C-C bonds in it. In order to show the nature of bonding between the H and C atoms, we have shown the orbital and charge-density contour plots of the stirrup conformer (Fig. 4). From the highest occupied molecular orbital (HOMO) plot of the stirrup conformer, hybridization between the *s* and *p* orbitals of carbon can be seen [Fig. 4(a)]. The figure also shows a bonding orbital between the *s* orbital of hydrogen and *p* orbitals of carbon atoms. The charge contour plot of the plane perpendicular to the C plane [Fig. 4(b)] shows a high charge density (violet) between the C-H and C-C bonds of the stirrup conformer, which confirms a sharing of electrons between the H and C atoms of the sheet. Thus it suggests a covalent nature of bonding among the atoms of the sheet.

We have carried out vibrational frequency analysis on a 4×4 supercell of the stirrup conformer with 16 Å vacuum. It shows positive frequencies for all the normal modes of vibration of the stirrup conformer, indicating the inherent stability of the structure. The highest vibrational frequency mode of the stirrup conformer corresponds to the C-H stretching mode, and occurs at a frequency of 3167 cm^{-1} . This frequency is IR active and is found to lie between the highest stretching mode vibrational frequency of the chair and the boat conformers (Table I), which is in accordance to the order of their stability.

Apart from the three conformers discussed above, we have also carried out some test calculations for other configurations, such as four up–two down, five up–one down, etc., in one hexagon. However, these structures (configurations) are found to be energetically less favorable (by ~ 0.13 eV/atom or more) with respect to the stirrup conformer. Thus any attempt (other than these three conformers) to increase the number of C-H bonds on one side of the sheet disrupts the parity as well as the periodic puckered nature of the structure. A detailed physical insight into this problem of double sided hydrogen coverage and the associated strain was dealt with using cluster expansion approach.²²

In summary, we present here our first-principles DFT based calculations to propose a different conformer of graphane, called stirrup. This structure has an intermediate stability

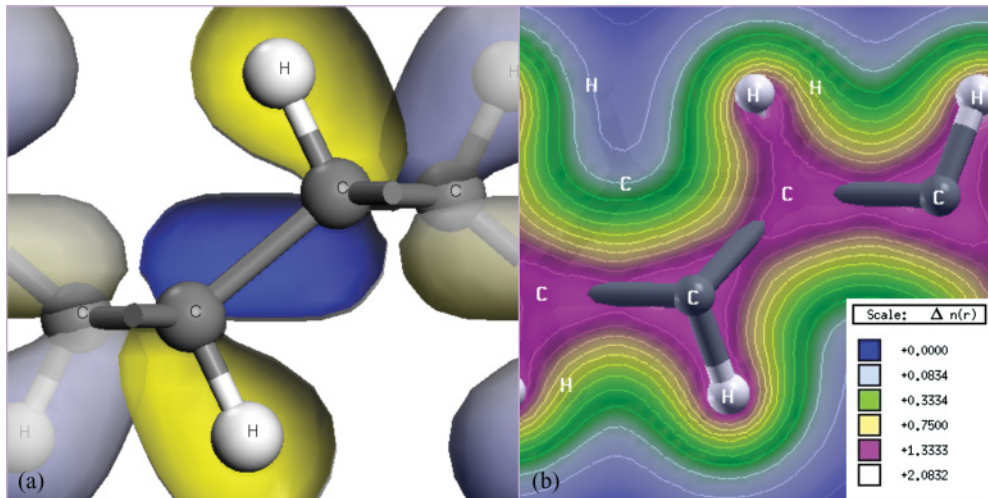


FIG. 4. (Color online) Lateral view of stirrup structure showing (a) orbital plot of highest occupied molecular orbital (HOMO), (b) charge-density contour plot perpendicular to the C plane.

between the chair and boat conformers of graphane. The ground-state electronic properties of this conformer have been compared to the other two conformers of graphane and are found to be similar. It is an insulator with a direct

energy-band gap of 3.1 eV at the Γ point. Any other alternative hydrogenation of the graphene sheet disrupts the symmetric puckered geometry of the structure and turns out to be energetically less favorable.

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