Ab-initio investigation on the stability of H-6 Carbon - Electronic Supplementary Information

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A few years ago H-6 Carbon had been proposed as an all sp^2 three-dimensional Carbon allotrope, with mechanical properties comparable to graphene. However, results on the stability of H-6 Carbon presented in the literature are rather contradictory and confusing, and it is not yet clear if this hypothetical allotrope is stable or not. Studying systematically the stability of H-6 Carbon, using ab-initio density functional theory and phonon band structure calculations, we show that H-6 Carbon is unstable, converted spontaneously to diamond. According to our findings, the instability mechanism is not the same with that of compressed rhombohedral graphite, but is related to the synergetic action of the interchain interactions of the parallelly arranged zig-zag chains and the strain induced by the 60° rotation (with respect to graphite) of the interconnected zig-zag chains. This synergetic action eliminates the barrier provided by the intrachain interactions, causing the transition of H-6 Carbon to diamond.

1 Details from the optimization of the H-6 Carbon structure

The optimized unit cell lengths a and c of either H-6 Carbon or diamond, depend only on the functional used, they are independent of the number of k-grid points and the mesh cutoff values used in our calculations, and of course they are different for H-6 Carbon and diamond. Their values ($a = a_{H6}$ and $c = c_{H6}$ for H-6 Carbon, and $a = a_{dia}$ and $c = c_{dia}$ for diamond) are presented in the first column of Tab. 1.

Optimizations do not affect the fractional coordinates of H-6 Carbon or diamond, which remain the same with those presented in section 2 of the main manuscript.

The total energy per atom of the optimized structures obtained from those optimizations for the specific values of k-grid points and mesh cutoff value are also presented in Tab. 1.

Based on these findings we conclude that either H-6 Carbon is stable, (but there is a small energy barrier between H-6 Carbon and diamond, which was overcame during the optimization, whenever diamond structure was found as the optimum structure), or H-6 Carbon is unstable, corresponding to a saddle point of the PES. The calculations presented in subsection 3.1 of the main manuscript show that H-6 Carbon structure is unstable, corresponding to a saddle point of the PES and not to a true energy minimum.

Functional, a and c (Å)	Mesh cutoff	k-grid points 16x16x7	24x24x10	32x32x14
LDA-CA $a_{H6} = 2.624$ $c_{H6} = 6.363$ $a_{dia} = 2.506$ $c_{dia} = 6.140$	100	-154.5305 H-6	-155.4046 diamond	-154.5299 H-6
	200	-155.4043 diamond	-154.5303 H-6	-154.5302 H-6
	300	-155.4042 diamond	-154.5301 H-6	-154.4046 diamond
GGA-PBE $a_{H6} = 2.656$ $c_{H6} = 6.416$ $a_{dia} = 2.532$ $c_{dia} = 6.203$	100	-162.3113 diamond	-162.3113 diamond	-162.3112 diamond
	200	-162.3129 diamond	-162.3129 diamond	-162.3129 diamond
	300	-161.4729 H-6	-162.3139 diamond	-162.3138 diamond

Table 1 Total energy per atom in eV units of the optimized structure for the specified functional, mesh cutoff value (in Ry units) and Monkhorst-Pack k-grid points. With "H-6" and "diamond" below each energy value, we indicate whether H-6 Carbon or diamond structure was found as the result of the optimization. The values of a and c of the optimized structures for the corresponding functional are shown in the first column.

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2 Details of the TB Hamiltonian used by Tamor and Hass

As already mentioned in the main manuscript, the TB Hamiltonian used by Tamor and Hass utilizes the Slater-Koster[1] parameters of Tománek and Louie[2] for first nearest neighbour interactions. The SK parameters for the interatomic distance d are scaled as $V_{ll'm}(d) = V_{ll'm}(d_0)(d_0/d)^2 f_c(d)$, where $d_0 = 1.42$ Å and $f_c(d)$ is a cutoff function defined to be 1 if $d \leq 1.7$ Å, 0 if $d \geq 2.4$ Å and $(1 - \sin[\pi(d-2.05)/0.7])/2$ if $1.7 < d < 2.4$ Å. The cohesive energy U_{coh} is $U_{coh} = U_{atr}/N + U_{rep}/N + \psi_1 n_b^2 + \psi_2 n_b$, where U_{atr} is the sum of the eigenenergies of the occupied spin states, U_{rep} is a sum of pair potentials $E_{rep}(d_{ij})$ of the form $E_{rep}(d) = e^{-3\varepsilon}(U_0 + U_1\varepsilon + U_2\varepsilon^2) f_c(d)$, where $\varepsilon = d/d_0 - 1$, n_b is the number of bonds per atom defined as $n_b = \sum_{i>j} f_c(d_{ij})/N$ and U_0, U_1, U_2, ψ_1 and ψ_2 are constants.

Obviously, the use of the cutoff function f_c is a convenient way to describe a smooth decay of FNN interactions for $d > 1.7$ Å, and ensures that any SNN interactions with interatomic distances $d > 2.4$ Å are eliminated. As already discussed in the main manuscript, such a decay introduces unphysical interactions between atoms with interatomic distances in the range $[1.7, 2.4]$ Å and must be used very carefully. If the results of interest depend on such interatomic interactions, then the energy calculations will be affected by the unphysical nature of the cutoff function f_c, and it is most likely that they will be wrong.

As already mentioned in the main manuscript, the 1-4 interaction is under the influence of the unphysical effects introduced artificially by the f_c function, and therefore, the energy calculations along the transition pathway, which are used for the calculation of the energy barrier, are not reliable.

For a more reliable estimation of the energy along the transition pathway, we present in the main manuscript two different sets of calculations for the cohesive energy U_{coh}, using the TB method of Tamor and Hass, but with $f_c(d) = 1 - \theta(d - d_0)$. For the one set, $d_0 = 1.7$ Å and for the other, $d_0 = 2.2$ Å. As already mentioned in the main manuscript, the former ignores the 1-4 interaction for $d_{14} > 1.7$ Å and the latter, for $d_{14} > 2.2$ Å. Thus, there are not differences between the two sets of U_{coh} values for $d_{14} < 1.7$ and $d_{14} > 2.2$ Å, but they are differences for $1.7 < d_{14} < 2.2$ Å. For d_{14} slightly smaller than 2.2 Å, (where the 1-4 interactions are still weak), the U_{coh} values of the former set are rather more reliable. For d_{14} slightly larger than 1.7 Å, (where the 1-4 interactions are stronger), more reliable are the U_{coh} values of the later. Therefore, a more reliable estimation of U_{coh} as a function of λ can be found if we take the lower energy branches of the cohesive energy curves for $d_0 = 1.7$ Å and $d_0 = 2.2$ Å of Fig. 3(c) of the main manuscript, up to their crossing point, as shown with ΔU_{TB} in Fig. 3(f).

References

1 J. C. Slater and G. F. Koster, *Phys. Rev.*, 1954, **94**, 1498–1524.

2 D. Tománek and S. G. Louie, *Phys. Rev. B*, 1988, **37**, 8327–8336.