New class of carbon allotropes

UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI FISICA

F. Delodovici[1], N. Manini[2], D.Proserpio [3], L. Burchfield[4], M. Al Fahim [5]

[1,2] Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy
[3] Dipartimento di Chimica, Università di Milano, Via Golgi 12, 20122 Milano, Italy
[4,5] Alfields, Inc. PO Box 3091, Richland, WA 99354, USA

Introduction

In this work we study two new carbon allotropes consisting in a combination of sp^2 and sp^3 hybridized atoms: single-ring novamene and protomene. We carry out a detailed computational analysis, based on DFT techniques, of their structural and electronic properties. We analyze their structural stability, finding that these new allotropes are just less stable than diamond and graphite [1]. We investigate the possibility of induce a transition from metallic to semiconductor regime, by switching the sp^2 to sp^3 with a small energy cost. We also suggest how hundreds new allotropes of carbon could arise by the combinations of simple sp^2 carbon structures.

Method

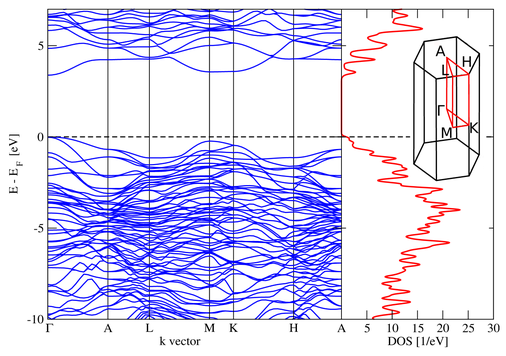
To obtain a reliable equilibrium structure for the single-ring novamene and protomene, we resort to DFT simulations. We study the electronic structure by mean of the local density approximation (LDA) and of the generalized gradient approximation (GGA). A plane-waves basis is used with a kinetic energy cutoff of 408 eV, with standard ultrasoft pseudopotentials to account for the 1s core electrons of carbon as implemented in the Quantum Espresso package [2].

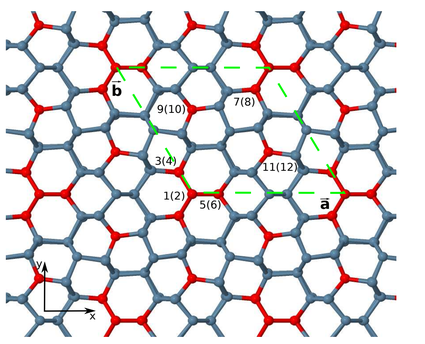
Simulations

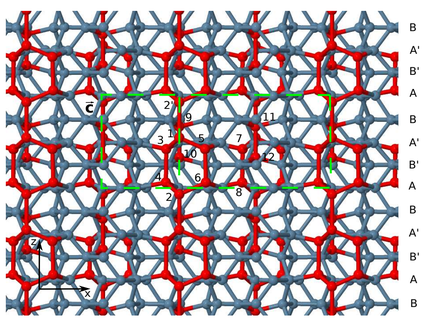
- The starting point: initial rough configuration built from symmetries analysis.
- Full relaxation of the nuclei positions allowing also the cell primitive vectors to change.
- Convergence conditions: $F_{tot} < 4$ pN, $\Delta E_{tot} < 10^{-3}$ eV.
- Electron band and total energies are computed starting for the fully-relaxed structures.

Protomene

Protomene show an hexagonal crystal structure, with 48 atoms per primitive cell.
6 pairs of sp^3 carbons can switch to sp^2 hybridization and back with a small energy cost per dimer (LDA): 0.573 eV.
The removal of dimers closes the gap in the electronic band structure (compare with the No-dimers configurations).

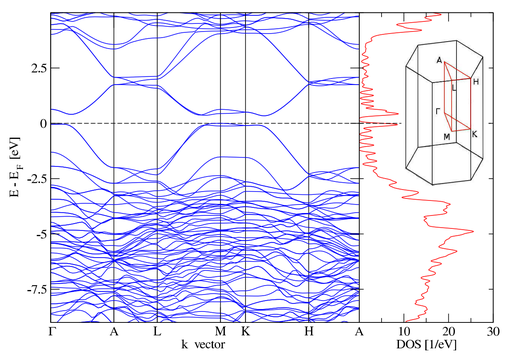


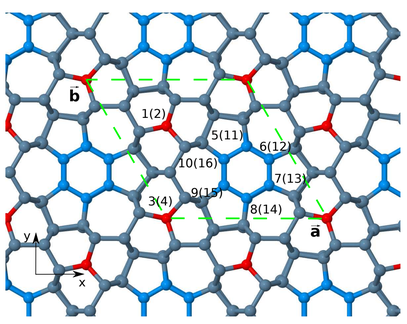


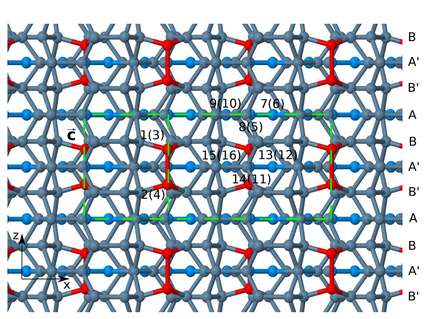


Single-ring novamene

Single-ring novamene has an hexagonal lattice, with 52 atoms per primitive cell.
12 carbons form a double benzenic ring and 4 more atoms can switch from sp^3 to sp^2 hybridization. The energy cost per dimer (LDA) is: 1.09 eV.
Also in this case, The removal of dimers closes the gap in the electronic band.







References

[1] L. A. Burchfield, M. Al Fahim, R. S. Wittman, F. Delodovici, and N. Manini. Novamene: A new class of carbon allotropes. *Heliyon*, 3(2):e00242, 2017.

[2] P. Giannozzi et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter*, 21(39):395502, 2009.

[3] V. L. Deringer, G. Csnyi, and D. M. Proserpio. Extracting crystal chemistry from amorphous carbon structures. *ChemPhysChem*, 18(8):873–877, 2017.

Numerical results

The table shows some of the main energetic and structural results obtained with LDA (GGA) simulations. The reference binding energy is the diamond one:

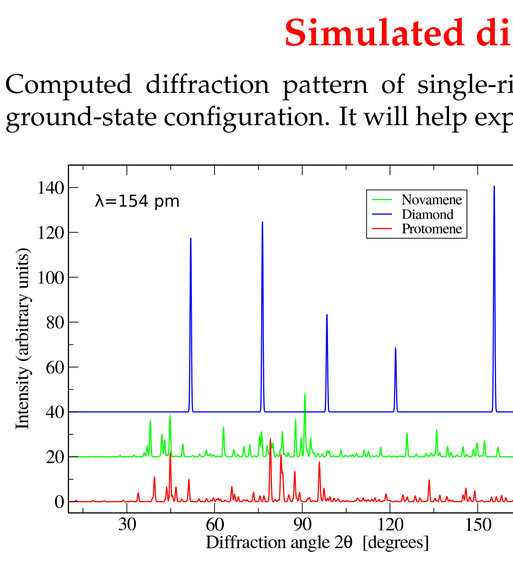
$$\text{LDA } E_b^{diam} = -8.908 \text{ eV}$$
$$\text{GGA } E_b^{diam} = -8.252 \text{ eV}$$

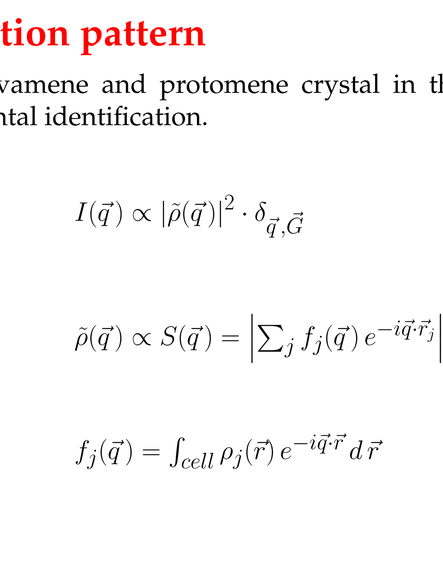
We also present the results for diamond and graphite as a comparison.

Structural parameters	protomene no dimers (GGA)	protomene ground state (GGA)	novamene ground state (GGA)	Diamond (GGA)	Graphite (GGA)
N_{atoms} per cell	24	48	52	2	4
N corner dimers	–	4	–	–	–
N central dimers	–	2	2	–	–
ΔE_b [eV]	0.2713 (0.1882)	0.1997 (0.1315)	0.2272 (0.1350)	0 (0)	−0.1460 (−0.3176)
Band gap [eV]	0.000 (0.000)	3.380 (1.274)	0.336 (0.371)	4.220 (4.445)	0.000 (0.000)
a,b [pm]	807 (817)	807 (816)	842 (851)	352 (357)	243 (246)
c [pm]	247 (251)	483 (498)	500 (509)	352 (357)	590 (644)
Density $\mathrm{kg\,m^{-3}}$	3432 (3303)	3512 (3338)	3381 (3248)	3649 (3055)	2639 (2366)

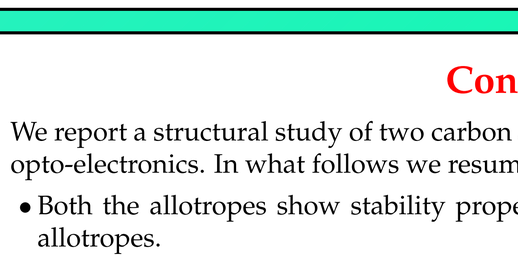
No-dimer configurations

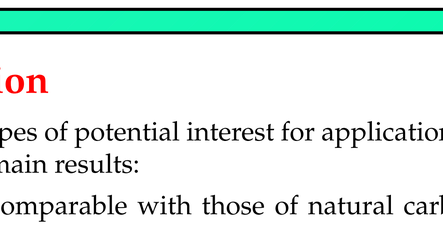
Protomene





Single-ring novamene





Simulated diffraction pattern

Computed diffraction pattern of single-ring novamene and protomene crystal in their ground-state configuration. It will help experimental identification.

$$I(\vec{q}) \propto |\tilde{\rho}(\vec{q})|^2 \cdot \delta_{\vec{q},\vec{G}}$$

$$\tilde{\rho}(\vec{q}) \propto S(\vec{q}) = \left|\sum_j f_j(\vec{q})\, e^{-i\vec{q}\cdot\vec{r}_j}\right|^2$$

$$f_j(\vec{q}) = \int_{cell} \rho_j(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}\, d\,\vec{r}$$

Conclusion

We report a structural study of two carbon allotropes of potential interest for application in opto-electronics. In what follows we resume the main results:

- Both the allotropes show stability properties comparable with those of natural carbon allotropes.
- An insulator-metal transition appears in both allotropes, with a small energy cost.
- We suggest that a large number of possible new allotropes can be formed based on different combinations of benzenic rings of carbon [1, 3].

These results can be extended towards an understanding of how induce and manage the transition in electronic properties e.g. by mean of mechanical stress, termal gradient or light beams.