Effects caused by vacancies in carbon nanocluster C_{96} and polyaromatic molecule $C_{96}H_{24}$

O.S. Karpenko

Chuiko Institute of Surface Chemistry NAS of Ukraine,
UKRAINE, Kyiv, 17 General Naumov Str., E-mail: karpenkooksana@ukr.net

Abstrac – The equilibrium spatial and electronic structure of hexagon-shaped carbon nanocluster (CNC) C_{96} limited to six zigzag edges, analogical polyaromatic molecule (PAM) $C_{96}H_{24}$ and CNCs, PAMs with defects (monovacancies, divacancies) have been calculated within the density functional theory method (DFT) with the exchange-correlation potential B3LYP and the basis set 6-31G+(d,p).

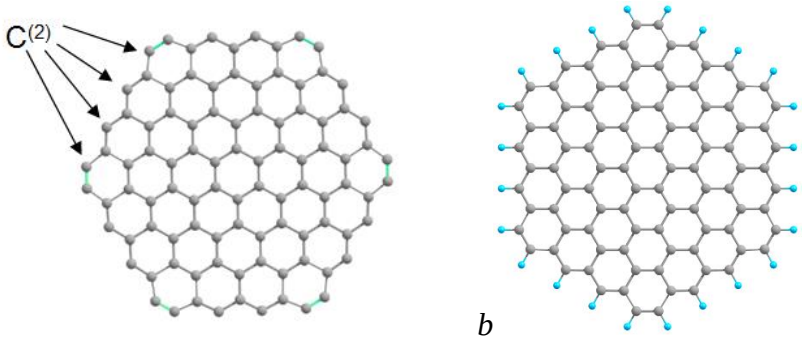
Keywords – density functional theory (DFT), graphene, carbon nanoclusters, monovacancies in graphene, divacancies in graphene.

Introduction

The ideal graphene consist of sp^2-hybridized carbon atoms [1, 2]. The structure of edges in CNCs samples is important for the chemistry of graphene, but an analysis of literature has shown that a lot of quantum chemical studies of graphene with zigzag edges have not been fully clarified yet.

Results and discussion

CNC C_{96} (Fig. 1*a*) has six zigzag edges, each of which has four doubly coordinated carbon atoms ($C^{(2)}$). PAM $C_{96}H_{24}$ was built from related CNC by attaching hydrogen atoms to the peripheral doubly coordinated carbon atoms $C^{(2)}$ (Fig. 1*b*).



a *b*

Fig.1. Carbon nanocluster C_{96} with doubly coordinated carbon atoms (*a*), polyaromatic molecule $C_{96}H_{24}$ (*b*).

The structures with vacancies (Fig. 2) have been obtained from C_{96} and $C_{96}H_{24}$ by removing one carbon atom ($C_{96\text{-}1(1)}$ and $C_{96\text{-}1(1)}H_{24}$), two non-adjacent carbon atoms ($C_{96\text{-}2(1)}$ and $C_{96\text{-}2(1)}H_{24}$), two adjacent carbon atoms ($C_{96\text{-}1(2)}$) or two pairs of adjacent carbon atoms ($C_{96\text{-}2(2)}$).

It have been established that the ground electronic state of CNCs C_{96}, $C_{96\text{-}1(1)}$, $C_{96\text{-}2(1)}$ and $C_{96\text{-}1(2)}$, PAMs $C_{96}H_{24}$, $C_{96\text{-}1(1)}H_{24}$, $C_{96\text{-}2(1)}H_{24}$, despite its have even amount of electrons, is not singlet.

The equilibrium spatial structure of CNC C_{96} is such that the 2pz atomic orbitals of the outer edge cyclic chain form a conjugate system loosely-coupled with π-system of the central part of the CNC. This suggests that the outer edge chain is relatively isolated and does not participate in the formation of a common conjugate π-system, delocalized throughout the CNC. The degree of separation of the outer edge chain increases from CNC C_{96} to defect-containing

CNCs $C_{96\text{-}1(1)}$ and $C_{96\text{-}2(1)}$. For systems $C_{96\text{-}1(1)}H_{24}$ and $C_{96\text{-}2(1)}H_{24}$, obtained from PAM $C_{96}H_{24}$, the formation of one or two monovacancies does not violate a single conjugate system.

The spectrum of single-electron energy levels of CNCs C_{96}, $C_{96\text{-}1(1)}$ and $C_{96\text{-}2(1)}$ exhibits that some MOs distributed over outer cyclic chain remain vacant but theirs energies fall into the energy intervals of the highest occupied MOs.

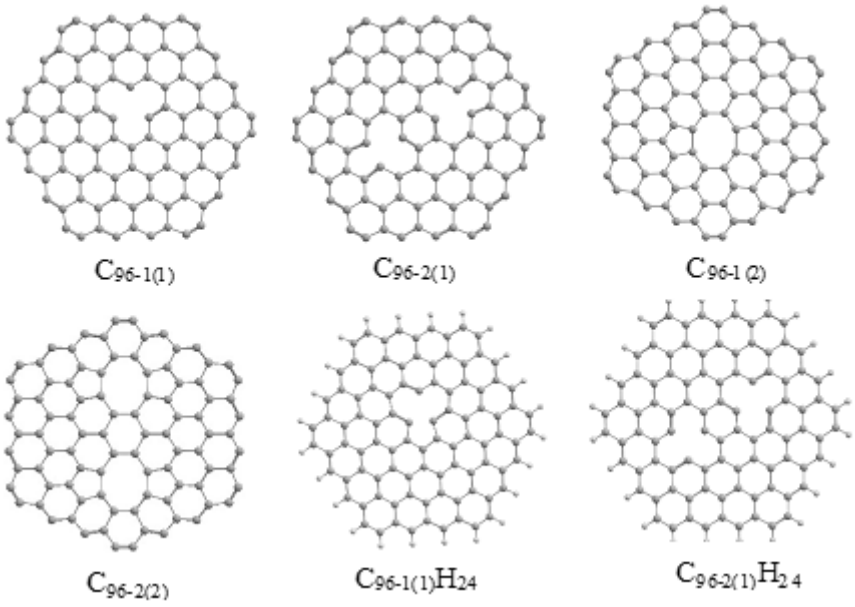


Fig.2. CNCs and PAMs with defects (monovacancies and divacancies)

The calculated energies of formation of one and two monovacancies in CNC C_{96} indicate «loosening» of the structure during the transition from C_{96} to $C_{96\text{-}1(1)}$, while for PAM $C_{96}H_{24}$ the introduction of vacancies «seals» the structure.

The formation of divacancies in the CNC C_{96} (removing the $C^{(2)}$ molecule from it) is more favourible energetically in comparison with the sequential removal of two adjacent carbon atoms.

The spectra of one-electron density states of CNC in the binding-energy scale of carbon 1*s* (C1*s*) core-level allow to identification the different types of carbon atoms depending on the degree of hybridization of their atomic orbitals, the availability of vacancies and their position in the CNC.

Conclusion

Modeling of CNCs structures and properties as PAMs (when carbon atoms $C^{(2)}$ saturated with hydrogen atoms) is not correctly both for defect-free and defect-containing hexagon-shaped CNCs.

Acknowledgments

This work was supported by the National Research Foundation of Ukraine (grant 2020.02/0050).

References

[1] Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., Firsov, A.A. 2004. Electric field effect in atomically thin carbon films. Science, V. 306(5696), 666–669. https://doi.org/10.1126/science.1102896

[2] Novoselov, K.S., Geim, A.K., Morozov, S.V. et al. Two-dimension gas of massless Dirac fermions in graphene. 2005. Nature, V. 438, 197–200. https://doi.org/10.1038/nature04233