



## Communication

## On the possibility of planar graphyne and graphdiyne chains

Frank J. Owens

Department of Physics, Hunter College of the City University of New York, 695 Park Ave., New York, 10065 NY, United States



## ARTICLE INFO

## Keywords:

Planar chains of graphyne and graphdiyne

Band gap

Vibrational frequencies

## ABSTRACT

Density Functional Theory is used to show the possibility of the existence of planar chains of graphyne and graphdiyne. The electronic and vibrational properties are calculated as a function of the chain length. Periodic boundary conditions are employed to calculate the dependence of the band gap on the wave vector. Both graphyne and graphdiyne are predicted to be semi-conducting having a non zero band gap at the zone center. This gives them potential for interesting electronic applications.

## 1. Introduction

Until 1964 the only known forms of carbon were diamond and graphite. Since then a number of different structures of carbon have been fabricated. These include cubic carbon molecule  $C_8H_8$ , a dodecahedron structure  $C_{20}H_{20}$ , a soccer ball structured molecule  $C_{60}$ , carbon nanotubes and grapheme. [1–5]. Some of these structures such as  $C_{60}$  and graphene were theoretically predicted prior to their synthesis. Such predictions often serve to motivate efforts to synthesize the structures. In 1987 a planar structure of carbon consisting of benzene rings bonded to each other by acetylenic links was predicted by the MNDO semi empirical method. [6] Subsequently more advanced computational methods such as density functional theory were used to determine its properties. [7–10] Fig. 1 shows the predicted structure of this material called graphyne. The benzene rings are connected to each other by a linear chain of two carbon atoms. It has the same symmetry as graphene but unlike graphene, it is predicted to have a small band gap at the center of the Brillouin zone. [7] Because of this it could have much more potential for electronic applications such as field effect transistors. Unfortunately only trace quantities of graphyne, insufficient for experimental measurements, have been fabricated. However, large area films of graphdiyne have been fabricated on copper surfaces suggesting that chains could be formed in a similar manner. [11] In graphdiyne the benzene rings are connected to each other by a linear chain of four carbon atoms.

The object of this work is to use density functional theory to examine the possibility of the existence of planar chains of graphyne and graphdiyne and determine their electronic and vibrational properties as a function of chain length. Also of interest is to determine how the lengths of the acetylenic links affect properties. There has been no previous first principles calculations of the electronic properties of single chains of graphyne or graphdiyne except for a semi empirical calculation using Huckel theory. [12] However, there is a need for more advanced molecular orbital methods to reliably predict the properties

of these chains.

## 2. Methods

DFT at the B3LYP/6–31 G\* level has been employed to obtain the minimum energy structures of graphyne and graphdiyne chains. The calculations employed the Gaussian 2003 software. [13] The normal modes of vibration are calculated for each structure to verify that the calculated structures are at a minimum on the potential energy surface indicated by the absence of imaginary frequencies. The separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), referred to as the energy gap, is calculated. This is done by using the local spin density approximation (LSDA) and the 6–31 G\* basis set to do a single point calculation on the minimum energy structures. This is a recommended method for predicting electronic structure. [14] Periodic boundary conditions are used to calculate the separation between the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) versus the wave vector. This is done using the VSCX/6–31 G\* model which has been shown to be an effective method to calculate this dependence on other low dimensional structures such as carbon nanotubes. [15].

## 3. Results

Fig. 2 shows the calculated minimum energy structure of 3 benzene chains having acetylenic linkages of different lengths. All of the calculated structures have no imaginary frequencies and are thus at a minimum on the potential energy surface. Fig. 2a is a chain where the benzene rings are bonded to each other by one intermediate carbon atom. Interestingly this structure at minimum energy is not predicted to be planar as alternate benzene rings are not in the same plane. Because planarity of the structure is an important determinant of the unique electronic properties, no further analysis of this structure will

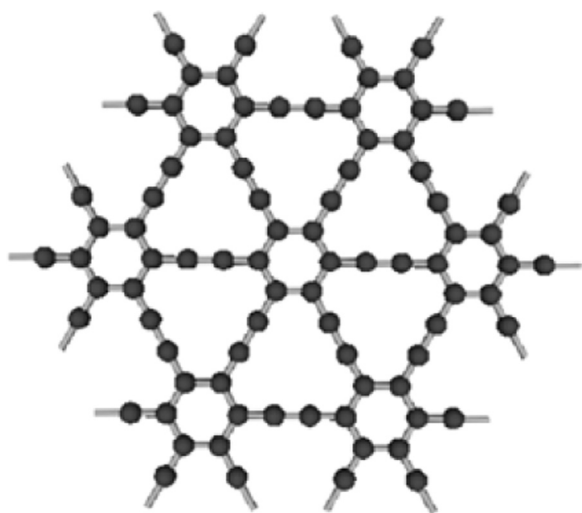


Fig. 1. Illustration of the structure of graphyne.

be presented. Fig. 2b shows the structure of a planar graphyne chain where the acetylenic link consists of two carbon atoms.

Fig. 2c shows the structure of a graphdiyne chain where the linkage between the benzene rings consists of four carbons. Both the graphyne

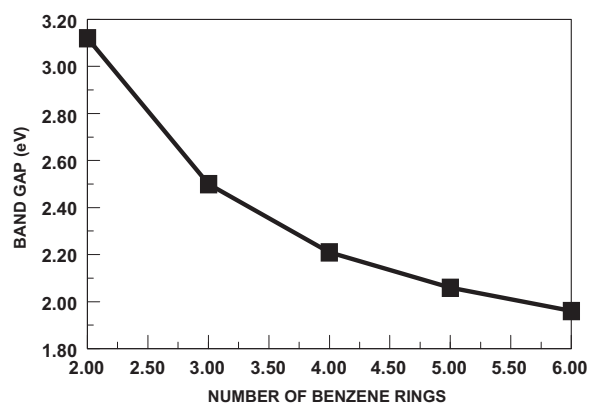


Fig. 3. Calculation of the band gap at center of the Brillouin zone of the graphyne chain versus the number of benzene rings in the chain.

and graphdiyne structures are planar and thus should have interesting electronic properties which could have applications potential.

Fig. 3 plots the band gap at the center of the Brillouin zone versus the length of the graphyne chain. The decrease in the band gap with increasing chain length is generally predicted for similar chain like systems such as polyacetylene and pentacene. [16,17]. Fig. 4a illustrates the unit cell for graphyne used to calculate the dependence of the

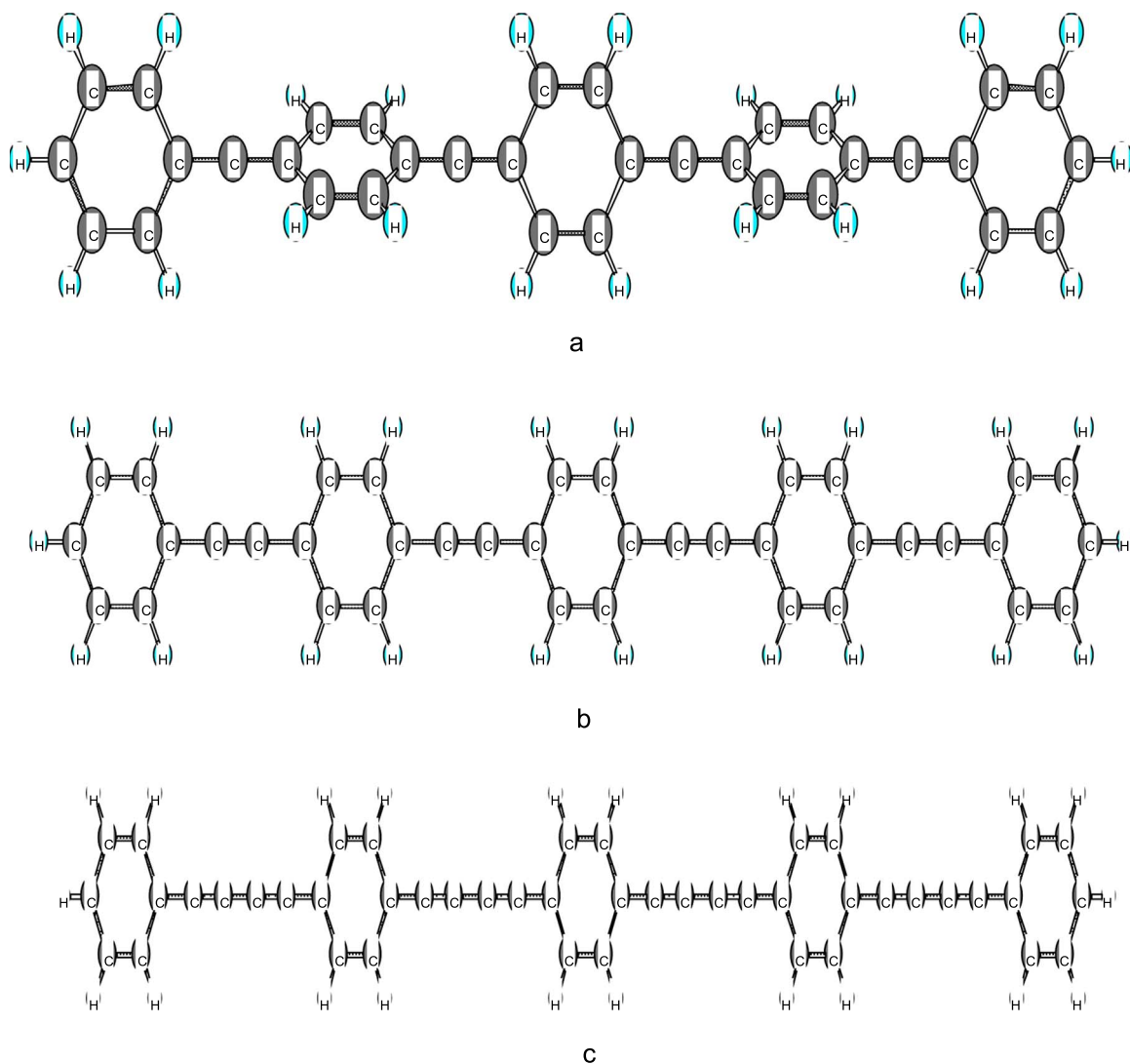
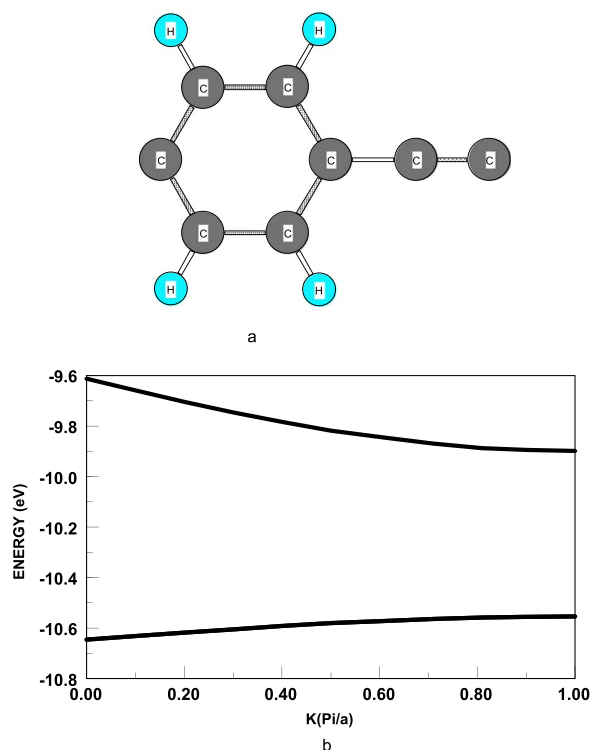


Fig. 2. Illustration of the calculated minimum energy structure of benzene chains having a one carbon link (a) a two carbon link (graphyne) (b) and a four carbon link (graphdiyne) (c).



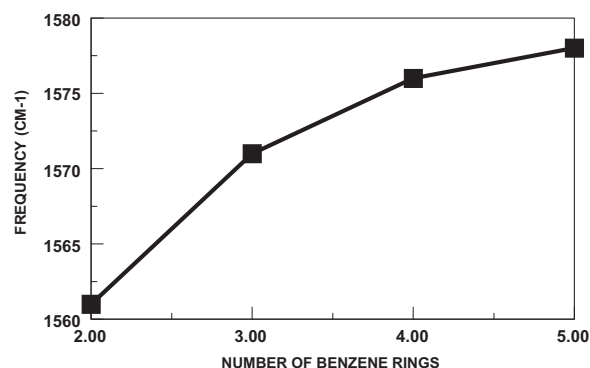
**Fig. 4.** (a) The unit cell used to calculate the dependence of the band gap of the graphyne chain on the wave vector (b) Calculated dependence of the band gap on the wave vector.

LUMO and HOMO levels on the wave vector. The results shown in Fig. 4b, indicate that the graphyne chain is semiconducting having a band gap at the zone center of 1.0 eV.

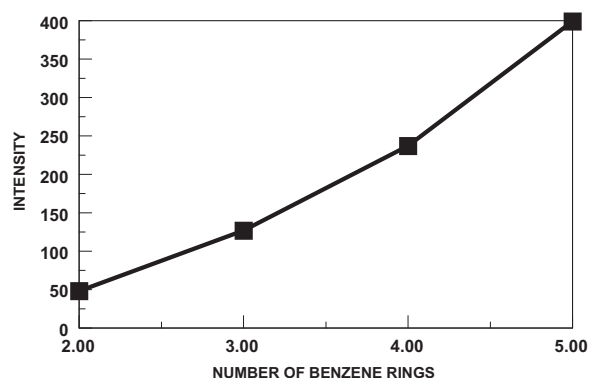
The effect of chain length on the vibrational frequencies has also been investigated. Fig. 5 is a plot of the most intense vibrational frequency of the graphyne chain in the vicinity of  $1560\text{ cm}^{-1}$ , which is a stretch motion of the C–C bonds of the acetylenic links, versus the chain length. Fig. 6 shows how the intensity of this vibration increases as the chain length increases. This effect is likely a manifestation of the emergence of Van Hove singularities in the density of states near the band gap when the chain becomes longer and effectively more one dimensional. These singularities in the density of states contribute to a resonance enhancement of Raman spectra.

All of the effects observed above are also observed in the graphdiyne chains,

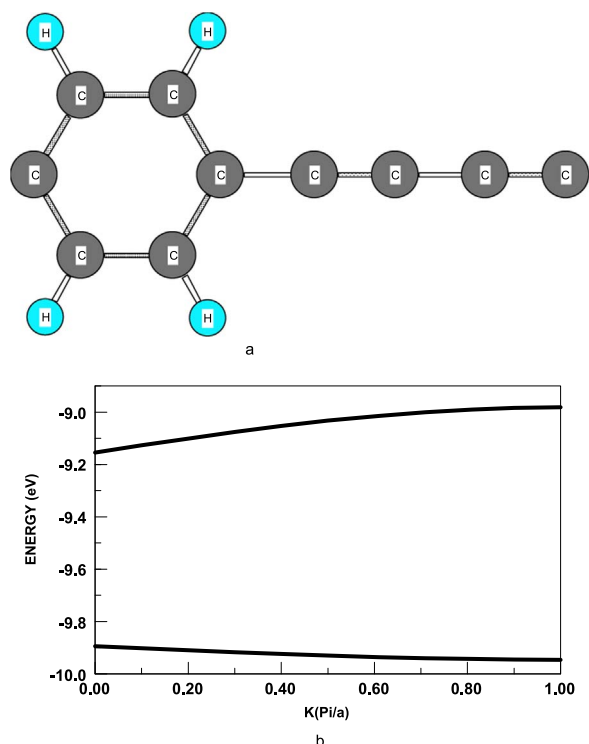
The graphdiyne chains are also semiconducting. Fig. 7a shows the unit cell of graphdiyne used to calculate the dependence of the HOMO and LUMO levels on the wave vector using periodic boundary conditions. Fig. 7b shows the result. The energy gap at the center of the zone



**Fig. 5.** Plot of the frequency of the C–C stretch vibration of the acetylenic bond versus number of benzene rings in the chain.



**Fig. 6.** Plot of the intensity of the Raman line due the C–C stretch versus number of benzene rings in the chain.



**Fig. 7.** (a) The unit cell used to calculate the dependence of the band gap of the graphdiyne chain on the wave vector (b) Calculated dependence of the band gap on the wave vector.

is 0.73 eV indicating this chain is also semiconducting.

#### 4. Conclusion

The existence of planar chains of graphyne and graphdiyne is shown to be possible using density functional theory. Electronic and vibrational properties have been calculated as a function of the chain length. Periodic boundary conditions have been employed to calculate the dependence of the band gap on the wave vector. The calculations indicate that both single planar chains are semiconductors. Unlike graphene they have a band gap at the center of the Brillouin zone which gives then potential for development of interesting electronic devices such as field effect transistors. There have been previous reports of calculations of the electronic structure of graphyne ribbons consisting of many parallel chains of benzene rings bonded by acetylenic links between the rings and the chains. [9] Although it would not be expected that the electronic structure would be the same because of the difference in structures, It is off interest to compare the electronic

structure of the single graphyne chains with the wider graphyne ribbons. In the case of the wider sheets the band gap was predicted to be approximately independent of the sheet length whereas for the single chains reported here the band gap was dependent on the length of the chain decreasing as the chain length increased. This is advantageous for use of the chains in electronic devices as it allows a method to engineer the magnitude of the band gap. Also the calculated magnitude of the band gap at the zone center is 1.0 eV smaller than the gap of wider sheets which is approximately 4.0 eV.

## References

- [1] P.E. Eaton, T.W. Cole, J. Am. Chem. Soc. 86 (1964) 964.
- [2] L.A. Paquette, R.J. Ternaski, D.W. Balooch, D.W. Kentgen, J. Am. Chem. Soc. 105 (1983) 5446.
- [3] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.E. Smalley, Nat. (Lond.) 318 (1985) 162.
- [4] S. Iijima, Nat. (Lond.) 35 (1991) 56.
- [5] A. K. Geim and K. S. Novoselov, vol. 6, 2005, p. 183.
- [6] R.H. Baughman, H. Eckhardt, M. Kertesz, J. Chem. Phys. 87 (1987) 6687.
- [7] J. Kang, et al., J. Phys. Chem. C115 (2011) 20466.
- [8] N. Narita, S. Nagi, S. Suzuki, K. Nakao, Phys. Rev. B58 (1998) 1109.
- [9] J. Zhou, et al., J. Chem. Phys. 134 (2011) 174701.
- [10] B. Bhattacharya, N.B. Singh, U. Sarkar, J. Phys. Conf. Ser. 566 (2014) 012014.
- [11] G. Li, et al., Chem. Commun. 46 (2010) 3256.
- [12] Kondo, et al., Chem. Phys. 312 (2005) 289.
- [13] Gaussian 03, Revision B.04, M. J. Frisch et. al., Gaussian, Inc., Pittsburgh PA, 2003.
- [14] M.S. Hybertsen, S.G. Louie, Phys. Rev. Lett. 65 (1985) 1418.
- [15] H. Wang, B. Wang, W. Chen, M. Hayashi, J. Phys. Chem. A112 (2008) 1783.
- [16] F.J. Owens, Physica E25 (2005) 404.
- [17] F.J. Owens, Solid State Commun. 185 (2014) 58.