Solid State Communications 250 (2017) 75–78

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Fast-track 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 graphidyne. 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 graphidyne 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 Brillioun 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 graphidiyne 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

http://dx.doi.org/10.1016/j.ssc.2016.11.004
Received 17 August 2016; Received in revised form 17 October 2016; Accepted 6 November 2016
Available online 12 November 2016

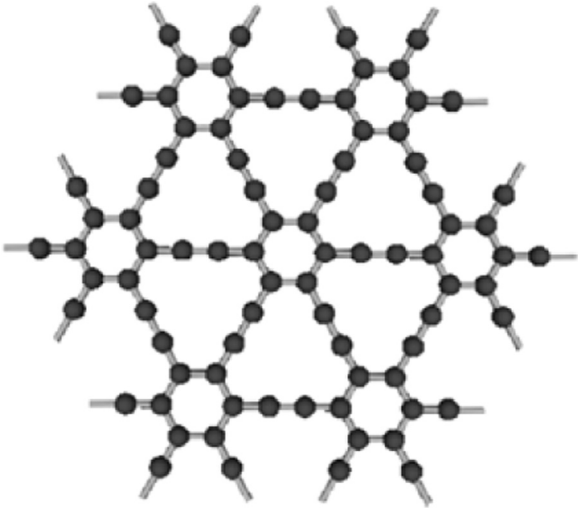

Fig. 1. Illustration of the structure of graphyne.

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

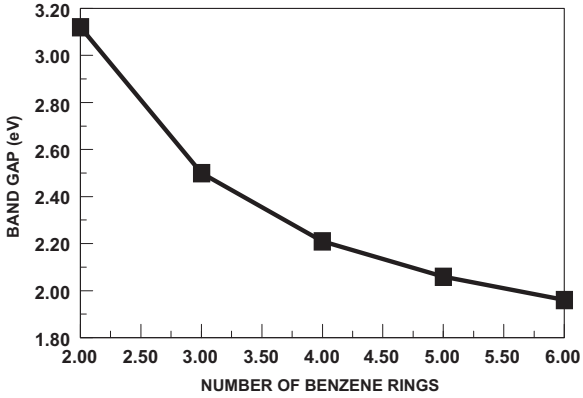

Fig. 3. Calculation of the band gap at center of the Brillouin zone of the graphyne chain versus the number of benzene rings in the chain.

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 polyacetelyne and pentacence. [16,17]. Fig. 4a illustrates the unit cell for graphyne used to calculate the dependence of the

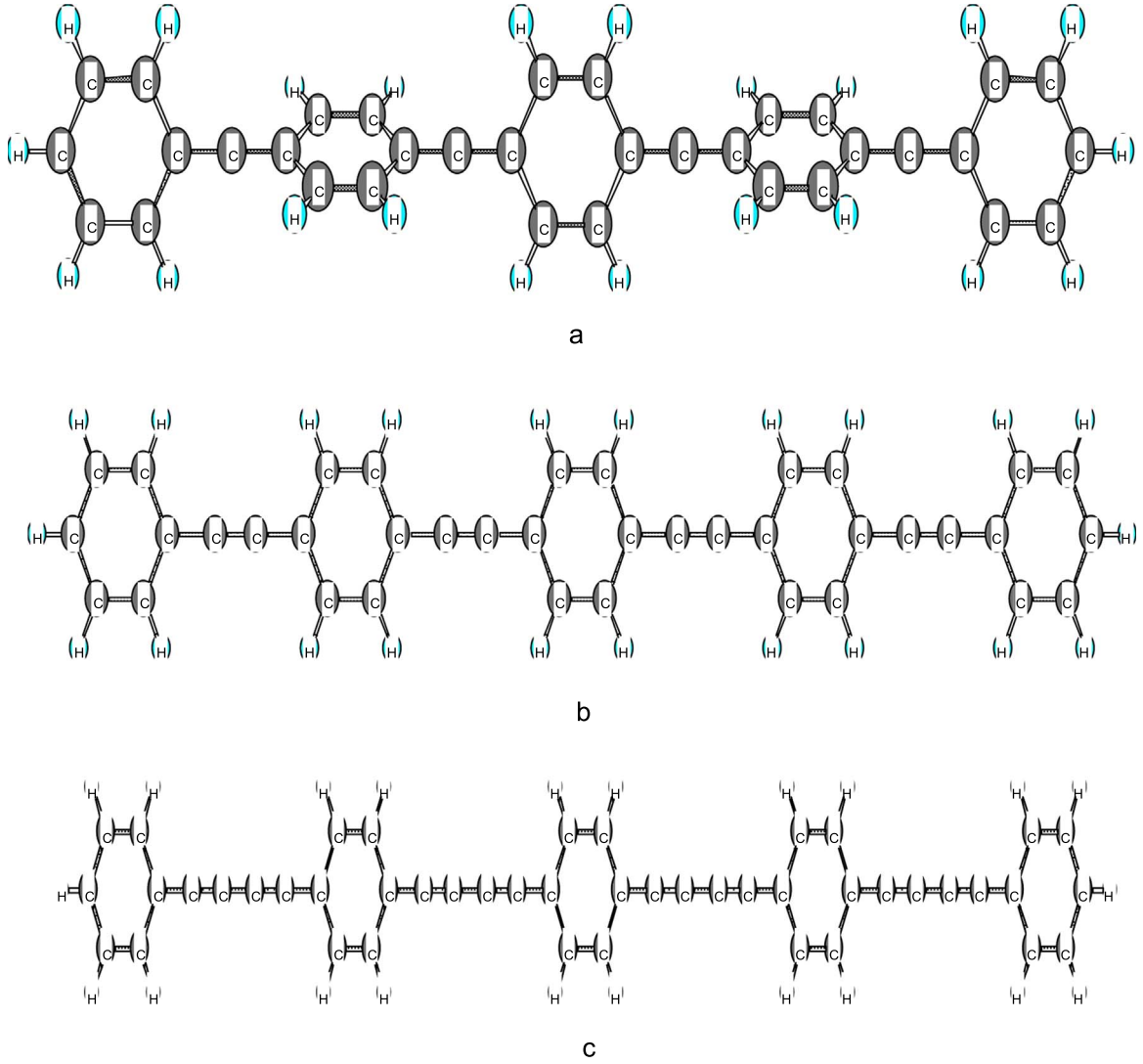

Fig. 2. Illustration of the calculated minimum energy structure of benzene chains having a one carbon link (a) a two carbon link (graphyne) (b) and a four carbon link (graphdiyne) (c).