



Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Theoretical prediction of some novel nanotubes composed of macrocyclic structures: A DFT study

Hamid Reza Masoodi*, Sotoodeh Bagheri, Reza Ranjbar-Karimi

Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, P.O. Box 77176, Rafsanjan, Iran

ARTICLE INFO

Article history:

Received 9 August 2016

In final form 8 November 2016

Available online xxxx

Keywords:

Nanotube

 π -conjugated macrocycle

Benzene

Borazine

Alumazene

ABSTRACT

Our interests in this paper are the elucidation of structural and electronic properties of some π -conjugated macrocycles composed of borazine and alumazene rings as well as the investigation of their potential utility for the creation of new nanotubes. Here, the calculations are performed at B3LYP/6-31+G(d) and M06-2X/6-31+G(d)//B3LYP/6-31+G(d) levels of theory. The results suggest that the self-assembly of the macrocyclic compounds can be considered to form new nanotubes through π - π stacking. Also, meaningful correlations are found between the stability and photoconductivity applications of the nanotubes and the number of stacked π -conjugated macrocycles.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

One of the interesting subjects in materials, chemical, and physical sciences is the creation of fully π -conjugated macromolecules with well-defined shapes, because of their potential applications in organic electronics [1–5]. The first synthesis of hexameric arylene ethynylene macrocycles from AB-type monomers dates back 40 years, when Staab and Neunhoeffer prepared the hexameric phenyleneethynylene macrocycle in 4.6% yield through sixfold Stephens–Castro coupling of the copper salt of *m*-iodophenylacetylene [6]. In the following, the synthesis, novel molecular structures, electronic and optoelectronic properties, and supramolecular chemistry of some π -expanded cyclic compounds have been examined in various papers to provide an introduction to the new field of conjugated macrocyclic structures [3,7,8]. In addition, X-ray analyses of macrocyclic compounds revealed unique molecular and packing structures, reflecting planar cyclic frameworks with medium to large inner cavities. However, tedious synthetic procedures are necessary to synthesize cyclic structures, which often hamper the experimental study of such materials [3]. In this regard, molecular modeling and theoretical calculations can be key issues in predicting the properties of conjugated nanosized macrocycles.

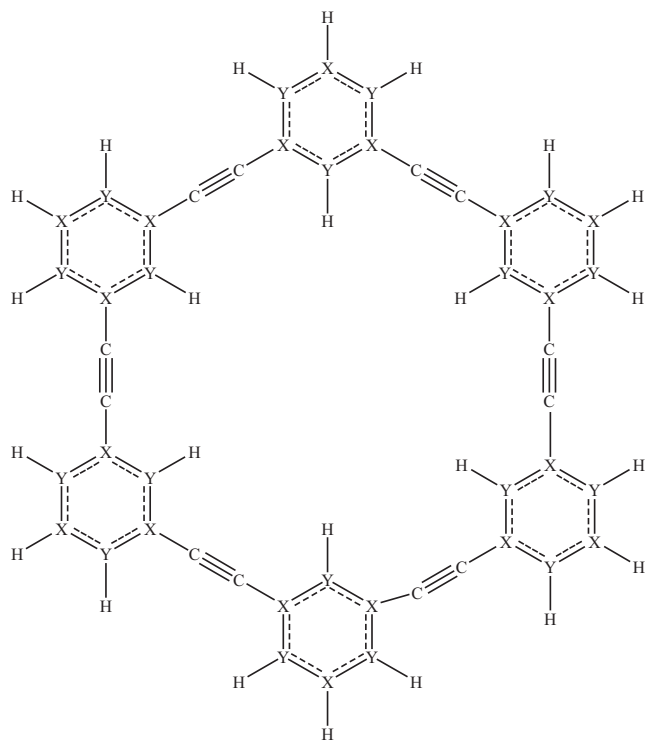
Conjugated macrocycles have infinite π -conjugations with a large inner cavity, and thus these π -systems have attracted considerable attention for their roles as large, supramolecular building

blocks that generate π -stacked structures [3,9,10]. The π -expanded macrocycles can be expected to form self-assembled nanostructures such as nanowires, nanotubes, and nanoparticles using π - π interactions. For example, Moore and co-workers examined the solid-state assembly of phenylacetylene macrocycles bearing hydrogen-bonding functionalities. They indicated, using X-ray crystallographic analysis, that the extended channels result from the stacking of the cyclic layers in a way that maintains registry between the macrocyclic cavities, and these channels are filled with solvent molecules [11].

Although benzene might be the primarily conceivable candidate to produce π -conjugated macrocycles, inorganic benzene analogues can also be used in this regard. For example, borazine ($B_3N_3H_6$) is isoelectronic and isostructural with benzene. Also alumazene ($Al_3N_3H_6$), which is an aluminum analogue of borazine, can be another candidate. To the best of our knowledge, there is no report concerning nanotubes composed of π -conjugated macrocycles when borazine or alumazene rings act as building blocks. In the present work, we theoretically investigate some structural and electronic properties of these nanotubes. Computational results are widely used to predict and design the possibility of so far entirely unknown compounds [12–16]. For example, boron nitride nanotubes were successfully synthesized [17] shortly after a theoretical prediction was made [18]. As shown from Scheme 1, six membered rings connected by carbon–carbon triple bonds are hexagonally arranged in a planar conformation with high symmetry (D_{6h}). Depending on how borazine and alumazene are connected to $C\equiv C$ bond, the two types of macrocycles can be visualized. The parallel array is assembled layer-by-layer, yielding new

* Corresponding author.

E-mail address: h.r.masoodi@vru.ac.ir (H.R. Masoodi).



Scheme 1. Schematic representation of considered macrocycles. Types of I, II, III, IV and V correspond to (a) X = C, Y = C (b) X = N, Y = B (c) X = B, Y = N (d) X = N, Y = Al and (e) X = Al, Y = N, respectively.

types of nanotubes. Here, the nanotubes consist of face-to-face intermolecular π -stacking between the macrocycles. Also for modeling nanotubes, the π - π interactions are extended in the space up to four stacked π -conjugated macrocycles. Although the macrocycles may be shifted or rotated with respect to each other, the conformation with D_{6h} symmetry is proposed on the basis of sandwich configuration of benzene dimer. Benzene dimer configurations namely T-shaped, parallel-displaced and sandwich were investigated using experimental and theoretical viewpoints [19–21]. The benzene dimer in the sandwich configuration is stabilized by London dispersion forces but destabilized by repulsive quadrupole/quadrupole interactions. Fig. 1 shows a typical nanotube.

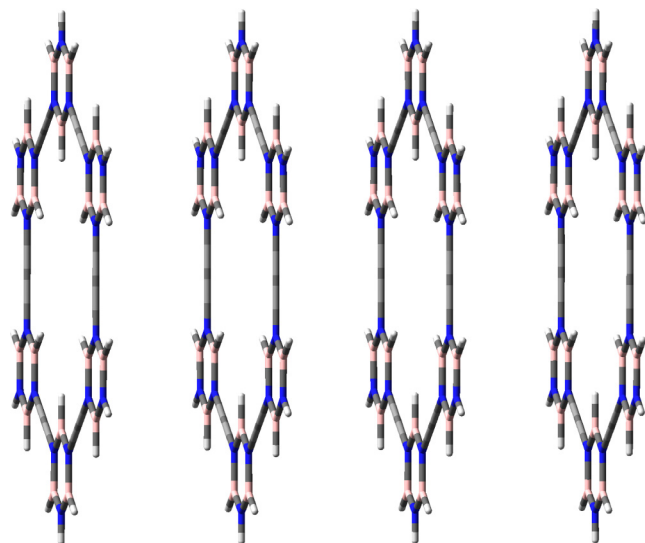


Fig. 1. A typical nanotube composed of four macrocycles.

2. Computational details and methodology

All calculations have been implemented with the Gaussian 09 suite of programs [22] at the spin-restricted level. The availability of methods with small scaling law such as DFT allows reasonable accuracy for modeling sufficiently large systems (e.g., nanotube) [23,24]. The basis set dependence of the DFT results shows that the economical 6-31+G(d) basis set is generally sufficient for calculating the HOMO and LUMO energies to use in correlating with molecular properties [25]. B3LYP is the most popular DFT model. Here, the geometries have been optimized at the B3LYP/6-31+G(d) level by symmetrical constraint (D_{6h}). Nevertheless, Zhao and Truhlar showed that the M06-2X functional has the best performance for π - π stacking [26]. To obtain credible energy properties, the single point energies of the species were further refined at the M06-2X/6-31+G(d)//B3LYP/6-31+G(d) level of theory.

3. Results and discussion

In order to compare the stability of macrocycles, we first calculated the cohesive energy or the binding energy (BE) per atom for any macrocycle according to the following formula:

$$BE = \frac{aE_B + bE_{Al} + dE_N + eE_C + fE_H}{a + b + d + e + f} - E$$

where a, b, d, e and f are the number of B, Al, N, C and H atoms, respectively. E_B , E_{Al} , E_N , E_C and E_H are the ground state total energies of B, Al, N, C and H, respectively, and E is the total energy of macrocycle. As shown from Table 1, the energetic order of the considered compounds is as following: I > III > II > V > IV. It is observed that borazine and alumazene rings when are connected to $C\equiv C$ bond through their B and Al atoms, the obtained macrocycle is more stable. It may be related to delocalization of π electrons between B, Al atoms and $C\equiv C$ bond. Jenneskens et al., indicated that heteronuclear analogues of benzene (such as borazine and alumazene) typically show localization of the lone pairs on the electronegative atoms and their values of resonance energy is negligible. This result was also confirmed by energetic and magnetic criteria of aromaticity [27]. According to these findings, it may be deduced that the influence of N atoms on acidic character of B and Al (Lewis acid) is negligible. In following, one may expect that delocalization of π electrons between $C\equiv C$ bond and B/Al and thus, the resonance in compounds III/V to be more intense than that in systems II/IV, respectively. It is well known that a direct correlation exists between resonance and stability of compound.

The magnitude of cavity of macrocycles is characterized by distances from the center of the macrocycles to the H atom of any six membered ring (d_1) and $C\equiv C$ bond (d_2). The d_1 and d_2 values are given in Table 1. While the d_1 value in considered macrocycles increase as V > III > I > II > IV, this trend for d_2 is V > IV > III > I > II. The increase in d values is accompanied by lower strain of central ring of macrocycle. Ring strain is a type of instability that has a negative correlation with ring size [28]. As expected, a direct cor-

Table 1
Binding energies (kJ/mol) and geometrical parameters (Å) in considered macrocycles.^a

Type of macrocycle	BE	d_1	d_2
I	527.58, 533.57	4.41	5.97
II	471.57, 477.71	4.17	5.89
III	490.25, 495.01	4.79	6.25
IV	382.71, 392.27	4.07	6.50
V	400.73, 409.73	5.99	7.56

^a The normal and italicized data correspond to calculations at B3LYP/6-31+G(d) and M06-2X/6-31+G(d)//B3LYP/6-31+G(d) levels, respectively.

Download English Version:

<https://daneshyari.com/en/article/5378511>

Download Persian Version:

<https://daneshyari.com/article/5378511>

[Daneshyari.com](https://daneshyari.com)