



Computational investigation of the adsorption of molecular hydrogen on the nitrogen-doped corannulene as a carbon nano-structure



Adel Reisi-Vanani¹, Leila Alihoseini

Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran

ARTICLE INFO

Article history:

Received 23 September 2013

Accepted 17 November 2013

Available online 28 November 2013

Keywords:

Hydrogen storage

Binding energy

BSSE

Physisorption

Corannulene

Carbon nanostructure

ABSTRACT

The effect of the nitrogen substitution in corannulene as a carbon nanostructure on the molecular hydrogen adsorption was evaluated at MP2/6-31G(d) level of theory. Two orientations of the hydrogen were used on the concave and convex sides of corannulene. The average binding energy was calculated and corrected for the basis set superposition error (BSSE) using counterpoise method. Results showed that 4N-substituted, 2N-substituted and intact corannulene have the most adsorption energy, respectively. The increment of the binding energy was dependent on the number and position of the nitrogen atoms. Doping with N atoms leads to decrease the gap and the kinetic stability. The isomers with two N atoms in alternate bridge and rim positions and two N atoms in alternate hub position are the best and the worst for the hydrogen storage, respectively. For 4N substituted corannulene, the isomer with four N atoms in hub position is the best for hydrogen adsorption.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen has been proposed as an ideal energy carrier and clean fuel for the future and is expected to be used as a replacement of the fossil fuels, because of health, its abundance, high chemical energy, environmental problems and renewable resources [1]. Hydrogen has the highest heating value per mass among all of the chemical fuels. Furthermore, it is the most abundant element in the universe and can be produced from water. It can produce only water as a byproduct when used in a fuel cell, so it is environmentally friendly [1].

Current hydrogen storage options which include compressed or liquefied hydrogen gas have several inadequacies such as low capacity and safety problems. There are different advanced hydrogen storage materials including metal hydrides, carbon-based and organometallic materials. In metal hydrides, the hydrogen uptake capacity is low (about 2 wt.%, due to the presence of heavy metals) and the hydrogen adsorption on metal hydrides is chemisorption, and thus desorption of hydrogen occurs at temperatures above 500 K [2–4]. In organometallic materials, hydrogen adsorption is physisorption but they have low density and high surface area and are porous materials. Low hydrogen uptake at room temperature is the main disadvantage of them as adsorbents [5,6]. Carbon-based materials, including nanotubes, nanofibers, nanoscrolls, buckybowls, activated carbon materials and graphene sheets have been analyzed experimentally and theoretically [1,7–16]. However, as a result of weak interactions between H₂ and pure carbon, these materials do not show sufficient storage capacity for commercial use under room temperature working conditions. Adjustment of

C-based materials to enhance interactions between H₂ and adsorbents and then enhance the physisorption of H₂ is essential for the development of the hydrogen storage [17,18].

Encapsulation of smaller molecules in the bowl-shaped geometry has turned attention to possible applications in hydrogen storage [19]. Corannulene (the smallest bucky bowl) is a bowl shaped nanostructure material that is a polycyclic aromatic hydrocarbon composed of five perfluorinated aromatic rings around a central five-member ring (Fig. 1). Corannulene is one of the simplest curved 2D carbon nanostructures and can be represented as one third of a C₆₀ fullerene molecule with hydrogen termination.

Corannulene was first synthesized by Lawton and Barth in 1966 [20], but remained silent until the discovery of buckminsterfullerene by Kroto et al. in 1985 [21]. Corannulene is commercially available, relatively easy to synthesize and has a small curvature, so one can compare it with the fullerene. Moreover, both concave and convex surfaces of corannulene molecule are exposed to react with the hydrogen molecules [22]. The hydrogen adsorption in corannulene-based materials was evaluated by Zhang et al. [23]. They have shown that corannulene has potential advantages as the hydrogen storage material over the planar graphite and even carbon nanotubes. Also, in lithium doped corannulene, lithium atoms are more stably doped over the six-member rings than over the five-member ring of corannulene with the concave side more favorable than the convex side of the corannulene for doping. The doping of the lithium atoms enhances the hydrogen adsorption due to three factors: Lithium-doped corannulene complexes have higher dipole, the interaction between the lithium atom and hydrogen is stronger than the interaction between carbon atom and hydrogen and the doping of lithium atoms provides more space in the doping complexes for hydrogen adsorption [24]. Rellán-Piñero et al. have considered the interaction

E-mail address: areisi@kashanu.ac.ir (A. Reisi-Vanani).

¹ Tel.: +98 3615912358; fax: +98 3615552930.

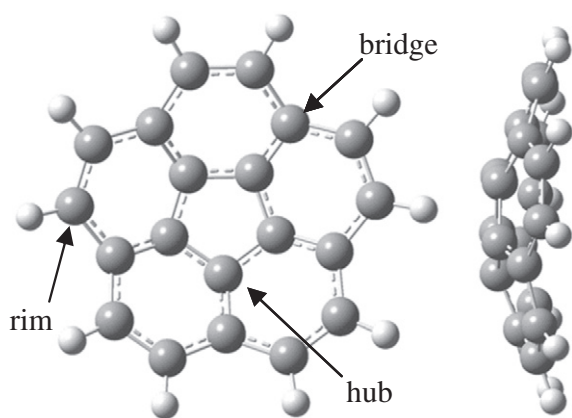


Fig. 1. Optimized bowl-shaped structure of the corannulene molecule ($C_{20}H_{10}$) and type of the carbons.

of corannulene with alkali cations by DFT and MP2 methods [25]. Interaction of the hydrogen molecules with some of the carbon nanostructures such as C_{60} , C_{36} and several B and Be-doped carbon nanostructures was studied by MP2 method [13]. Banerjee et al. have shown that for interaction of the alkali and alkaline earth metal ion doped corannulene molecules with dihydrogen, the smaller and larger size ions show the higher binding energy on the convex and concave sides, respectively. The clean surface of the molecule interacts with the hydrogen very weakly and the binding strength is significantly improved after decorating the molecule by alkali or alkaline earth metal ions [22].

In this study, we have studied the hydrogen adsorption of the nitrogen doped corannulene and used a different route to increase the electronic density of the corannulene. We have investigated the effect of doping of two and four nitrogen atoms and their position on the hydrogen adsorption of corannulene. Binding energy with respect to BSSE correction has been calculated and the best isomer was assigned for the hydrogen adsorption. The effect of the dipole moment on the binding energy and kinetic stability of the isomers with respect to HOMO–LUMO (H–L) gap energy has been investigated.

2. Computational methods

2.1. Ab initio calculations

Geometry optimization of the corannulene, hydrogen molecule, 22 isomers of $C_{18}N_2H_{10}$ (presented in [26]) and 7 isomers of $C_{16}N_4H_{10}$ was done at the MP2/6-31G(d) level of theory to account for weak Van der Waals forces that are responsible for the hydrogen molecule–corannulene physisorption interaction. MP2/6-31G(d) frequency calculations were performed to ensure that the molecular system was at a local minimum. For evaluation of the interaction of H_2 –N-doped corannulene systems, two orientations of the hydrogen were used (perpendicular and parallel) on the concave and convex sides of the corannulene (Fig. 2) and full geometry optimizations were performed. To obtain the most stable adsorption site of the each isomer, on the N-doped corannulene ring, several possible configurations (on pentagonal or each of the hexagonal rings) have been considered and the optimization has been carried out. Adsorption of the hydrogen in head-on orientation is more stable than parallel orientation that it is in good agreement with Scanlon et al. studies [16], so throughout this study, head-on orientation has been used. All calculations were performed by Gaussian 03 software [27]. Gauss View 5 program [28] was used for visualization of the results.

2.2. Calculation of the interaction energy

As an indication of stability for the hydrogen adsorption, the average binding energy of the hydrogen molecule and adsorbent molecules was calculated by the following:

$$E_{BE}(AB) = E(AB) - (E(A) + E(B)) \quad (1)$$

where, $E(AB)$ is the energy of the hydrogen–adsorbent complex, $E(A)$ and $E(B)$ are the energy of the adsorbent and hydrogen molecules, respectively. It is well known that physisorption energies must be corrected by BSSE. Therefore, we used the counterpoise correction suggested by Boys and Bernardi in 1970 [29]. The counterpoise corrected binding energies were calculated by the following:

$$E_{BE}^{CP}(AB) = E_{BE}(AB) + \delta_{AB}^{BSSE} \quad (2)$$

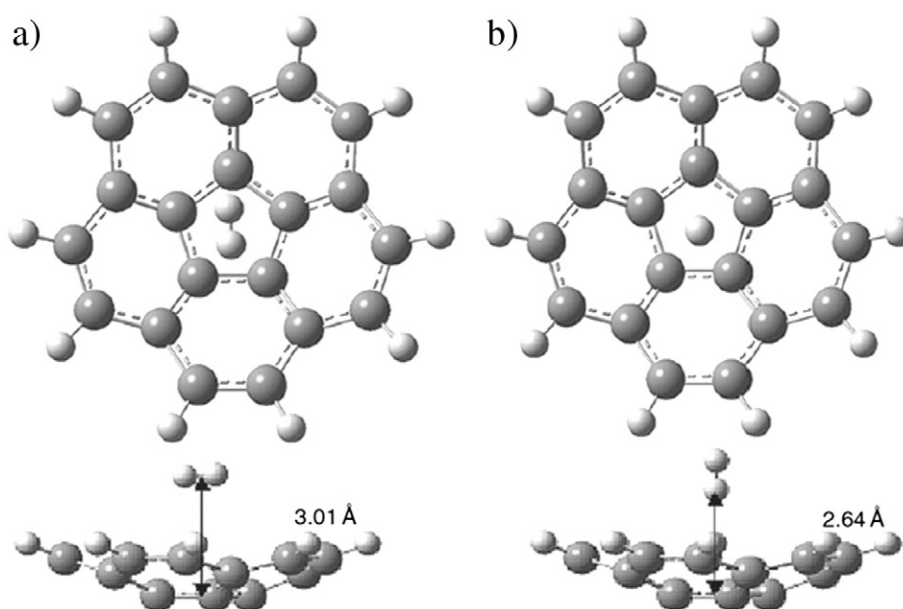


Fig. 2. Adsorption of a hydrogen molecule on corannulene. MP2/6-31G(d) (a) parallel orientation; (b) head-on orientation. From reference [23].

Download English Version:

<https://daneshyari.com/en/article/5422268>

Download Persian Version:

<https://daneshyari.com/article/5422268>

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