Computational and Theoretical Chemistry 981 (2012) 31–37

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

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

Cycloaddition of ethene on a series of single-walled carbon nanotubes

Daniel B. Lawson *, Alice Walker

Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI 48128-1491, United States

ARTICLE INFO

Article history:
Received 30 September 2011
Received in revised form 21 November 2011
Accepted 22 November 2011
Available online 27 November 2011

Keywords:
Carbon nanotubes
Ethene
Cycloaddition
Carbon–carbon bond

ABSTRACT

The binding energy of ethene to several $(n,0)$ and (n,n) single wall carbon nanotubes where $n = 5–9$ are investigated by B3LYP density functional theory (DFT). The calculated binding energies indicate the cycloaddition reactions to be exothermic for the smaller diameter nanotubes (5,0) and (6,0) and increasingly endothermic as the diameter of the nanotube increases. The binding energy of ethene to the smallest SWCNT of this work, the (5,5) SWCNT, is exothermic and increasingly endothermic as n increases for the remaining (n,n) SWCNTs. Bonding alters the hybridization of the CC bonds of both the ethene and the C atoms of the nanotube to which the ethene is bound. The HOMO and LUMO orbitals include the ethene and are delocalized over the length of the tube.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

A single wall carbon nanotube (SWCNT) is an allotrope of carbon often described as a sheet of graphene rolled into a cylinder [1]. SWCNTs come with different C atom arrangements and a variety of diameters. Correspondingly, SWCNTs have numerous physical and chemical characteristics that depend on their structure. It is the arrangement of the C atoms in the nanotube that determine whether the SWCNT is semiconducting or metallic in nature [2]. The stiffness, conductance and transport properties of the SWCNTs in conjunction with their length suggest a variety of applications ranging from use as strong fabrication materials [3–6] to applications as sensitive chemical detectors [7–9]. The chemical stability of SWCNTs is indicative of the fact that most of the interactions between gas molecules and SWCNTs do not involve direct bonding. The sp^2 CC bonds of the nanotubes render SWCNTs relatively inert [10].

There are numerous experimental [11–14] and theoretical studies [15–19] of the binding of small gaseous molecules to SWCNTs. Of particular interest in this work are those studies related to the interactions of ethene with carbon nanotubes. A recent study [20] used grand canonical Monte Carlo simulations to model the adsorption of various hydrocarbons including methane, ethane, ethene, propane, and propylene into interstitial regions between the bundles of SWCNTs. The SWCNTs were modeled as smooth structureless nanocylinders and each hydrocarbon CH_n group was treated as single interaction sites. The work indicates that adsorption is more favorable for the larger hydrocarbons due to the increase of the number of interaction site associated with each hydrocarbon. Another Monte Carlo simulation [21] consisted of various alkanes and alkenes adsorbed to bundles of uniform but varying sized SWCNTs including (10,0), (20,0), (30,0) and (40,0). Here, the SWCNTs consisted individual C atoms in fixed positions and all interactions between hydrocarbons and SWCNT were modeled by Lennard-Jones 12–6 potential. This work indicates that at low pressure, more alkanes are adsorbed in the interstitial spaces than the corresponding alkenes and at high pressures the opposite occurs. And, a recent experimental [22] work generates low temperature adsorption isotherms of krypton and ethene on multi-walled carbon nanotubes (MWCNTs) and compares these adsorptions with graphite. The MWCNTs result in a higher condensation pressure and a lower heat of adsorption with respect to the planar surface of graphite. The condensation pressure increases as the nanotubes diameter decreases. By contrast, an inverse gas chromatography study [23] of the adsorption of a variety of saturated and unsaturated volatile organic compounds onto nonmicroporous carbons including MWCNTs indicates that the adsorption of the various compounds on the MWCNTs is less energetically favorable than adsorption onto graphite.

Two other studies of interest, one theoretical [24] and one, both theoretical and experimental [25], look at the interaction of ethene with benzene. In the latter study, two-color multiphoton ionization spectroscopy is used to evaluate the binding energies in the neutral ground state from dissociation threshold measurements of the cluster cations. The ethene and ethyne absorb to the benzene ring through a CH–π interaction. The former study mentioned ab initio methods to calculate the interactions of ethene in a variety of geometrical configurations relative to benzene. The computed binding energies are all below 3 kcal mol^{-1} indicating the interactions to be purely dispersion.

* Corresponding author. Tel.: +1 313 593 4921; fax: +1 313 593 4937.
E-mail address: dblawson@umich.edu (D.B. Lawson).

2210-271X/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.comptc.2011.11.040

In this work we computationally investigate the interaction of ethene with SWCNTs of various sizes. Our interest lies with the formation of the CC bonds with the outer wall of the SWCNT. Thus we focus on the interaction of the hydrocarbon-C atoms with the C atoms of the SWCNT.

2. Computational details

Initial SWCNT geometries where obtained using the graphical molecular editor GABedit [26]. The program has a nanotube option within the molecular builder portion of the program. Hydrogens were manually added to the terminal C atoms with open valences and the new structure was initially optimized using the UUF force field of the rendering program. Ethene molecules where then placed on the exterior surface of the nanotubes according to the orientations as described in the next section. The resultant geometries where fully optimized using the semiempirical method PM6 as incorporated in MOPAC2009 [27]. Single point DFT calculations were performed using the resultant PM6 geometries. The DFT used in this work consisted of the Becke exchange functional and the correlation functional of Lee, Yang, and Parr or also known as B3LYP [28]. All B3LYP calculations where performed with a combination of Gaussian03 [29] and NWChem [30] using a standard 6-31g* split valence with a single polarization function add to C [31]. These calculations where completed either in-house on a group of multiprocessor Linux machines or using NCSA-TeraGrid Resources.

3. Considered orientations of the ethene relative to SWCNT

In this work we consider the binding of a single ethene to armchair or (*n*,0) SWCNT and to zig-zag or (*n*,*n*) SWCNT where in both cases *n* = 5–9. There are six orientations associated with the (2 + 2) cycloaddition of the ethene to the benzoid rings of each SWCNT giving a total of 60 different structures. Fig. 1 indicates the numeric referencing applied to the resulting structures for both the (*n*,0) SWCNT and the (*n*,*n*) SWCNT and Fig. 2 provides the names for the various orientations of the ethene relative to the SWCNT. For example, binding of the ethene in the 2,3 position of the (*n*,0) SWCNT, as indicated in Fig. 2a, is referred to as 2,3-*ortho*-ethene-(*n*,0) SWCNT. The *ortho*- designation is attributed to the C atoms of the ethene being oriented *ortho*- relative to the benzenoid rings of the nanotubes. Note that this conformation places the ethene CC bond parallel to the length of the SWCNT. Fig. 2b indicates a configuration that places the ethene C atoms *ortho*- to the benzenoid ring, however, the ethene CC bond is now diagonally oriented relative to the length of the SWCNT. This configuration is called 1,2-*ortho*-ethene-(*n*,0) SWCNT and would be degenerate with 3,4-*ortho*-ethene-(*n*,0) SWCNT, 4,5-*ortho*-ethene-(*n*,0) SWCNT and the 1,6-*ortho*-ethene-(*n*,0) SWCNT. The 2,3-*ortho*-ethene-(*n*,0) SWCNT is degenerate with only the 6,5-*ortho*-ethene-(*n*,0) SWCNT as the ethenes run parallel to the axis of the SWCNT. For a shorthand notation, we refer to the 1,2-*ortho*-ethene-(*n*,0) SWCNT as o-diagonal and the 2,3-*ortho*-ethene-(*n*,0) SWCNT as o-lateral. Fig. 2c and d also indicate the ethene bound *para*- to the benzenoid rings. And, there is a 1,4-*para*-ethene-(*n*,0) SWCNT, a 2,5-*para*-ethene-(*n*,0) SWCNT and a 3,6-*para*-ethene-(*n*,0) SWCNT where the latter two are degenerate. We refer to the structures depicted in Fig. 2c as p-lateral and the structure of Fig. 2d as p-diagonal. The next set of ethene SWCNT orientations correspond to the ethene oriented *meta*- relative to the phenyl rings. Fig. 2e indicates a 1,3-*meta*-ethene-(*n*,0) SWCNT and Fig. 2f shows a 2,5-*meta*-ethene-(*n*,0) SWCNT. There are three other *meta*-orientations energetically equivalent to the 1,3-*meta*-ethene-(*n*,0) SWCNT including 2,4-*meta*-ethene-(*n*,0) SWCNT, 4,6-*meta*-ethene-(*n*,0) SWCNT and a 1,5-*meta*-*ethene*-(*n*,0) SWCNT. We refer to these latter arrangements as *m*-diagonal. Alternatively, there is a 2,6-*meta*-ethene-(*n*,0) SWCNT as depicted by Fig. 2f and a degenerate 3,5-*meta*-ethene-(*n*,0) SWCNT and these structures are referred to as *m*-equatorial.

As with the (*n*,0) configuration, the C atoms of ethene arrange themselves with pairs of C atoms of the (*n*,*n*) SWCNT either *ortho*-, *meta*- or *para*- relative to the benzenoid rings. Fig. 2g shows the 1,6-*ortho*-ethene-(*n*,*n*) SWCNT and Fig. 2h shows the 5,6-*ortho*-

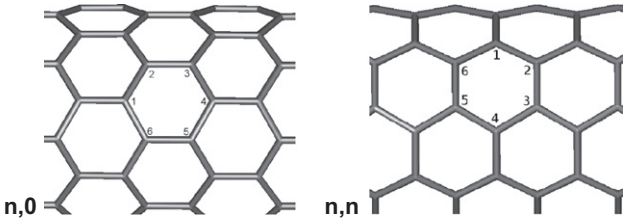

Fig. 1. Carbon atom indexing scheme of (*n*,0) and (*n*,*n*) SWCNT.

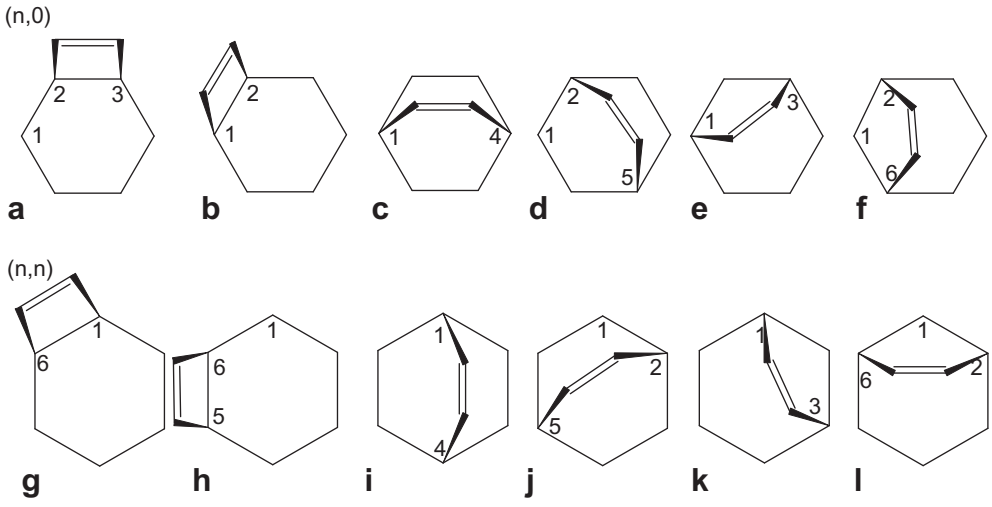

Fig. 2. Geometry designations used to describe ethene SWCNT complexes. (a) 2,3-*ortho*-ethene-(*n*,0) SWCNT, (b) 1,2-*ortho*-ethene-(*n*,0) SWCNT, (c) 1,4-*para*-ethene-(*n*,0) SWCNT, (d) 2,5-*para*-ethene-(*n*,0) SWCNT, (e) 1,6-*ortho*-ethene-(*n*,*n*) SWCNT, (f) 5,6-*ortho*-ethene-(*n*,*n*) SWCNT, (g) 1,4-*para*-ethene-(*n*,*n*) SWCNT, (h) 2,5-*para*-ethene-(*n*,*n*) SWCNT.

Download English Version:

https://daneshyari.com/en/article/5394798

Download Persian Version:

https://daneshyari.com/article/5394798

Daneshyari.com