Synthetic Metals 210 (2015) 80–84

Contents lists available at ScienceDirect

Synthetic Metals

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

Stereochemical effect of covalent chemistry on the electronic structure and properties of the carbon allotropes and graphene surfaces

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ARTICLE INFO

Article history:
Received 16 January 2015
Received in revised form 28 June 2015
Accepted 5 July 2015
Available online 29 July 2015

Keywords:
Graphene
Graphene chemistry
Stereochemistry
POAV
Hybridization

ABSTRACT

We consider the covalent chemistry of the carbon allotropes with an emphasis on the newest member—graphene. We focus on the effect of such chemistry on the geometric and electronic structure of the functionalized materials and the way in which the conjugation is modified by such processes. We conclude that there are two limiting cases: (a) Conventional addition chemistry leading to the formation of σ-bonds to the graphitic surface in which there is full rehybridization of the derivatized carbon atoms from sp^2 to sp^3; thus these carbon atoms are effectively removed from conjugation and from the electronic band structure (referred to as destructive rehybridization). (b) Covalent chemisorption with formation of an organometallic hexahapto-metal bond that largely preserves the graphitic band structure (constructive rehybridization) and accompanies the formation of bis-hexahapto-metal bonds such as those in (η^6-SWNT)Cr(η^6-SWNT) which serve to interconnect adjacent graphitic surfaces and significantly reduces the internanotube junction resistance in SWNT networks. The formation of η^2 di-hapto bonds represent an intermediate case of covalent chemistry and is known to be important in carbon nanotubes and particularly the fullerenes but this situation has been treated in detail in previous publications.

1. Introduction

In 2004 graphene joined the fullerenes and carbon nanotubes as the third new form of conjugated carbon materials to take its place in the spotlight of scientific research [1,2]. All of these materials are composed of the same basic building block—tri-coordinate, formally sp^2 hybridized carbon atoms which are predominantly contained within six-membered rings thereby leading to polybenzenoid structures. These carbon allotropes are normally divided into two categories: molecules and materials, with the fullerenes being the only members of the first category. Nevertheless, in either case these substances can be viewed as continuous arrays of conjugated carbons as the fullerenes have no boundaries and (except for the terminal carbon atoms), carbon nanotubes and graphene are periodic structures which can in principal be extended without limit. Thus the question of functionalization of these continuous polybenzenoid structures has been of interest from the first isolation of the fullerenes as any chemistry, apart from redox processes, must involve an addition reaction which will normally saturate the carbon atoms that become functionalized and lead to sp^3 hybridized carbon atoms. Furthermore the question of covalent functionalization of graphene surfaces is an important question that must be addressed if the carbon allotropes are to play a role in assembling functional electronic structures based on polybenzenoid carbon surfaces [3].

In the case of graphene the sp^3 carbon atoms have been shown to act as scattering sites and their presence leads to a reduction in the conductivity and mobility of the samples that have been examined [4]. Nevertheless it is of interest to understand the effect of the introduction of sp^3 carbon centers on the electronic structure of the surrounding carbon atoms and the manner in which it modifies the geometrical strain and conjugation. Effects such as these have been studied for many years in organic chemistry and their ability to influence the stability and reactivity

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http://dx.doi.org/10.1016/j.synthmet.2015.07.004
0379-6779/

of molecules is well known [5]. For example, it has long been recognized that the geometries of the annulenes limit the reach of the Huckel (4n + 2)π-electron rule and it is the interplay of the geometrical requirements of the remainder of the molecule with the electronic structure of the π-system that ultimately determines the chemical stability of these compounds [6]. Within organic chemistry the necessity of balancing these two contributions is often considered under the title of steric inhibition of resonance.

In the present paper we compare the properties and the effect of geometry on conjugation in the carbon allotropes both before and after addition chemistry with model compounds drawn from the literature of organic chemistry in order to benchmark these materials against well-known molecules which can be structurally and physically characterized.

We begin by briefly reviewing the structures and stereochemical features of the fullerenes and single-walled carbon nanotubes (SWNTs) in the context of their functionalization (addition) chemistry in order to provide a benchmark for the analysis of graphene prototype structures which we draw from the literature on the 15,16-dihydropyrenes and theoretical calculations. The dihydropyrenes have been studied for a number of years by Boekelheide and Mitchell and their properties are well known [7–10]—there is an obvious relationship between pyrene and the 15,16-dihydropyrenes and between graphene and its addition products as discussed in more detail below.

2. Experimental and computational

Normally π-electron systems are considered to be planar and this is the case for undistorted graphene in the absence of scrolling (which can lower the total energy by van der Waals forces). In order to treat nonplanar π-electron systems it is convenient to use the π-orbital axis vector (POAV) analysis to divide the structural distortions into one-center and two-center terms as shown in Fig. 1 [5]. The one-center term makes use of the POAV1 pyramidalization angle and the vector defined by this procedure which is constructed to make equal angles to the three σ-bonds at the conjugated carbon atoms. While the vector defining the POAV1 rehybridized π-orbital direction depends on the geometrical construction defined above and shown in Fig. 1a, the corresponding POAV2 vector is based on the rehybridized π-orbital which is constructed to be orthogonal to the three σ-bonds. The POAV2 hybridizations and the resulting direction of the rehybridized π-orbital are obtained analytically by solving a set of homogeneous linear equations [11]. In the case of C_{3v} symmetry (equal angles between the 3 σ-bonds), the two constructions are identical; thus the POAV1 approach assigns an equal average σ-bond hybridization to the 3 σ-bonds, whereas the POAV2 approach solves for the individual hybridizations of each σ-bond hybridization in addition to the π-orbital [5].

The geometries of the compounds were obtained from X-ray crystal structures or from theoretical calculations and used directly in the analysis. For the ring current analysis of the experimental proton NMR chemical shifts, the C—H bond lengths of the X-ray structures were normalized to 1.1 Å [14,15].

3. Results and discussion

3.1. Analysis of covalent σ-bonding requirements (full rehybridization from sp^2 to sp^3)

3.1.1. Fullerenes

The effect of the spheroidal structure of C_{60} on its electronic structure is now well known—because the fullerenes are curved in two-dimension the geometry of the π-system imposes a very strong pyramidalization of the carbon atoms [16,17], but maintains a high degree of alignment of the π-orbitals (perfect in C_{60}) [18]. Thus the fullerenes readily undergo 1,2 addition reactions because this relieves the strain of pyramidalization without disrupting the favorable π-orbital alignment [17,19–22]. Nevertheless it is important to note that the larger high symmetry fullerenes become faceted and because the pyramidalization is concentrated at the vertices of the (12) five-membered rings the minimum pyramidalization angle in such fullerenes remains quite large ($\theta_P > \sim 9°$) [23].

3.1.2. Carbon nanotubes

The carbon nanotubes are only curved in 1-dimension and thus in general the degree of pyramidalization required for the formation of structures of equivalent diameter is much less than in the case of the fullerenes (by about a factor of $^1/_2$ at small diameters); for example, the diameters (d) of C_{60} and the (5,5) SWNT are both about $d = 7$ Å, but the difference in the required pyramidalization angles is apparent in Fig. 2 and Fig. 3 [25].

It is apparent from Fig. 3 that the nonplanarity in carbon nanotubes not only leads to pyramidalization but also produces significant π-orbital misalignment which is distributed unequally among the π-bonds depending on their orientation with respect to the nanotube axis. Thus it is apparent that bonds which do not lie parallel or perpendicular to the nanotube axis will experience some degree of π-orbital misalignment and particularly for the smaller carbon nanotubes this may be quite severe. In fact for diameters smaller than C_{60}, it is likely that π-orbital misalignment is more

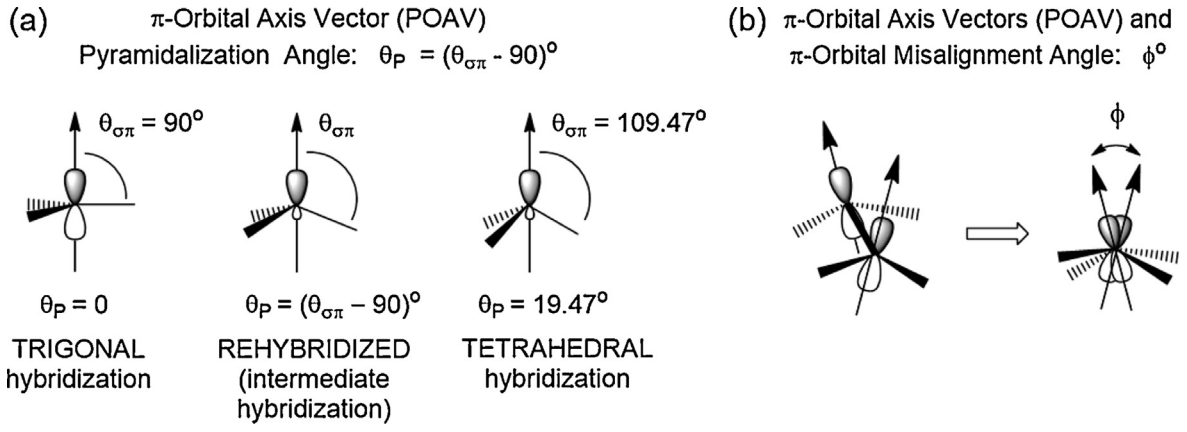

Fig. 1. Geometrical construction of the π-orbital axis vector (POAV), the POAV pyramidalization angle (θ_P) and π-orbital misalignment angle (φ) [6,11–13].