



Letter

Correlating geometry of multidimensional carbon allotropes molecules and stability

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ABSTRACT

It is well-known that the convex surfaces of graphene, carbon nanotubes and fullerenes exhibit different reactivities due to the pyramidalization angles of the carbon atoms. The higher the angle, the more propitious the site towards chemical additions. Given the high impact of the stability of these particular materials with respect to their application in electronic devices, we determine the importance of their curvature on their stability. This is done by means of DFT calculations in which binding energies of common degradation agents are characterized with respect to carbon bond curvatures. It is found that there is a clear correlation between the radius of curvature and oxidative instability under photochemical and thermal stresses.

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1. Introduction

Among known carbon allotropes, the low-dimensional fullerenes [1,2], nanotubes [3–5] and graphenes [6–8] are of paramount importance to the development of new nano-based technologies. This is mainly due to their exceptional electron-poor electronic properties, their singular structures and the ease with which they can be obtained [9,10]. One of the most relevant proposed uses are as electron acceptors in organic photovoltaic devices, as first demonstrated for fullerenes [11].

Intense theoretical and experimental effort has been used to elucidate and design the electronic and structural properties of such materials [12,13]; yields of devices in certain respects are competitive with inorganic counterparts [14–16]. Carbon-allotropes composites with polymers are used for organic devices and in particular for photovoltaic (OPVs) that have attracted significant interest as lightweight, low-cost and renewable energy sources [17,18]. However, one hindrance to expanding commercialization of these devices is their stability under operating conditions [19]. Degradation processes such as morphological changes

[20,21] and reactions with water and air in the presence of light hinder further cost-effective development [22,23]. In effect, the photo-oxidation of organic materials used in the active layer can be treated by considering the stability of the materials, or by exploiting expensive encapsulations that may limit market opportunities [24]. Work has been done to identify the techniques and types of macro(molecules) that will enable high-stability OPVs [25,26]. However, the importance and high impact stability of electron acceptors has not been addressed to our knowledge.

PCBM, a pioneer acceptor material [27], remains the most widely used, and has been shown to enhance, in most cases, the stability of donor polymers by polymer singlet state quenching and radical scavenging which otherwise go on to cause cascading polymer degradation [28], a result supported by combined spectroscopic and degradation studies [29]. Given that PCBM degrades under the combined action of light and oxygen [25,30], it is worth considering its own stability with respect to other classes of acceptor carbon allotropes, especially given that it has been suggested that PCBM is primarily degraded at the carbon sphere [28]. Furthermore, the direct relation between the stability of the acceptor material and the photovoltaic device has been highlighted [31]: oxidized fullerene cages (PCBM) have deeper LUMO levels and act as electron traps in a device. Therefore this work focuses on the stability of a range of fullerenes with regards various oxidative

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attacks, and increases the scope of possibilities by comparing it against other carbon allotropes. We provide: (1) a simple method to estimate the relative stabilities of carbon-allotrope class materials against oxidation reactions; and (2) a detailed link between structure and degradation that has not yet been reported in detail. While it is understood that each material may lend itself in varying ways as physical barriers to contaminants, it is nevertheless a fundamental and important object to systematically study the correlation of the curvature of these carbon structures and their degradation energetics by well-established routes.

As the electronic properties of the carbon allotropes arise from sp^2 -hybridized carbon atoms, their distortion induces pronounced property modifications. It is well known that bending the hexagonal planar arrangement that make up graphene into carbon nanotubes (cylindrical bending) or fullerenes (spherical bending) determines several properties derived from chemical reactivity [32–34]. Chemical reactions, such as acidic attacks on carbon nanotubes [35], are understood to be dependent on the (m, n) index of the tube, which defines its radius of curvature. Experience shows that the more bent a carbon surface is, the more easily attacked it becomes [36]. This is generally accepted accordingly to the π -orbital axis vector analysis (POAV) [37,38], which provides an appropriate description of the electronic structure on non-planar conjugated molecules. This theory explains how pyramidalization angles are key to the differences in chemical potentials between curved and planar carbon structures. Moreover, carbons residing on curved surfaces should exhibit increased chemical reactivities due to diminished electronic delocalization and higher σ -bond characters [39,40]. Hirsch et al. considers the influence of the carbon-atom pyramidalization angle on the reactivity of carbon nanotubes [41]. However, we could not find work linking this intrinsic parameter of carbon curvature to oxidation, and material stabilities for devices.

2. Results and discussion

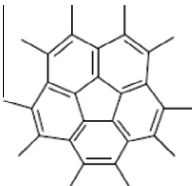
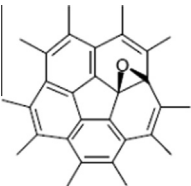
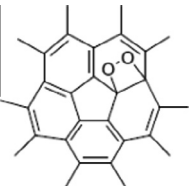
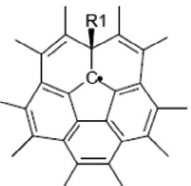
Three different attack routes are studied, a collision with atomic oxygen, a radical attack [42] and a molecular singlet oxygen attack,

and illustrated in Table 1. They were chosen as they model reactive species playing roles in degradation process of OPVs. In the atomic oxygen attack, it is assumed that an epoxide is formed, rather than a ketone or bridging ether, in accordance with prior studies [43,44]. Radicals can add to fullerene double bonds. In this case, we used a hydroxyl radical as probe. For the 1O_2 attack, a superoxide is formed and the singlet and triplet configurations are studied (S_0 and T_0 , respectively) [42].

Generally, the molecules chosen for this study comprise a nanoribbon model molecule which is strained over two parallel edges towards the center of the molecule, allowing one to fully control the radius of curvature, and as a consequence the pyramidalization angle. Where there is no curvature, i.e., the molecule is completely planar, we assume that the radius goes to infinity. The edges are zigzag and hydrogen-passivated and we attribute to this model a graphene-like character. The strain was applied by a controlled constrained distance linking the edge carbons from one side to the other, and the distance along the edge atoms of the same side was not allowed to relax. This defines a chord which was used to calculate the radii of the curvature. This is depicted with more details in Fig. 1c. More generally, the angular defect that gives rise to the curvature of any given system (Fig. 1a) forms a pyramid which has a circumscribed sphere in 3D space. The vertices of this pyramid bear the information of a pyramidalization angle and are related to the radius of the circumscribed sphere. Fig. 1b indicates the normal to the plane that bears the base of the pyramid. This normal defines the pyramidalization angle.

To study the effect of curvature on fullerene systems, we picked several medium-size fullerenes, namely C_{60} , C_{70} , C_{78} , C_{80} , C_{82} and C_{84} and attacks were performed on the asymmetric fullerenes at the equator and pole. No prior symmetry consideration was performed; this does not influence the final results [*vide infra*]. Although these two attacks were made in different regions, one should keep in mind that it is not enough to describe all the chemical environments that arise from this lack of symmetry. This is clearly seen for the case of C_{70} : for radical attacks, it has five possible regio-isomeric structures of a rC_{70}^* radical [45], where r is generic. Two out of these structures are located in what we term here

Table 1
Oxidation products resulting from the oxidation of C_{60} -based materials with atomic oxygen, singlet oxygen and radical species [1–3].

C_{60} -type material	Reactive species		
	Atomic oxygen	Singlet oxygen	Radical species
			

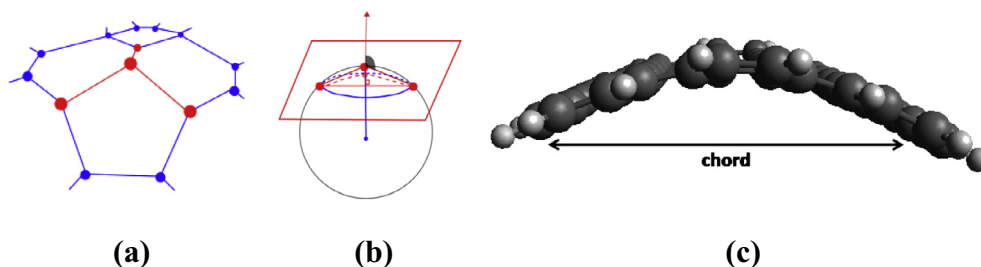


Fig. 1. a) and b) Definition of the curvature in terms of the radius of a circumscribed sphere and the relation with the pyramid formed by the angular defect. In b), the pyramidalization angle is calculated as 180° minus the angle shadowed; c) Definition of the chord caused by lateral strain.

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