



Exploring structures and properties of new geodesic polyarenes



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ABSTRACT

We have employed the self-consistent charge density-functional tight-binding, the density functional theory and the classical molecular dynamics methods to study new geodesic polyarenes, which can be synthesized via the regiospecific cove-region closure and HF elimination. We show that the shape of new polyarenes may be altered and controlled by the presence of C₆₀ fullerenes. The high intrinsic curvature of the geodesic arenes facilitates fusion with C₆₀ fullerenes. This propensity to fuse is consistent with the hypothesis of an optimal value of the bond-puckering angle at which graphene-like structures show maximum reactivity.

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1. Introduction

Geodesic arenes are a family of polycyclic aromatic hydrocarbons that has recently received a lot of attention, due to their potential use in the synthesis of fullerene isomers [1,2] and isomerically pure single-wall carbon nanotubes [3]. In a very recent paper Amsharov et al. presented an elegant method for obtaining geodesic arenes, which involves a regiospecific cove-region closure via HF elimination [4]. The method also uses activated $\gamma\text{Al}_2\text{O}_3$ as catalyst, which mediates the reaction at slightly elevated temperatures (100–150 °C). The advantage of this approach is the high chemoselectivity and regioselectivity, since the chlorinated or brominated analogues remain completely intact under these conditions. The reaction only takes place if the fluorine atom is positioned directly in the cove region. The method allows for a total control of the geodesic-arenes synthesis process and can be used to generate large non-planar carbon-based nanostructures.

Inspired by the geodesic-arenes study we perform a computational investigation of novel geodesic arenes, which can be obtained via the cove-region closure method. In the study we aim to answer the following three main questions: what are the common features of the 3-dimensional structures of various geodesic arenes; how the curvature and the shapes of the geodesic arenes be controlled when they are synthesized; does the intrinsic

curvature of the geodesic arenes facilitate their fusion with C₆₀ fullerene and production of hybrid nanostructures. To answer these questions we use a combination of theoretical methods including DFT, SCC-DFTB, and MD. All these methods have been previously used to describe various properties of carbon-based systems and, in most cases, the results and predictions derived from the calculations have been quite accurate.

2. Computational methods

The SCC-DFTB method (as implemented in the DFTB+ software [5]) is used in all calculations in this study to obtain the geometries of the investigated structures. These geometries are starting points for the DFT and MD calculations. Some information on the energetics of these systems are also obtained from the SCC-DFTB calculations. DFTB is based on the second-order expansion of the Kohn–Sham total energy in the Density-Functional Theory (DFT) with respect to the charge density fluctuations [6,7]. The zeroth-order approach is equivalent to the standard non-self-consistent tight-binding scheme, while at the second order a transparent, parameter-free, and readily calculable expressions for the generalized Hamiltonian matrix elements can be derived. These are modified by a self-consistent redistribution of the Mulliken charges (SCC) [8]. The DFTB method has been extensively used for modeling of carbon nanostructures and was shown to be in good agreement with more sophisticated methods in the determination of equilibrium geometries, energies and vibrational modes [6,9–12].

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However, as shown in our recent study [13], the DFTB method does not always properly describe the energetics of the C_{60} -graphene fusion reaction. Therefore, to elucidate the energetics of the C_{60} fullerene – arenes fusion we need to use the DFT calculations with the M06-2X functional, which allows for an accurate description of both the C–C bond-breaking and the noncovalent interactions. Due to the computational limitations we employ the ONIOM method [14] (as implemented in GAUSSIAN 09 software [15]) for single-point calculations with the atoms close to the bond-formation region described at the M06-2X/6-31+G* level of theory and other atoms described at the PM6 level of theory [16,17]. Throughout the text we use the notation M06-2X/6-31+G*/PM6 for these ONIOM calculations at 0 K.

MD studies are performed using the CHARMM27 parameter set [18], using the standard aromatic carbon (CA) and hydrogen (HP) parameters for all arenes and the C_{60} fullerene. The approach comprises two steps; in the first step systems consisting of 27 C_{60} fullerenes and a variable number of geodesic arenes are placed in a periodic box, their energies are minimized for 100 steps, and then gradually heated from 0 to 450 K with 50 K increments in short MD runs involving 250000 steps of 1.0 fs each. In the second step we perform a 10 ns MD run on the NPT ensemble with the constant temperature of 450 K (as used in the experimental synthesis of **1** and **2**) [4] and the pressure of 1 atm. The MD calculations are performed using the NAMD ver. 2.8 software suite.

3. Results and discussion

In their recent paper, Amsharov et al. showed only a few geodesic arenes synthesized by cove-region elimination with compound **1** (indaceno[3,2,1,8,7,6,*pqrstuv*]picene) being the simplest possible 'domino' piece for the synthesis of larger nanostructures involving two cove regions. The bond-puckering angle (defined in Figure 1

[13] as the divergence of the two six-membered or five-membered rings connected by one chemical bond from the perfect, flat surface of graphene, for which the puckering angle is 0°) for this system is equal to 18.7° , for the crystal structure, and 19.5° for the SCC-DFTB-minimized structure. This is similar to the 20.9° bond-puckering angle in an isolated fullerene. We can modify this puckering angle and the entire curvature of the arene by introducing additional benzene rings to **1**. Two such simple modifications are presented in Figure 1; both introduce two additional cove regions that force a larger curvature of the whole system. System **3** has the bond-puckering angle of 32.9° , while system **4** has the angle of 29.8° , with both systems having structures close to a half-sphere.

These results are interesting for two reasons. First, they show that by manipulating the topology of the arene any desired shape, including C_{60} fullerene-like shape, can be obtained. Additionally, as the previous studies show, these structures have strong tendency to cyclization and the energy barriers associated with the cage formation are low (on the order of 0.3 eV [19]). Second, the values of the puckering angle for **3** and **4** are close to the optimal bond-puckering angle (equal to 30.9°) [13], which allows for low-barrier bond formation between aromatic carbon–carbon systems (found e.g. in nanocones [20,21]). To study arene– C_{60} fullerene fusion and to estimate the energy barrier for the C_{60} fullerene chemical attachment an approach similar to that used in previous studies [13,9] is used. In short, we consider a bond dissociation/formation path where the coordinates of two carbon atoms forming the C–C bond of interest are incrementally changed and frozen, and all other atoms are free to relax. In all cases we start from two structures: the fully minimized structure of the arene–fullerene system chemically bonded via two C–C bonds of around 1.6 Å in length and a structure with the arene and fullerene systems separated and interacting via two carbon atoms separated by approximately

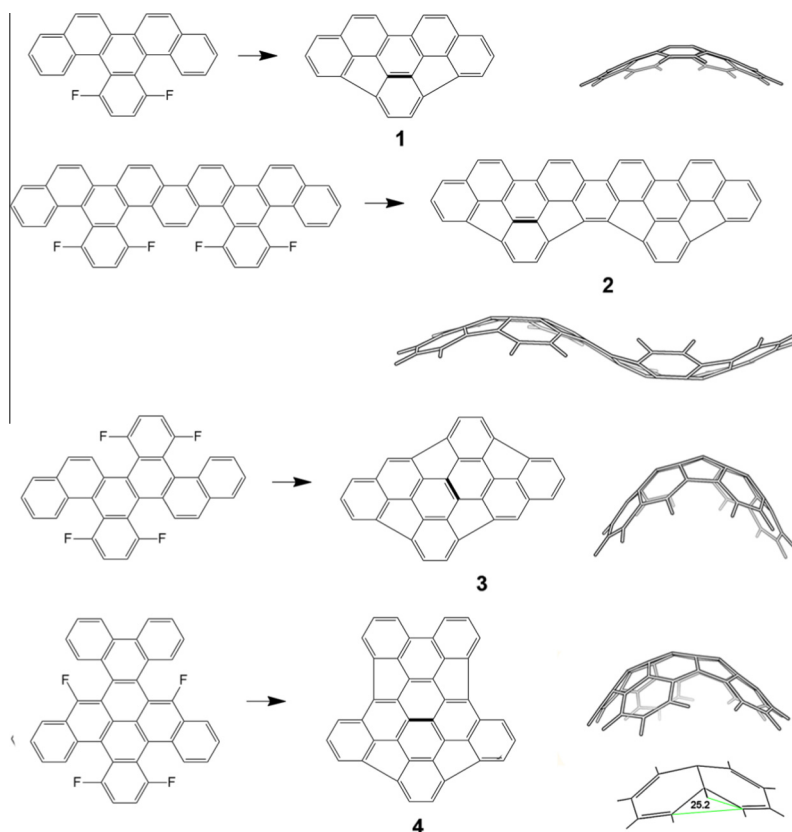


Figure 1. Geodesic arenes of different topologies studies in this work. Their shapes and the definition of the bond puckering angle are shown. The bond in bold indicates the bond to which C_{60} attaches, as shown in Figure 2 and 3.

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