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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

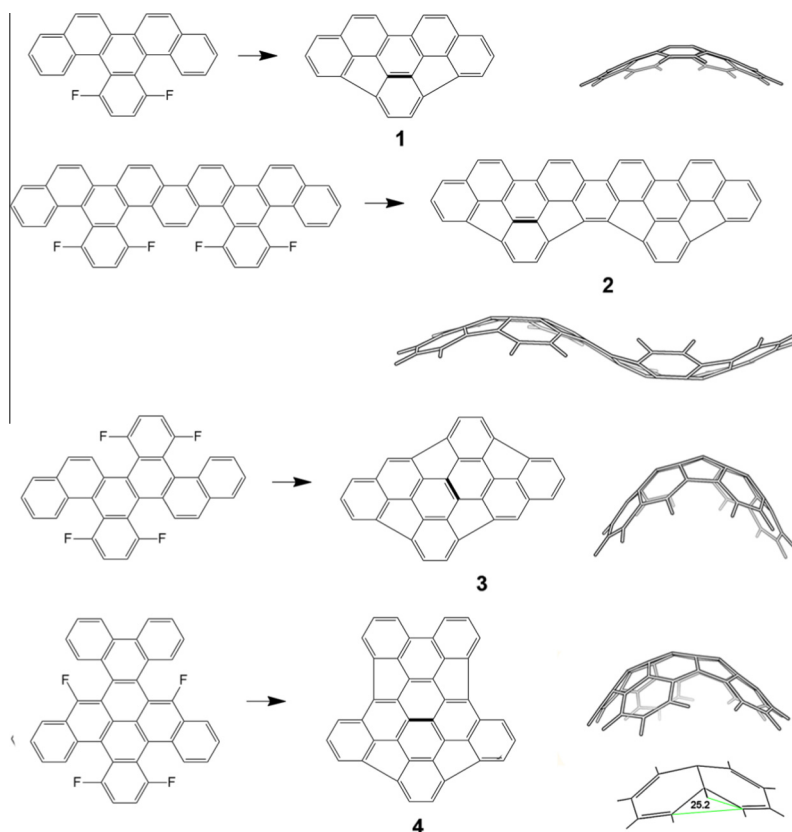


Figure 1. Geodesic arenes of different topologies studies in this work. Their shapes and the definition of the bond pucker angle are shown. The bond in bold indicates the bond to which C_{60} attaches, as shown in Figure 2 and 3.

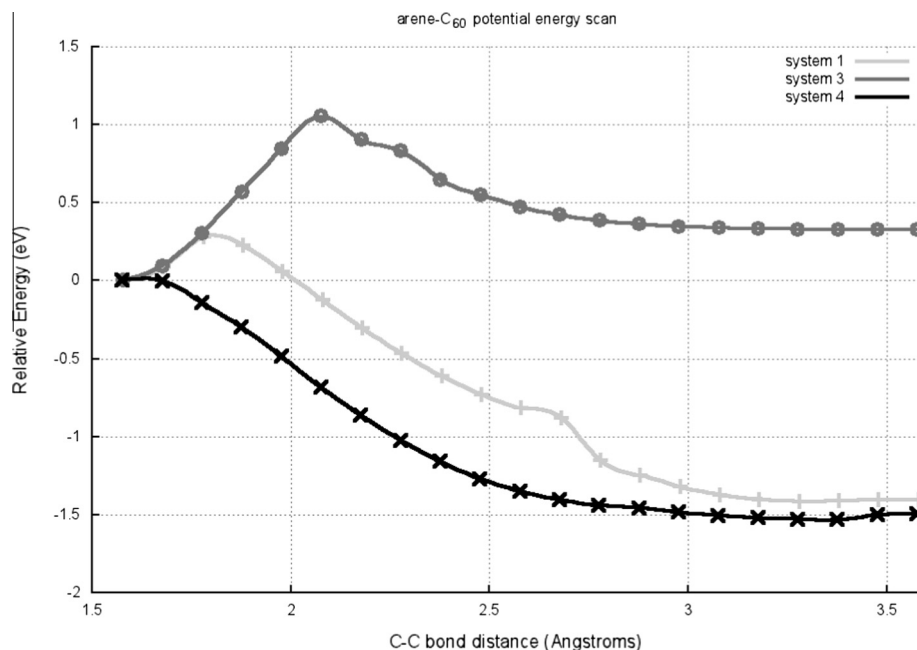


Figure 2. C_{60} -arene potential energy surfaces along the reaction coordinate for systems 1, 3 and 4.

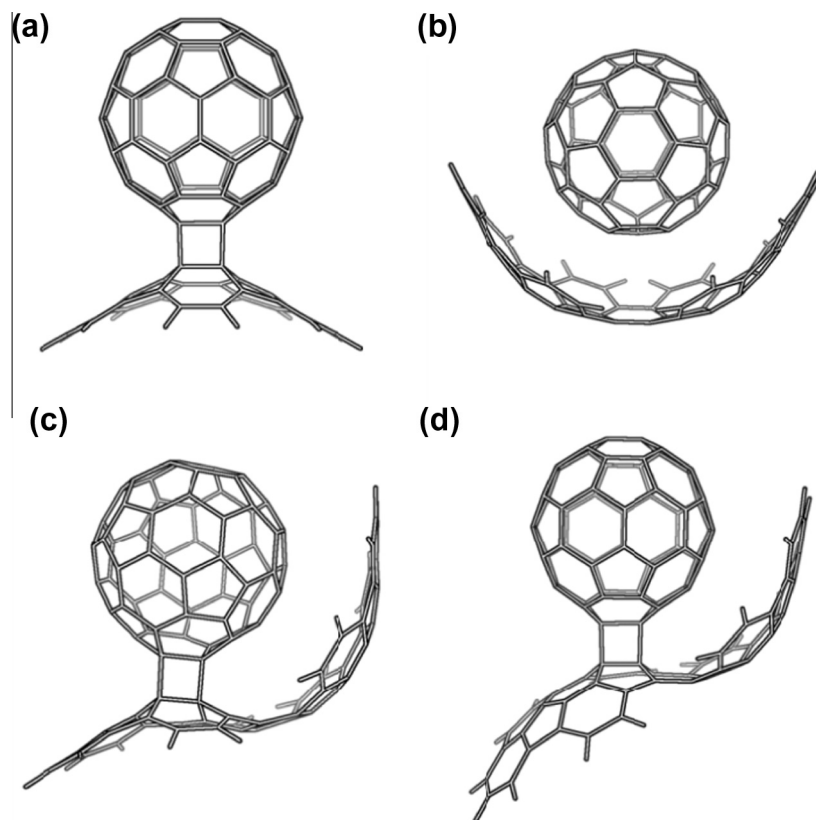


Figure 3. Minimum-energy structures of C_{60} fullerene – geodesic arene systems: (a) fullerene bonded to **1**; (b) fullerene interacting with **2** via van der Waals forces; (c) fullerene bonded to **2** via C–C bonds formed between two six-membered rings (geometry 1); (d) fullerene bonded to **2** via C–C bonds formed between a six-membered and a five-membered ring (geometry 2).

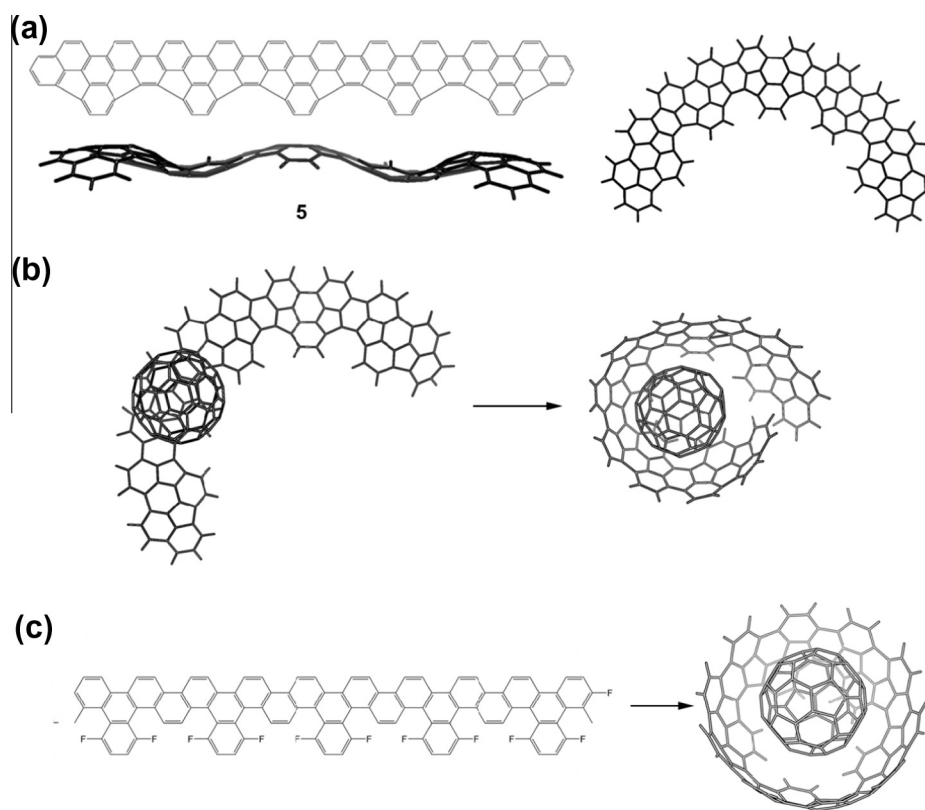
2.2 Å. We then vary the C–C bond distance by 0.1 Å in the 1.6–3.5 Å range. For selected cases we also calculate additional points along the reaction coordinate, particularly points positioned close to the bond breaking transition state. Such an approach applied before to study the activation energy for the C_{60} – C_{60} fusion provided a value

of 1.11 eV in good agreement with the experimental estimate of 1.25 eV [22].

Potential-energy scans along the reaction coordinate are presented in Figure 2 with the exact energies reported in Table 1. We find that the barrier for the dissociation of C_{60} fullerene from

Table 1Total energies of the system for the C₆₀-arene potential energy surfaces along the reaction coordinate for systems **1**, **3** and **4**.

C–C distance (Å)	System 1		System 3		System 4	
	Energy (Hartree)	Relative energy (eV)	Energy (Hartree)	Relative energy (eV)	Energy (Hartree)	Relative energy (eV)
1.58	-1534.56783	0.000	-1839.29702	0.000	-2069.04553	0.000
1.68	-1534.56472	0.085	-1839.29351	0.095	-2069.04562	-0.003
1.78	-1534.55765	0.277	-1839.28576	0.306	-2069.05068	-0.140
1.88	-1534.55956	0.225	-1839.27607	0.570	-2069.05646	-0.298
1.98	-1534.56567	0.059	-1839.26589	0.847	-2069.06343	-0.487
2.08	-1534.57244	-0.125	-1839.25833	1.053	-2069.07061	-0.683
2.18	-1534.57903	-0.305	-1839.26386	0.902	-2069.07724	-0.863
2.28	-1534.58506	-0.469	-1839.26643	0.832	-2069.08314	-1.024
2.38	-1534.59031	-0.612	-1839.27320	0.648	-2069.08811	-1.159
2.48	-1534.59461	-0.729	-1839.27685	0.549	-2069.09217	-1.269
2.58	-1534.59786	-0.817	-1839.27958	0.474	-2069.09514	-1.350
2.68	-1534.60012	-0.879	-1839.28155	0.421	-2069.09716	-1.405
2.78	-1534.61019	-1.153	-1839.28288	0.385	-2069.09847	-1.441
2.88	-1534.61373	-1.249	-1839.28373	0.362	-2069.09905	-1.456
2.98	-1534.61641	-1.322	-1839.28422	0.348	-2069.10011	-1.486
3.08	-1534.61826	-1.372	-1839.28455	0.339	-2069.10080	-1.504
3.18	-1534.61936	-1.402	-1839.28482	0.332	-2069.10141	-1.521
3.28	-1534.61979	-1.414	-1839.28488	0.330	-2069.10169	-1.528
3.38	-1534.61970	-1.412	-1839.28494	0.328	-2069.10189	-1.534
3.48	-1534.61943	-1.404	-1839.26500	0.327	-2069.10074	-1.502
3.58	-1534.61934	-1.402	-1839.28498	0.328	-2069.10044	-1.494

**Figure 4.** Exploring the geometries of a long, geodesic arene **5**; (a) structure and minimum-energy geometry of **5**; (b) two snapshots from MD simulations (as described in the text) showing change in arene geometry upon interactions with fullerene; (c) a hypothetical topology of a fluorinated arene which may lead to a closed, cage-like structure.

1 is located at the C–C distance of approximately 1.78 Å and is equal to 0.28 eV. This result suggests that the C–C bond between **1** and C₆₀ fullerene is likely to be unstable and the system can dissociate relatively easily. Interestingly, this result is also completely different from the result obtained for system **3** which shows a fullerene-like behavior. The approximate energy barrier found for the C₆₀ dissociation for this system is equal to 1.05 eV at the C–C bond

distance of 2.08 Å. However, system **4**, which has a similar bond puckering angle, behaves in a completely different manner. For this system we find no stable bound geometry.

The former studies of the fullerene dimer fusion have shown that the [2+2] cycloaddition reaction may be a rate-limiting step for the fusion, since it can be only initiated when two C–C bonds of the fusing fullerenes face each other [23]. We have therefore

decided to take a closer look at the differences in the molecular structures and topologies of systems **1**, **3** and **4** which can explain the different behaviors during the [2+2] cycloaddition. For system **4**, the chemical attachment of a fullerene involves a C–C bond located at the edge of the four six-membered rings. Such a situation is similar to chemical bonding to a graphene sheet and [13], despite an intrinsic curvature of system **4**, is energetically unfavorable. In systems **1** and **3** the fullerene binding occurs to the C–C bond located between two six-membered rings, and not at the edge of two additional five-membered rings, similarly to the C₆₀–C₆₀ binding case. As we can see from the calculations, such a scenario is energetically favorable, if the molecule has a proper curvature. For system **1** the bond puckering angle is equal to 18.7° (isolated molecule) and changes to 31.8° for the system bound to C₆₀. For system **4** the bond puckering angle is equal to 32.9° (isolated molecule) and is altered to 35.8° upon bonding to C₆₀. The latter values are much closer to the optimal bond-puckering angle (equal to 30.9°) and suggest that for system **4** only a small change in geometry is required to facilitate C₆₀ fullerene binding. It may also lead to a relatively easy functionalization by other chemical groups.

The propensity of geodesic arenes to change their shapes and curvature upon fullerene binding, observed in the first part of this study, is an interesting property that is further investigated in this work. Otero et al. showed that C₆₀ fullerene can be synthesized

using a C₆₀H₃₀ arene precursor via surface-catalysed cyclodehydrogenation, provided that the precursor has the required topology which forces a cage-like geometry [19]. In the case of geodesic arenes studied by Amsharov et al. showed that going to more complex arenes (e.g. from **1** to **2**) does not result in cage-like compounds, as the minimum-energy structure of **2** shows only a small curvature. One can alter the shapes of the arenes studied by Amsharov et al. by changing the topologies of benzene rings (as in **3** and **4**), but compound **2** itself also provides a scaffold for potentially interesting carbon systems. This is provided one can find a way to control its shape and the transition from a mostly flat to a largely curved structure (see Figure 4, system **5**). As seen before, the addition of fullerene molecules alters the shape of **2**, hence it can perhaps also be used to alter the shape of the more complex arenes to obtain **5**.

Our MD studies on a mixture of C₆₀ fullerenes and various geodesic arenes show, that it should be indeed possible to control their shapes. In all simulations the starting points are minimum-energy (minimally-curved) geometries of **2** and **5**, and similarly for arenes. Almost immediately upon a C₆₀ fullerene non-bonded attachment most of these arene molecules switch to more curved geometries encircling the fullerenes (see Figure 4). In the case of MD simulations of C₆₀ fullerene – **5** mixture (the longest system studied) some of the arenes have both ends coming very close to each other (starting from 16.3 Å and ending within 3.5 Å for the closest C–C distance), suggesting that perhaps a reaction involving connecting

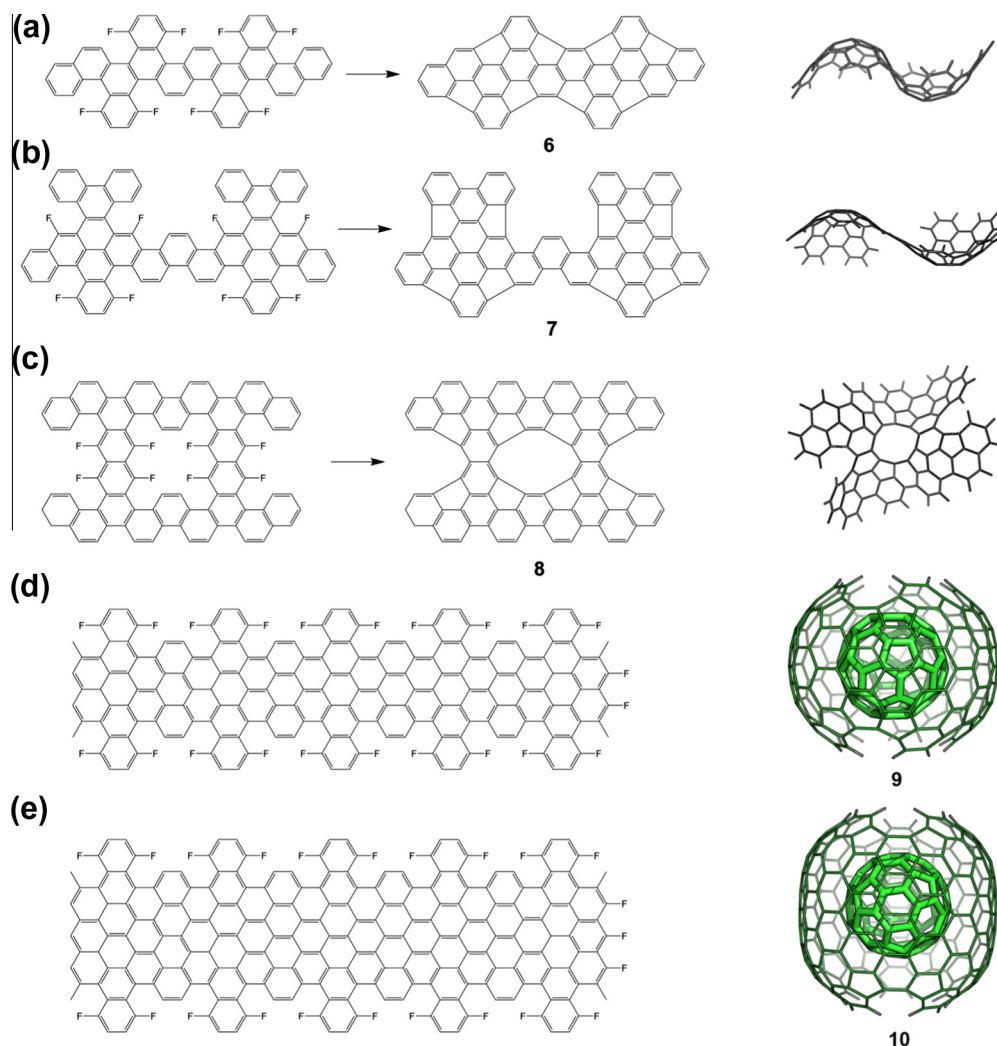


Figure 5. Exploring the geometries of a large geodesic arenes; (a–c) structures of **6–8**, their fluorinated precursors and minimum-energy geometries; (d–e) structures of fluorinated precursors of **9** and **10** and their minimum-energy cage-like geometries, possible in the presence of C₆₀ fullerenes.

these ends to form a closed structure is also feasible. It is worth mentioning, however, that in the original work, the HF elimination occurred only for the cove-region fluorine atoms. On the other hand, the proposed mechanism of such elimination [4] requires only a close distance between the F and H atoms undergoing elimination (equal to 1.7 Å in **1**) and our MD simulation shows that during the evolution of **5** such a H–F distance is common.

Figure 5 shows a number of geodesic arenes with different topologies and their optimized three-dimensional structures. We can see that by synthesizing different arenes we can control their shapes to a large extent. For example, systems **6** and **7** have large curvatures resembling buckyballs and may be potentially useful as precursors in the synthesis of fullerenes or nanotubes. All these systems may also be precursors of complex materials, e.g. molecular traps for C₆₀ and larger fullerenes. Due to the large surface of delocalized π -electrons, these systems should strongly interact with fullerenes, nanotubes, and other similar structures via attractive π – π stacking interaction. We have estimated the energies of these interactions for some of the investigated structures at the DFTB level of theory at 0 K. As expected, for some of the systems they are relatively high, particularly for system **2** (–56.0 kcal/mol), system **5** (–89.9 kcal/mol), system **9** (–156.9 kcal/mol), and system **10** (–157.8 kcal/mol). These values are much larger than e.g. interaction of the well-known double concave hydrocarbon

buckycatcher (–45.3 kcal/mol), where the experimental binding constant value is $K_a = 8600 \pm 500 \text{ M}^{-1}$ [24]. There is a number of similar, smaller systems for which binding energies have been estimated previously; these include corannulene (16–24 kcal/mol) [25], a quadrannulene derivative (37 kcal/mol) [26] and another buckycatcher with two corannulene units (37–39 kcal/mol) [27] and other fullerene host systems [28].

4. Conclusions

In conclusion, we have shown that new geodesic arenes may provide a wealth of interesting scaffolds, which can be used to synthesize buckyball-like molecules, parts of nanotubes, and other, new carbon-based materials. By synthesizing specific fluorine-functionalized arenes one can control the topology of these systems and obtain molecules with desired properties. Some of these arenes can be readily functionalized e.g. by attaching C₆₀ fullerenes, due to their high intrinsic curvature and fullerene-like topology. Others, which are characterized by high affinity towards C₆₀ fullerenes, can serve as buckycatchers. We have identified which structural features are responsible for specific properties, which should facilitate the rational design and synthesis of new molecules and materials based on geodesic arenes.

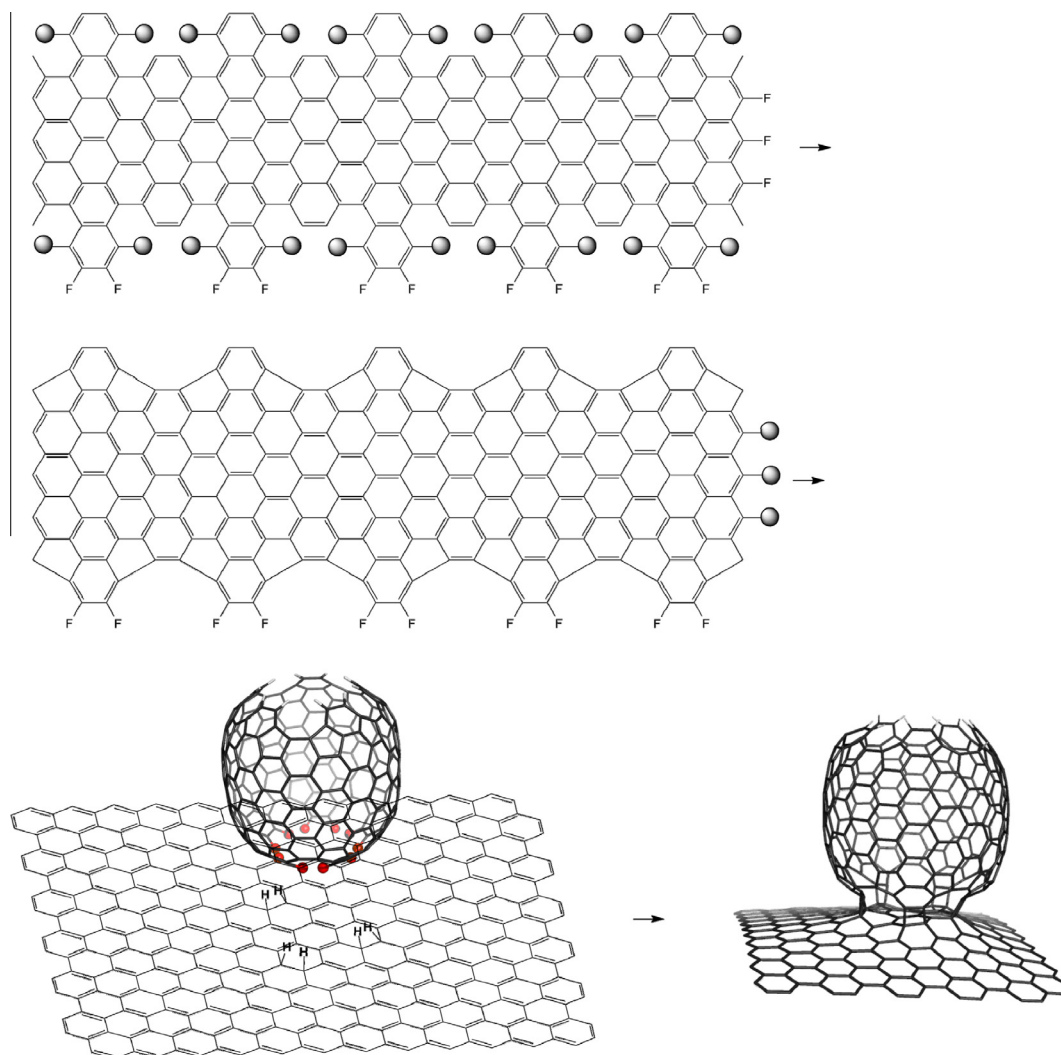


Figure 6. A hypothetical series of HF elimination leading to a pillared graphene-like structure. Fluorine atoms depicted at circles represent those F atoms that undergo the elimination reaction in that particular step.

There is one more interesting carbon-based system, which has not yet been synthesized, but warrants a short discussion within the context of this study. This system is pillared graphene, which has been predicted to have remarkable structural, thermal, and electronic transport properties [29–32], but has not been synthesized yet. Based on the results of this investigation and the possibility of an HF elimination reaction occurring not only in the cove region, but also between regions separated by a larger distance within the same molecule (intramolecular, as in **9** or **10**) or between two distinct molecules (intermolecular), we may speculate that geodesic arenes may be a starting point in the synthesis of pillared graphene. A schematic representation of such a hypothetical synthesis is presented in Figure 6. The synthesis is initiated by the synthesis of a precursor of **10**. This molecule undergoes a two-step intramolecular HF elimination; first of them results in a curved structure, while the second forces the closure of the molecule. These are followed by an intermolecular HF elimination with a partially hydrogenated graphene surface(s) to yield the final product, a pillared graphene-like structure.

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