4.2 (4+2) and (2+2) Cycloadditions of Benzyne to C$_{60}$ and Zig-Zag Single-Walled Carbon Nanotubes: The Effect of the Curvature


J.P.M. participated in the design of the project, performed all the calculations, analyzed the results, and co-wrote the manuscript.
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(4 + 2) and (2 + 2) Cycloadditions of Benzyne to C$_{60}$ and Zig-Zag Single-Walled Carbon Nanotubes: The Effect of the Curvature

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Supporting Information

ABSTRACT: Addition of benzyne to carbon nanostructures can proceed via (4 + 2) (1,4-addition) or (2 + 2) (1,2-addition) cycloadditions depending on the species under consideration. In this work, we analyze by means of density functional theory (DFT) calculations the reaction mechanisms for the (4 + 2) and (2 + 2) cycloadditions of benzyne to nanostructures of different curvature, namely, C$_{60}$ and a series of zigzag single-walled carbon nanotubes. Our DFT calculations reveal that, except for the concerted (4 + 2) cycloaddition of benzyne to zigzag single-walled carbon nanotubes, all cycloadditions studied are stepwise processes with the initial formation of a biradical singly bonded intermediate. From this intermediate, the rotation of the benzyne moiety determines the course of the reaction. The Gibbs energy profiles lead to the following conclusions: (i) except for the 1,4-addition of benzyne to a six-membered ring of C$_{60}$ all 1,2- and 1,4-additions studied are exothermic processes; (ii) for C$_{60}$ the (2 + 2) benzyne cycloaddition is the most favored reaction pathway; (iii) for zigzag single-walled carbon nanotubes, the (4 + 2) benzyne cycloaddition is preferred over the (2 + 2) reaction pathway; and (iv) there is a gradual decrease in the exothermicity of the reaction and an increase of energy barriers as the diameter of the nanostructure of carbon is increased. By making use of the activation strain model, it is found that the deformation of the initial reactants in the rate-determining transition state is the key factor determining the chemoselectivity of the cycloadditions with benzyne.

1. INTRODUCTION

Nanostructured allotropes of carbon such as fullerene C$_{60}$ and carbon nanotubes (CNTs) encompass an active area of research in many fields of nanoscience and nanotechnology. Three decades after its discovery, fullerene C$_{60}$ is still an attractive material due to its unique structure and specific properties. Numerous derivatives can be synthesized from C$_{60}$ with the purpose of promoting applications in biology, medicine, and optoelectronics, among others. There is also a great interest in CNTs due to their large values of modulus of elasticity, their high stability (they are stable up to 2800 °C in vacuum and 750 °C in air), their thermal conductivity, which is even better than that of some good thermal conductors like copper, and their particular electronic and optical properties, which depend on their sidewall curvature, chirality, and local environment can be similar to those of certain metals or semiconductors. In view of that, it is not difficult to imagine the synthesis of interesting materials developed from CNTs taking advantage of their outstanding thermal and electrical properties combined with high specific stiffness and strength. In fact, functionalized CNTs have been shown to be useful assemblies in fields of materials, medical, and biological sciences. However, the actual application of these nanomaterials is hampered because their selective purification is hard to achieve due to poor solubility of CNTs in conventional solvents or the formation of agglomerates because of their strong π-stacking tendencies. These problems can be partially or totally solved with proper chemical modifications. The most common chemical reactions used to functionalize carbon

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Scheme 1. Generalized Representation of the Reaction Mechanisms Studied in the Current Manuscript

"Biradical singly-bonded intermediates are represented as I; transition states and final products are labeled as TS and P, respectively. Two subscripts separated by a dash are used to indicate how the species are formed; in fact, they refer to chemoselectivity—regioselectivity. The left subscript takes the values of 4 2 and 2 2 to denote whether the 1,4- or 1,2-addition takes place, respectively, but it also acquires the value of 566 indicating the formation of biradical singly-bonded structures related to the attack on a 566 carbon center (i.e., a C566 center, see green dot in the fullerene structure). The right subscript takes the values of 5 and 6 to indicate whether a five- or six-membered ring (see 5-MR in blue, and 6-MR in red) is under attack; but it can also have the values of 5,6 and 6,6 to denote whether a [5,6] or [6,6] bond is attacked (see, respectively, orange and purple labels). An analogous terminology is used for SWCNTs.

nanostructures are the Diels−Alder reaction, the 1,3-dipolar (Prato) cycloaddition, photochemical silylation, carbene and nitrene additions, Bingel−Hirsch reaction, and (2 + 2) cycloadditions.31−36

There is experimental evidence describing the chemical functionalization of fullerenes through (2 + 2) arylene cycloadditions (1,2-additions). To our knowledge, the first study of the reaction of fullerenes and benzene was reported by Cooks et al.37 already in 1992. These authors found that the (2 + 2) benzene cycloaddition (BC) to C60, occurs at the [6,6] bonds of C60 (although they did not exclude the possibility of a [5,6] addition) to form mono-, di-, tri-, and teta-adducts. Three years later, the group of Nogami38 characterized by X-ray the adduct of the (2 + 2) cycloaddition of 4,5-dimethoxybenzene to C60. This adduct was shown to exhibit a benzylocyclobutene structure attached to a closed [6,6] bond of C60. In 2001, Nishimura et al. were able to synthesize, isolate, and characterize eight regioisomers corresponding to all possible [6,6] bisadducts generated by the (2 + 2) bisaddition of 4,5dimethoxybenzene to C60.39 More recently, Yang et al.40 claimed on the basis of NMR, UV−vis spectroscopy, and cyclic voltammetry, the formation of an unprecedented [5,6]-open adduct from the (2 + 2) cycloaddition of benzene to C60. In the case of C80, the first studies were reported by the group of Taylor.41,42 They found that C80 can accommodate up to 10 benzene addends. From the 1H NMR spectra, they concluded that benzene addition to C80 gives four possible monoadducts, three of them corresponding to (2 + 2) additions to [6,6] bonds and one being the result of a (4 + 2) cycloaddition (1,4-addition) in a six-membered ring (6-MR). In 1998, Meier et al.43 found by X-ray crystallography that one of the four monoadducts generated by the BC to C60 is a closed-cage [6,6] adduct. Two of the remaining three monoadducts were assigned to [6,6] bonds additions, and the last one on the basis of 13C NMR results was considered the result of a [5,6] attack to C60. The first successful BC to endohedral metallofullerenes (EMFs) was carried out in C60@C82 by Gu et al.44 who reported the formation of two different (2 + 2) monoadducts. The addition of benzene to La@C82 was shown to take place preferentially at the [5,6] bonds to yield close cyclobutene rings.45 Echegovian et al.46 reported that the BC with Sc2N@C82 produced two thermally stable cycloadducts corresponding to the addition of benzene to both a [5,6] and a [6,6] bond as confirmed by the X-ray crystal structures. These bonds were found to be elongated but not broken in the resulting cycloadduct (i.e., the carbon−carbon distance is ~1.65 Å in the final product).47 The (2 + 2) cycloaddition of Sc2N@C82 with 4,5-dipropoxybenzene also yields two adducts that were assigned to the [6,6]- and [5,6]-regioisomers.48 As far as we know, there is not a single experimental work reporting the (4 + 2) BC to (metallo)fullerenes. It has been claimed that small diameter carbon nanostructures like fullerene promote better the (2 + 2) cycloaddition.37,39

Within the chemical functionalization of CNTs, some proposals to reach covalent junctions between functional groups and nanotubes have been already provided.49−52 In the case of the BC to CNTs, more than one decade ago it was...
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suggested that the addition of aromes to single-walled CNTs (SWCNTs) could lead to the synthesis of paddle-wheel-like nanostructures.\textsuperscript{55} Later Langa and co-workers\textsuperscript{27,24} published the reaction between benzene and SWCNTs under microwave irradiation with a high degree of functionalization. The authors found that the arylene addition increases the mass of SWCNTs by a factor ranging from 5\% to 19\%, confirming thus the functionalization of these materials. In view of that, Nagase and co-workers\textsuperscript{55} recently described energy profiles of the (4 + 2) and (2 + 2) BC to armchair SWCNTs based on density functional theory (DFT) methodology. They determined that the (4 + 2) cycloaddition of benzene in a slanted position is the most favorable for large diameters of the nanotube. For small diameters (<10 Å), the (2 + 2) addition in a slanted bond is preferred thermodynamically, yet kinetically the most favorable attack is the one in the perpendicular position.

In summary, benzene reacts with fullerenes and EMFs through (2 + 2) cycloadditions that occur preferentially at [6,6] bonds, although there are several examples of [5,6] attacks. For SWCNTs, cycloadditions of benzene can produce both (2 + 2) and (4 + 2) adducts depending on the shape and curvature of the nanotube, as well as their intrinsic electronic nature. The mechanistic details of the BC to all these nanostructures of carbon have not been entirely elucidated yet, and the reasons for the chemoselectivity (preference of the (2 + 2) over the (4 + 2) BC) and regioselectivity (the [6,6] attack is more frequently found than the [5,6] addition in fullerenes) of the BCs have not been discussed to date. In this contribution, we aim to provide a comprehensive description and analysis of the chemo- and regioselectivity of the BC to different nanostructures of carbon. First, we present a study of both (4 + 2) and (2 + 2) additions to fullerene C_{60}. A generalization of the reaction mechanisms occurring in C_{60} is summarized in Scheme 1, wherein we have included terminology that is useful to identify every structure discussed through the whole manuscript. After defining the potential energy surface for the benzene cycloaddition (PES-BC) to C_{60}, we discuss the PES-BC of the (4 + 2) and (2 + 2) BC to zigzag SWCNTs. An equivalent terminology as defined in Scheme 1 is also used in the description of the reaction mechanisms studied for zigzag SWCNTs. We do not consider armchair SWCNTs because their reaction pathways were already discussed in the work by Nagase and co-workers.\textsuperscript{55} The effect of the sidewall curvature on the chemical reactivity of the nanostructures has been directly analyzed. To that aim, we have investigated both (4 + 2) and (2 + 2) additions to carbon nanostructures whose diameter ranges from 14.1 Å (large-diameter zigzag SWCNT) to 6.8 Å (i.e., fullerene C_{60}).

2. METHODOLOGY

All DFT calculations were performed using the Amsterdam Density Functional (ADF) program.\textsuperscript{60} Molecular orbitals (MOs) were expanded in terms of an uncontracted set of Slater-type orbitals (STOs) of double-\(\zeta\) (DZP) and triple-\(\zeta\) (TZP) quality containing diffuse functions and one set of polarization functions. STOs correctly describe the asymptotic, long-range, and near-the-nucleus (cusp) behaviors. However, their evaluation for systems with many tens of atoms can be computationally very expensive; therefore the frozen-core approximation\textsuperscript{55} was used, which freezes the core orbitals (i.e., the orbital 1s of the carbon atoms) during the self-consistent field procedure. It was shown that the frozen core approximation has a negligible effect on the optimized equilibrium geometries.\textsuperscript{57,58} Scalar relativistic corrections were also included, self-consistently by using the zeroth order regular approximation (ZORA).\textsuperscript{59,60}

Energies and gradients were calculated via the local density approximation (Slater exchange) with nonlocal corrections for exchange (Becke88)\textsuperscript{61} and correlation (Perdew86)\textsuperscript{62} (i.e., the B3PW functional). Moreover, energy dispersion corrections as developed by Grimme\textsuperscript{63} (D_{y}) were added to the DFT energy. It has been shown that dispersion corrections are essential for a correct description of the thermodynamics and kinetics of reactions with fullerenes and nanotubes.\textsuperscript{64} For open-shell systems, unrestricted calculations with broken symmetry were performed. This is particularly important in the case of biradical intermediates.

Geometry optimizations without symmetry constraints and analytical frequency calculations were performed in the gas phase at the BP86-D_{y}/DZP level of theory. Electronic energies were obtained in the gas phase with the TZP basis at the geometries optimized with the DZP basis (i.e., BP86-D_{y}/TZP/BP86-D_{y}/DZP). In the search for stationary points, the QUILD code (quantum regions interconnected by local descriptions)\textsuperscript{65} was used. QUILD works as a wrapper around the ADF program; it creates input files for ADF, then executes the program and collects energies and gradients generated by ADF. In addition, the efficiency of QUILD is reflected in the use of techniques such as adapted delocalized coordinates and the fact that this code constructs model Hessians with the appropriate number of eigenvalues.\textsuperscript{66} This latter feature is particularly useful for the search for transition state (TS) structures.

Relative Gibbs energies (\(\Delta G\)) were determined from electronic energies at the BP86-D_{y}/TZP/BP86-D_{y}/DZP level of theory together with corrections of zero-point energies, thermal contributions to the internal energy, and entropy determined in the gas phase at 298 K with the BP86-D_{y}/DZP method considering an ideal gas in standard conditions. It is likely that the entropy term may be overestimated by our gas-phase calculations based on harmonic frequencies; although we expect a comparable error for the different reaction pathways and, therefore, comparisons should not be affected by this possible overestimation of the entropy correction.\textsuperscript{67} Solvent effects were not included in the present calculations since the BC is usually carried out in rather nonpolar solvents. The absence of charge-separated species along the reaction coordinate suggests that solvent effects are unimportant in this reaction.

Finally, in the Supporting Information we provide a detailed description of the construction of the SWCNT models to be used in computational modeling (see Figure S1 and additional explanation; also see Table S1 and Figure S2 and discussion for a comparative study of the benzene cycloaddition to SWCNT constructed with different approaches). Moreover, for all structures we make sure that the number of cells is suitable for the purpose of our study; that is, electronic properties such as electronic energies were conveniently converged with respect to the size of the implemented model (see Table S2 and associated discussion).

3. RESULTS AND DISCUSSION

This section is divided into two parts. Section 3.1 contains a detailed study of the BC to C_{60} with an exhaustive description of the different reaction pathways. Then, by making use of the information in section 3.1, in section 3.2, the reaction...
mechanisms for zigzag SWCNTs are reported. The introduction of nanotubes of different diameter enables us to discuss the curvature effect of sidewall BC to different nanostructures of carbon. The effect of the curvature is studied with activation strain analyses at the transition state of the (2 + 2) and (4 + 2) reactions.

3.1. Benzyn Cycloaddition to C60. As far as we know, a detailed mechanistic study of the BC to C60 has not been consistently established yet. We, therefore, explore the PES-BC to C60 considering the four possible cycloadducts produced from the 1,2-addition to [5,6] and [6,6] bonds and the 1,4-addition to 5- and 6-MRs. The Gibbs energy profile in terms of changes in Gibbs energies for the formation of the four different adducts is depicted in Figure 1.

In the first stage of the reaction mechanism, a reactant complex (RC) is formed in which the main interactions between benzyn and C60 are noncovalent.88 We distinguish two arrangements of benzyn with respect to the fullerene surface, RCd and RCg, where d and T standing for displaced sandwiched and T-shaped configurations as schematized in Figure 1. Nevertheless, a detailed analysis of the structure and energy of those species is provided in Figures S3 and S4 in the Supporting Information. In the first TS structure, namely, TS\textsubscript{565-6} benzyn is attacking a C atom in the ring junction between one five-membered ring (5-MR) and two six-membered rings (6-MRs) of C60 to generate a biradical singly bonded intermediate, I\textsubscript{565}. In both the TS and intermediate, the CC of benzyn is oriented toward a 6-MR of the cage as shown in Scheme 1. TS\textsubscript{566-6} has a small imaginary frequency due to the flatness of the PES-BC, 23.21 cm\(^{-1}\), with a normal mode that suggests a reaction progress toward an intermediate structure with biradical character in which only one carbon in benzyn is covalently attached to a C60 center. The ability of benzyn to rotate in a very flat surface also gives rise to the formation of an orientational isomer, I\textsubscript{566}, isoenergetic to I\textsubscript{565}. More importantly, the description of the (2 + 2) and (4 + 2) BC to C60 can be consistently done from the idea of a rotating benzyn, the formation of biradical singly bonded intermediate structures being the rate-determining step of the (2 + 2) reaction but not for the (4 + 2) addition, see Figure 1. For all singly bonded intermediates and transition states, we determine that triplet (S\textsubscript{3} \approx 2.0) and open-shell singlet (S\textsubscript{1} \approx 1.0) biradical structures present similar energies (absolute energy differences of ca. 0.5 kcal/mol) indicating a weak spin coupling between the unpaired electrons of two fragments. However, these energy comparisons are done at the open-shell singlet optimized geometry; therefore, we deduce that a geometry relaxation for the triplet state could slightly stabilize it, and consequently, the ground state for biradical singly bonded structures could be the triplet state. Additionally, it is worth mentioning that small deformations of spherical C60 can bring about an appearance of fine structure in the electronic energy spectrum compared with the spherical case.89 Still, we assume that the system follows the singlet potential energy surface through the entire reaction pathway since the singlet-to-triplet spin-crossing is expected to be not allowed due to the small spin-coupling term of the dipole moment of the transition integral. In fact, the major change between the open-shell singlet and triplet spin densities is located in the two radical carbon atoms. Additional information in the electronic structure and spin–orbit interactions for carbon nanostructures can be found in the works by Andraž90 and Pincock et al.91–95.

As mentioned earlier, the biradical singly bonded intermediate I\textsubscript{565-6} and I\textsubscript{566-6} structures are the key structures leading to the different cycloadducts. I\textsubscript{565} presents the benzyn faced to a 5-MR, and thus it is the precursor of the 1,4-addition to a pentagonal ring, whereas I\textsubscript{566-6} faced to 6-MR leads to the formation of 6-MR-based cycloadducts. At these points, the (4 + 2) addition of benzyn can take place via TS\textsubscript{(4+2)-5} or TS\textsubscript{(4+2)-6} to yield P\textsubscript{(4+2)-5} and P\textsubscript{(4+2)-6} respectively. The (4 + 2) BC to C60 is kinetically hampered in view of the larger energy barriers (more than 20 kcal/mol) compared with its (2 + 2) BC counterpart. Moreover, the formation of P\textsubscript{(4+2)-6} is an endergonic process.

The possible rotation of benzyn in the intermediate structures is now evaluated to formulate a mechanistic pathway.
leading to the $(2 + 2)$ cycloadducts as schematized in Figure 2a. Coincidently the rotating-benzylene mechanism has been formulated very recently for EMA's by Zhao et al.\textsuperscript{74} There are two types of bonds to be attacked: [5,6] and [6,6] bonds. From I$_{566}$ only [5,6] bonds can be attacked to achieve the product resulting from the $(2 + 2)$ BC, P$_{122-5,6}$. Nevertheless, from I$_{666}$ both types of bonds are available to react giving rise to either P$_{122-5,6}$ or P$_{122-6,6}$. This situation shows that [5,6] adducts in C$_{60}$ are statistically favored. We have performed linear transit (LT) calculations to assess the energetic cost for the rotation of benzylene in the biradical singly bonded intermediates (see Figure 2b–d). Our LT results indicate that the carbon–carbon bond between benzylene and C$_{60}$ in both structures I$_{566}$ and I$_{666}$ can freely rotate since the rotation occurs in a practically barrierless process. In Figure 2, the dihedral angle $\varphi$ is monitored in order to describe the benzylene rotation. Bonds [6,6] and [5,6] are defined at $\varphi = 0^\circ$ and $\varphi = 124^\circ$, respectively. In this context, $\varphi$ in I$_{566}$ must be decreased from $103^\circ$ to $0^\circ$ to reach a [6,6] bond. The maximum point of the linear transit toward a [6,6] bond is given at $\varphi = 50^\circ$, and it provides an upper bound limit representing an energy barrier of 0.53 kcal/mol (see Figure 2b). This energetic cost is reported in Figure 1 as TS$_{22-5,6}$. This small energy barrier for the $(2 + 2)$ addition toward the [6,6] bond demonstrates that the rate-determining step for this process is given by the precursor TS$_{566}$. For the $(2 + 2)$ BC to a [5,6] bond, we were able to locate another biradical singly bonded intermediate, I$_{565-5,6}$ resulting from the rotation of benzylene toward a [5,6] bond ($\varphi = 124^\circ$) from either I$_{566}$ ($\varphi = 103^\circ$) or I$_{665}$ ($\varphi = 174^\circ$) (see Figure 2c,d, respectively). This reaction does not lead to a ring closure as observed for [6,6]. Unlike the barrierless ring closure on a [6,6] bond, the course of the $(2 + 2)$ BC is slightly hampered by an energy barrier of 3.4 kcal/mol characterized by a true transition state associated with the four-membered ring closure, TS$_{52-2,5,6}$.

Our complete analysis of the $(2 + 2)$ and $(2 + 2)$ cycloaddition to C$_{60}$ indicates that the $(2 + 2)$ BC to the [6,6] bond of C$_{60}$ is the most kinetically and thermodynamically favored reaction pathway. However, the difference in Gibbs energy barriers between [5,6] and [6,6] additions is small as a result we do not entirely discard the possibility of observing the $(2 + 2)$ BC on a [5,6] bond. These results are in line with the experimental observation that only $(2 + 2)$ BC are observed in fullerene and that both [6,6] and [5,6] additions have been reported in the literature, with the [6,6] addition being more frequently observed than the [5,6] one.\textsuperscript{77,80,40–42}

We have also investigated the possible open-cage structure of P$_{122-5,6}$ and P$_{122-6,6}$. Our results suggest that an open-cage structure of P$_{122-5,6}$ is not possible since we were not able to locate any structure with a long (\textgreek{r} > 2.8 \text{\AA}) attacked C–C [6,6]-bond. Nevertheless, an open-cage P$_{122-5,6}$ was characterized to be a local-minimum structure; yet the Gibbs energy in this structure is 4.3 kcal/mol above the energy of its closed-cage counterpart. Besides, the maximum point of a linear transit going from closed to open cage is calculated at 5.6 kcal/mol (see Figure SS in the Supporting Information). The structural deformation in the open-cage P$_{122-5,6}$ is significantly larger than that of the closed-cage cycloadduct (by 7.3 kcal/mol). This is partially but not fully compensated by the large interaction energy in open-cage P$_{122-5,6}$ due to better frontier orbital interactions among the deformed benzylene and C$_{60}$ moieties.\textsuperscript{75} We conclude that a closed-cage product is more likely to be observed. In this regard, our results resemble the work of Iyoda et al.,\textsuperscript{86} wherein the closed-cage product on a [6,6] bond is the most stabilized cycloadduct and it can be produced with a low-energy barrier, even though it is also suggested that the BC on a [5,6] may be kinetically competitive. On the other hand, when the reactant is 4,5-dibut oxybenzylene, Yang et al.\textsuperscript{46} suggested the formation of an open-cage [5,6] cycloadduct based on indirect evidence taken from $^1$H and $^{13}$C NMR, UV–vis spectra, and cyclic voltammetry results. From our calculations and taking into account similar experimental evidence,\textsuperscript{39,47} we conclude that the BC to C$_{60}$ can be conducted toward the formation of both cycloadducts P$_{122-5,6}$ and P$_{122-6,6}$ but we cannot support the hypothesis of open-cage structures.

3.2. Benzylene Cycloaddition to SWCNTs and the Curvature Effect. Models designed to construct SWCNTs under the Clar theory have been named finite-length Clar cells (FLCC), and we refer the reader to the seminal papers dealing with this subject.\textsuperscript{76,81,83} In this regard, we make use of complete Clar networks, which are fully benzenoid structures (see Scheme 2). These structures are more stable than their
counterpart Kekulé structures because aromaticity provides stability to conjugated systems due to the nature of molecular orbitals.\textsuperscript{53,83-86} However, by taking into consideration a molecular orbital model based on orbital-overlap arguments, the aromatic character of molecular systems involving $\pi$ electrons has been proposed to be strongly influenced by the geometry of the ring structure; as a result a regular or distorted geometrical arrangement indeed affects the aromaticity or antiaromaticity in the system.\textsuperscript{53,85} In addition, complete Clar network models for SWCNTs are fully benzenoid structures, have closed-shell singlet ground states (at variance with many non-FLCC), and reach faster convergence in their electronic properties with respect to the number of cells of the nanotube than conventional models for SWCNTs. In this FLCC classification, we select three different structures: (9,0), (12,0), and (18,0)-SWCNT. Additionally, we include some FLCC structures lacking completeness of the Clar network such as (8,0)- and (13,0)-SWCNT. All models are represented in Figure 3.

The BC to (9,0)-SWCNT is first described since the mechanistic details are exactly the same for all considered SWCNTs. As can be seen in Figure 4, the reaction starts with the formation of RC$_{48}$ (a true local minimum point in the PES-BC) followed by TS structures for either the (4 + 2) or (2 + 2) BC. We were not able to optimize a RC$_{48}$ structure. Like the BC to C$_{60}$ we confirmed TS$_{6666}$ to be a transition state structure with a frequency of 25.31 cm$^{-1}$ associated with a normal mode denoted $\text{RC}_{66}$ and the intermediate structure I$_{6666}$. To reach TS$_{6666}$, benzene has to be approximated to the nanotube surface with one of the arene carbon atoms at a distance of 2.01 Å and a dihedral angle (as described in Figure 5a) of $\phi = 66^\circ$. The formation of the intermediate structure I$_{6666}$ has a Gibbs energy barrier of 9.8 kcal/mol. Both TS$_{6666}$ and I$_{6666}$ have one of the benzyne carbon atoms directed toward a C$_{60}$ center of the nanotube and the other one toward the 6-MR (following the definitions introduced in Scheme 1). Therefore, the benzene rotation observed in the case of C$_{60}$ to yield the different cycloadducts also occurs in SWCNTs.

Once the biradical singly bonded intermediate I$_{6666}$ is formed, the final (2 + 2) cycloadduct formation can take place via two different pathways: the attack of benzene following a parallel orientation "p" with respect to the nanotube axis (shown in blue in Figure 4) or in an oblique fashion "o" (in red, Figure 4). One could therefore postulate the formation of the two possible intermediates that arise from these two orientations, that is, I$_{2(2+2):p}$ or I$_{2(2+2):o}$. The former could not be, however, characterized since the (2 + 2) BC evolves toward the ring closure before the rotation of benzene in I$_{6666}$ is completed (check LF calculation in Figure S6). As a matter of fact, the biradical singly bonded intermediate I$_{6666}$ localizes benzene with a distance of 1.54 Å and $\phi = 100^\circ$; and the rotation toward a parallel position means reducing $\phi$ to 0°. Analogously, the oblique position is found at $\phi = 120^\circ$. In the case of a (2 + 2) BC in parallel orientation, we in fact optimized a first-order saddle point at $\phi = 19^\circ$. The vibrational frequency calculation confirmed a small negative frequency of 75.31 cm$^{-1}$ due to the flatness of the PES-BC, and the associated normal mode suggests that this is a transition state for the rotation of benzene from I$_{6666}$ toward the parallel position (i.e., TS$_{6666}$). Nonetheless, the small energy barrier of 3.7 kcal/mol calculated with TS$_{6666}$ indicates that the reaction evolves to the formation of P$_{1(2+2):p}$ practically in a barrierless process (see details in Figure S6); thus I$_{2(2+2):p}$ and TS$_{2(2+2):p}$ could not be characterized. In the case of the oblique position, we optimized another first-order saddle point at $\phi = 105^\circ$ but with the unbound carbon atom in benzene closer to the unbound carbon atom in (9,0)-SWCNT (2.44 Å, this distance is 2.86 Å in I$_{6666}$). The vibrational frequency calculation confirmed a negative frequency of 279.31 cm$^{-1}$ associated with a normal mode resembling a ring closure; therefore we distinguish this structure as a true transition state for the ring closure of the (2 + 2) BC in oblique position, TS$_{2(2+2):o}$. Since TS$_{2(2+2):o}$ is not exactly localized at the oblique position ($\phi = 120^\circ$), we deduce that the reaction can proceed without previous formation of I$_{2(2+2):o}$. The energy barrier calculated with TS$_{2(2+2):o}$ is also...
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Figure 4. Gibbs energy profiles for the (2 + 2) (for blue and red lines, benzyne is, respectively, added in parallel and oblique position with respect to the nanotube axis) and (4 + 2) (black line) benzyne cycloadditions to (9,0)-SWCNT. Blue and red colored ΔG values stand for open-shell singlet structures.

Figure 5. Schematic representation of the rotation and bent orientation of benzyne in the different stationary structures before ring closure occurs. (a) A dihedral angle $\varphi$ is defined by the four blue-colored carbon atoms and used in the structural description of intermediate and transition state structures through the (2 + 2) BC. (b) A tilt angle $\theta$ is depicted and used in the structural description of the (4 + 2) BC. Gibbs energy barriers $\Delta G^\ddagger$ and some relevant distances between black-colored carbon atoms are given for TSs.

small, 2.6 kcal/mol, thus concluding that the (2 + 2) BC can equally proceed at parallel and oblique positions.

In the case of the (4 + 2) BC, $P_{(4+2)}\varphi$ is highly destabilized since its energy lies 9.2 kcal/mol above the energy of the reactants; consequently benzyne can only add to the parallel position with respect to the nanotube axis. In this regard, a TS structure was also obtained (with an imaginary frequency of 39.64 cm$^{-1}$, see linear transit in Figure S7 in the Supporting Information). In $RC_{66}$, benzyne is completely tilted with $\theta = 89.9^\circ$ (the tilt angle $\theta$ is defined in Figure Sb), and the arynes carbon atoms are localized at 3.27 Å from the nanotube surface. To reach $TS_{(4+2)}\varphi$, the tilt angle is reduced ($\theta = 139.1^\circ$) and benzyne is approximated to the nanotube surface at a distance of 2.50 Å, which is longer than the distance in $TS_{66}$ (compare Figure S, panels a and b). The structure $TS_{(4+2)}\varphi$ depicted in Figure Sb is a concerted transition state leading to $P_{(4+2)}\varphi$ with a Gibbs energy barrier of only 4.9 kcal/mol. We conclude therefore that the (4 + 2) BC to (9,0)-SWCNT in parallel position is both kinetically and thermodynamically favored. This notwithstanding, the binding energies of benzyne to (9,0)-SWCNT for the (4 + 2) and (2 + 2) differ only by a few kcal/mol as reported recently by Vasiliev et al. in a series of zigzag SWCNTs.\textsuperscript{87}
The mechanism as formulated in (9,0)-SWCNT can be also applied for the rest of the structures under consideration. In Table 1, we report reaction energies (ΔE) for the formation of benzene cycloadducts as well as the initial activation energy $E_i^+$ (i.e., the energy barrier from the reactant complex to the following TS). Results in Table 1 demonstrate that the (4 + 2) BC is always the preferred reaction pathway for finite-diameter zigzag SWCNTs because of the substantially lower $E_i^+$. It is also observed that the larger the curvature of the SWCNT, the lower the energy barriers and the larger the exothermicity of the (2 + 2) and (4 + 2) additions. Moreover, $P_{(4+2)r}$ is the most stabilized product in all the cases, and thus the kinetics and thermodynamics correspond to the same addition.

We also investigated the mechanistic details of the BC to nonbenzenoid centers like those reaction sites found at (8,0)- and (13,0)-SWCNTs and non-FLCC structures (the latter being zigzag SWCNTs uniformly cut at the tube ends with a high-spin ground state and electron localization at the edges). We reach the conclusion that the (4 + 2) BC in parallel position to nonbenzenoid centers and non-FLCC models of (n,0)-SWCNTs is still favored (see Figures S2 and S8 and Tables S1 and S3 and discussion in the Supporting Information for complete details).

Nagase and co-workers concluded that the activation energy for large-diameter (n,m)-SWCNTs is lower for the (4 + 2) BC but the (2 + 2) products are the most stable. Our results in Table 1 show that a gradual increase of the diameter of the SWCNT causes a steady increase in $E_i^+$ and $ΔE$ for both types of BC. This trend resembles the tendency observed by Nagase et al. in zigzag SWCNTs, however, the (4 + 2) addition is for all diameters preferred kinetically and thermodynamically over the (2 + 2) one.

To explain changes in reactivity due to the curvature of the nanostructure, we make use of the activation strain model, ASM, also known as distortion/interaction model. ASM is a helpful tool to better understand the origin of energy barriers. These barriers are analyzed in terms of strain and interaction energies being fragments participating in the formation or rupture of chemical bonds. Figure 6 schematizes the ASM for the BC to (9,0)-SWCNT.

In the ASM, activation energies can be separated into strain and interaction energies, that is, $ΔE = ΔE_{strain} + ΔE_{int}$. The strain energy, $ΔE_{strain}$, is the energy required to deform reactants from their equilibrium geometry into the activated complex, and the transition state interaction energy, $ΔE_{int}$, is the interaction energy between the deformed reactants in the transition state. This model can be extended through all the structures along the reaction coordinate; but here we only focus on the localized stationary points. Figure 6a shows that the (4 + 2) BC to (9,0)-SWCNT evolves with practically no deformation of the reactants, while for the (2 + 2) BC involves the formation of intermediate structures in which the reactants are significantly deformed before the ring closure. Despite the fact that (4 + 2) BC generates a more deformed 6-MR structure ($ΔE_{strain} = 80.5$ kcal/mol for $P_{(4+2)r}$), we confirm that the formation of the less-strained 4-MR structure produced through the (2 + 2) BC ($ΔE_{strain} = 56.7$ kcal/mol for $P_{(2+2)r}$) is not favored due to the preceding formation of a biradical singly bonded TS ($ΔE_{int} = 7.9$ kcal/mol for TS(666)), which cannot compete with the unstrained concerted transition state in the (4 + 2) BC ($ΔE_{strain} = 1.2$ kcal/mol for TS(466)); since the interaction energy is practically the same at the first TS of both BCs (−14.6 and −15.5 kcal/mol for the (4 + 2) and (2 + 2) BC, respectively), we conclude that the strain energy determines the course of the reaction. Therefore, those cycloadducts produced via a "less strained" reaction pathway will be favored. The same conclusion was reached by Houk and Osuna in a study of a series of (4 + 2) cycloadditions to PAHs.

It is more illustrative to carefully analyze the TS energy, $ΔE_{TS}$, at the first step of the BC to SWCNTs. Figure 7 shows the evolution of $ΔE_{int}$ and $ΔE_{strain}$ as a function of the diameter and shape of the nanostructures, and Table 2 reports some structural parameters for the species under consideration. Observe that benzene is farther and more tilted for tube-shaped structures with smaller diameters. This result agrees with the Hammond postulate that follows naturally from the ASM and states that more exothermic reactions have TSs with more reactant-like character.

In order to examine $ΔE_{int}$ for C60, the second TSs (i.e., those TSs related to the ring closure, TS(323) and TS(423)) must be taken into consideration since the first TS (TS(666)) is common for both BCs. Accordingly, it is

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Table 1: Initial Activation Energies ($E_i^+$) and Reaction Energies (ΔE) in Terms of Electronic Energy (kcal/mol) as a Function of the Diameter of the Structure (A)

<table>
<thead>
<tr>
<th>(n,m)</th>
<th>diameter</th>
<th>$E_i^+$ (4 + 2)</th>
<th>$E_i^+$ (2 + 2)</th>
<th>$ΔE$ (4 + 2)</th>
<th>$ΔE$ (2 + 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8,0)</td>
<td>6.26</td>
<td>1.25</td>
<td>4.74</td>
<td>−61.68</td>
<td>−59.49</td>
</tr>
<tr>
<td>(9,0)</td>
<td>7.05</td>
<td>1.32</td>
<td>5.67</td>
<td>−57.39</td>
<td>−53.92</td>
</tr>
<tr>
<td>(12,0)</td>
<td>9.39</td>
<td>2.36</td>
<td>7.94</td>
<td>−47.88</td>
<td>−45.17</td>
</tr>
<tr>
<td>(13,0)</td>
<td>10.18</td>
<td>2.42</td>
<td>7.81</td>
<td>−47.28</td>
<td>−42.61</td>
</tr>
<tr>
<td>(16,0)</td>
<td>14.09</td>
<td>5.22</td>
<td>8.90</td>
<td>−39.54</td>
<td>−37.61</td>
</tr>
</tbody>
</table>

$ΔE$ is the energy difference between products and reactants. $E_i^+$ is the energy difference between the first transition state and the reactant complex.
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Figure 7. Strain energy, \( \Delta E_{str} \), (top), and transition state interaction, \( \Delta E_{int} \), (bottom), as a function of the diameter and shape of the carbon nanotube. Black and blue bars, respectively, correspond to the (2 + 2) and (4 + 2) BCs. Green and red bars account for the TS energy (\( \Delta E_{str} + \Delta E_{int} \)) for the (2 + 2) and (4 + 2) BC, respectively. 

For SWCNTs, the first (2 + 2) TS is compared with the (4 + 2) TS.

### Table 2. Some Structural Parameters of the Main Transition State Structures for the Cycloaddition of Benzene to Different Carbon Nanostructures

<table>
<thead>
<tr>
<th></th>
<th>(2 + 2)</th>
<th>(4 + 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d_1 )</td>
<td>( d_2 )</td>
</tr>
<tr>
<td>C60</td>
<td>1.505</td>
<td>1.575</td>
</tr>
<tr>
<td>(8,0)</td>
<td>2.065</td>
<td>2.498</td>
</tr>
<tr>
<td>(9,0)</td>
<td>2.005</td>
<td>2.498</td>
</tr>
<tr>
<td>(12,0)</td>
<td>1.949</td>
<td>2.558</td>
</tr>
<tr>
<td>(13,0)</td>
<td>1.936</td>
<td>2.558</td>
</tr>
<tr>
<td>(18,0)</td>
<td>1.925</td>
<td>2.166</td>
</tr>
</tbody>
</table>

*Distances in Å and angles in degrees. Structures are TS(2+2),54 and TS(4+2),54.*

Consequently, the reacting carbon atoms in the nanotube have to adopt a closer situation to an sp²-type geometrical configuration, which causes more deformation.

The nearly null variation in \( \Delta E_{str} \) as a function of the diameter of the nanotube observed in Figure 7 can be partially explained in terms of frontier molecular orbital (FMO) theory. In Table S4 in the Supporting Information, HOMO and LUMO energies of each one of the fragments (i.e., benzene and (\( n_{60} \))-SWCNT) interacting in the corresponding TS for both (4 + 2) and (2 + 2) BCs are reported. We observe no significant variation of the HOMO and LUMO energies of the interacting fragments comparing the smallest against the largest diameter nanotube under study, a result that is attributed to the negligible variation in \( \Delta E_{str} \) as the curvature of the structure is increased, thus reinforcing our conclusions that the structural deformation is indeed the main factor determining the chemoselectivity of the cycloadditions with benzene.

### 4. CONCLUSIONS

In this work, we have studied the mechanisms for the sidewall cycloadditions of benzene to different nanostructures of carbon to account for the chemoselectivity (2 + 2 vs (4 + 2) additions) and regioselectivity ([5,6] vs [6,6] in fullerenes or parallel vs oblique addition in nanotubes) of the reaction. The (2 + 2) additions are preferred over the (4 + 2) for C60 and for the armchair SWCNTs of small diameter, whereas the zigzag SWCNTs and the armchair SWCNTs of large diameter favor the (4 + 2) attack. From the results obtained in the present work and previous studies (the following conclusions 2 and 4 are extracted from refs 74 and 55, respectively), we reach the following picture for the benzene cycloaddition to carbon nanostructures of different curvature:

1. In C60, once the biradical singly bonded intermediate structure is formed, the rotation of benzene in such an intermediate leads to the formation of closed-cage (2 + 2) cycloadducts in a practically barrierless process. The attack on a [6,6] bond of the cage produces the most kinetically and thermodynamically preferred reaction pathway, in good agreement with experimental evidence. Nonetheless, the attack on a [5,6] bond kinetically competes with the attack on a [6,6] bond; therefore the corresponding [5,6] product can be also observed as suggested in previous reports based on indirect experimental evidence.

2. For the \( X@C_{60} \) (\( X = S \) or \( X = Y \)) endohedral metallofullerenes, the situation is similar. The (2 + 2) addition is preferred over the (4 + 2) one and the [5,6] and [6,6] attacks compete, although the former is favored in the case of \( X: C_{60} \).

3. For zigzag SWCNTs, the parallel (4 + 2) cycloaddition of benzene in the parallel position to the SWCNTs is the most thermodynamically and thermodynamically preferred reaction pathway. When the diameter of the zigzag SWCNTs increases, the energy barrier increases and the exothermicity of the reaction decreases.

4. In armchair SWCNTs, the (4 + 2) cycloaddition of benzene in an oblique position is the most favorable for large diameters of the nanotube. For small diameters, the oblique (2 + 2) addition is preferred thermodynamically, whereas kinetically the most favorable attack is the one in the perpendicular (or orthogonal) position. Like zigzag nanotubes, when the diameter of the armchair SWCNTs...
increases, the reaction becomes less exothermic and the energy barrier increases.

The changes in chemoselectivity and regioselectivity can be explained in terms of structural strain and interaction between reactants. Thus, the sidewall (4 + 2) cycloaddition to zigzag SWCNTs evolves with practically no structural deformation making it the most favorable reaction pathway.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b11499.

Construction of conventional single-walled carbon nanostructures (i.e., non-Clar structures) and detailed explanation of how they are built, the four possible additions to conventional structure of (9,0)-SWCNT, comparison between reaction energies (considering reactants, reactant complex, transition states, and cycloadducts for both (4 + 2) and (2 + 2) additions) obtained with this model of (9,0)-SWCNT and the one constructed under the Clar theory with detailed discussion, performance of the size of the model implemented to construct (9,0)-SWCNT, potential energy surface for noncovalent interactions between benzyne and C_{60}, potential energy surface corresponding to the rupture of the attacked [5,6] bond of C_{60} in the (2 + 2) cycloadduct, linear transistors around the transition state structures involving the ring closure of the (2 + 2) and (4 + 2) cycloadditions of benzyne to (9,0)-SWCNT, cycloadditions of benzyne to benzodien and nonbenzenoid reaction sites, comparison of the reaction energies calculated on a benzenoid reaction site with the analogous nonbenzenoid ones, HOMO and LUMO absolute energies for interacting fragments in the first TS structure of the benzyne cycloadditions, orbital energies for fragments benzyne and (8,0)-SWCNT and benzyne and (18,0)-SWCNT, bibliography related to the construction of single-walled carbon nanotubes, Cartesian coordinates and Gibbs and electronic energies for all optimized structures of reactants, reactant complexes, transition states (with their respective imaginary frequency), and cycloadducts, including structures derived from conventional nanotube models and nonbenzenoid centers, as well as six-unit-cell structures (PDF)

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REFERENCES

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[Text continues with scientific articles and references related to cycloaddition reactions to carbon nanostructures]