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Research paper

Reactivity of cycloparaphenylenes: Studying the possible growth of single-walled carbon nanotubes with DFT methods

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We perform a theoretical study on a set of carbon nanorings (CycloParaPhenylenes or CPP) envisioned as molecular templates for the selective synthesis of carbon nanotubes. The shape of these precursors, originating from bending n phenylene units in *para* position until forming the corresponding nanoring [n]CPP, may drive the growth of armchair single-walled nanotubes. This kinetic and thermodynamic study covers a set of molecules with different diameters, analyzing the exothermicity and the reaction path of a CPP-based radicaloid mechanism. The methodology employed is based on validated density functionals for mechanistic studies, shedding light on the viability of this synthetic pathway.

1. Introduction

Nanotechnology is a challenging and growing field of knowledge that has aroused a big interest in the scientific community along the last years; one of the outstanding advances in this field are Carbon NanoTubes (CNTs), and the development of this technology has been one of the main worldwide goals in last decades. Currently, CNTs comprise a wide range of usage, from raw application in industry to more sophisticated ones in the lithium-ion batteries [1]. More specific investigations are devoted to disclose new (clean and selective) synthetic ways, envisioning more sophisticated applications (e.g. for organic electronic applications) and overcoming the traditional synthesis based on arc-discharge [2], laser ablation [3] or chemical vapor deposition [4], to name just a few of them. Interestingly, the use of molecular templates as chemical precursors is an emergent and relatively novel strategy from the synthetic point of view, ideally affording the size-specific growth of CNTs. This technique is based on employing n-ring CycloParaPhenylene ([n]CPP, see Fig. 1) molecules as adequate substrates for the spontaneous self-assembly and growth of the corresponding armchair CNT under certain reaction conditions [5,6], thanks to progress in epitaxial growth of Single-Walled (SW) CNTs [7]. Note that the design and bottom-up synthesis of CNT segments has progressed enormously along last years [6,8,9], and that synthesis of chiral or zig-zag CNTs could be also accomplished using other cyclic nanorings as precursors, although these other routes will not be studied here.

Only very recently some experimental evidences for the specific synthesis of SWCNT following this strategy were presented [10], after treatment of [12]CPP spin-coated on a C-plane saphire substrate with a flow of ethanol gas at high temperatures. The histograms with the CNT diameters distribution showed pronounced peaks consistent with the diameter (1.5–1.6 nm) of the [12]CPP used as a precursor [11], confirming TEM images and thus the successful synthesis. The authors comprehensively revised the two main possible reaction mechanisms proposed so far for CPP-initiated CNT growth, namely: (i) a neutral and classical Diels-Alder mechanism involving [n]CPP and acetylene C_2H_2, as diene and dienophile respectively, studied before in this context by Scott et al. [12]; and (ii) the ethynyl ($C_2H^{\cdot}$) radical addition mechanism, which is formed *in situ* from C_2H_2, also studied extensively before by Morokuma et al. [13,14]. Importantly, the authors did not experimentally observe any production of CNTs using $C_2H^{\cdot}$ or C_2H_2 as reactive agents, but the intrinsically entangled reaction conditions (i.e. temperature, reaction plate, and carbon source) did not allow to clearly isolate the reasons for that. Thus, they finally proposed a viable CPP radical-mediated mechanism involving the *in situ* generation of the $CPP^{\cdot}$ species, together with C_2 as carbon source from the flow of ethanol. The latter mechanism would necessarily operate at high temperatures (400–500 C) to provide the homolytic C–H cleavage of the [n]CPPs. This experimental information clearly opens new possibilities for the growth mechanism and rates of SWCNT, and prompts for accurate and systematic theoretical studies exploring the role of the $CPP^{\cdot}$ species.

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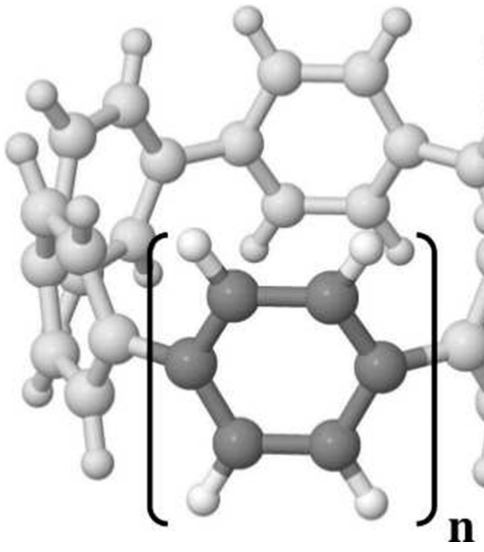
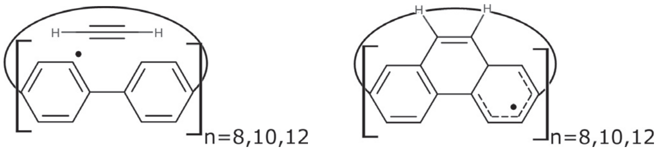


Fig. 1. Chemical structures of the [*n*]CPP systems.

Considering these experimental evidences, and the previous theoretical works as said before addressing the Diels-Alder [12] and the ethynyl radical addition mechanisms [13,14], we will focus next on a mechanism involving the CPP· specie but substituting C_2 with acetylene C_2H_2 as carbon source (see sketch below).



Sketch: Reactants (left) and product (right) of the mechanism studied.

We will try to find out whether this mechanism could also be operative in practice, through a detailed mechanistic study using state-of-the-art (cost-effective and accurate) quantum–mechanical methods based on Density Functional Theory (DFT), and compare its energetics with other existing mechanisms also employing C_2H_2 as a carbon source. Note that, contrarily to previous studies, we will also address the influence of the underlying density functional expression, including some models (i.e. BMK or mPW1k) specifically derived for reaction kinetics as well as more sophisticated methods as double-hybrid density functionals (i.e. B2-PLYP). We will first explain the computational methods and technical details in Section 2, before passing to their benchmarking using some model system (Section 3.1) and to the corresponding extension to the set of [*n*]CPPs selected (Section 3.2).

2. Computational methods

For kinetic and mechanistic studies, larger-than-defaults EXact-like eXchange (EXX) weights are needed for accurate energy barrier heights [15]. It has been documented before that conventional density functionals (e.g. B3LYP) underestimate the reaction barrier heights [16] and/or might fail to locate the transition state for non-covalently bound complexes [17]. In order to control these flaws of common density functionals, we have thus selected a number of modern expressions ordered for their increasing EXX weights (in %), to address the possible impact of this issue on thermochemistry and thermochemical kinetics of these systems: M06-L (0%) [18], M06 (27%) [18], BMK (42%) [19], mPW1k (43%) [20], M06-2X (54%) [18], and M06-HF (100%) [18]. We have also added to the study the double-hybrid B2-PLYP method [21], with a 53% of EXX together with 27% of MP2 correlation, to address the influence of going to higher orders of the hierarchy of DFT methods [22]. The 6-31G** and 6-311G** basis sets were initially used for studying basis set effects, and restricted (unrestricted) calculations were done for closed-shell (open-shell) species, with ultrafine grids always imposed for numerical integration.

The gas-phase Gibbs free energy of activation ($\Delta^{\ddagger}G$) and reaction (Δ_rG) was calculated after locating and fully optimizing each transition state (reactants and products), verifying their nature by the presence (absence) of imaginary frequencies, and obtaining their zero-point energies correspondingly. The Berny algorithm [23], as implemented in the Gaussian'09 package [24], was used for that purpose with the regular convergence of forces lower than $4 \cdot 10^{-4}$ Hartree/Bohr. If not otherwise indicated, all calculations were performed at 1 atm and 298 K, with the energy of reactants taken as origin for Gibbs free energy profiles.

3. Results and discussion

3.1. Initial benchmarking of DFT methods

The large number of librational degrees of freedom existing in [*n*]CPPs (arising from the mutual orientation of neighbouring phenyl rings) precludes a brute-force procedure without selecting in advance the reaction sites. However, previous evidences show that the reaction mechanisms explored so far (e.g. Diels-Alder) are highly local and occur in bay regions of the phenyl rings [25,26]. We will thus first proceed to benchmark the methodology using biphenyl as model system, taking advantage of its small size compared with the whole [*n*]CPP, and C_2H_2 as the other reactive agent. Using biphenyl as test case will allow us not only to try and discard different approaches to find the transition states that, in practice, is the hardest yet crucial part of the study, but also to bracket the $\Delta^{\ddagger}G$ and Δ_rG values according to the exchange-correlation functional choice, and to compare with previous estimates [14] although at a different temperature. We assume in the following that any evolution from reactants to products, passing through transition states, only depends on individual molecules; i.e., the growth would follow independent and continuous additions of C_2H_2 units. Fig. 2 sketches the mechanism studied, showing the chemical structure of all the species involved as well as the notation followed to identify them.

Table 1 gathers the $\Delta^{\ddagger}G$ values for energy barrier heights to both transition states starting from the previous point on the energy diagram, that is $\Delta^{\ddagger}G(\text{TS-1}) = G(\text{TS-1}) - G(\text{Reactants})$ and $\Delta^{\ddagger}G(\text{TS-2}) = G(\text{TS-2}) - G(\text{Intermediate})$, with values roughly grouped in the 10–14 kcal/mol for $\Delta^{\ddagger}G(\text{TS-1})$ and 3–6 kcal/mol for $\Delta^{\ddagger}G(\text{TS-2})$. The dependence on the weight of the EXX introduced into the methods also emerges from the results, as it was expected, with the exception being the M06-L functional due to the parameterization strategy followed in that particular case [27]. To further confirm the underlying and marked dependence of the results on the EXX weight for hybrid density functionals, we now compare BMK (42%) with mPW1k (43%) and found differences as low as 0.2–0.3 kcal/mol for both $\Delta^{\ddagger}G$. Finally, we can see how the M06-2X and M06-HF results are the closest ones to the benchmark B2-PLYP values, although the latter could also over-localize electronic (spin)-densities in more extended systems due to the presence of a too high EXX weight.

Taking into account the following concomitant facts: (i) the marked dependence of the results on the density functional choice, and (ii) the importance of medium-range effects in the structure and energetics of barrier heights, we select for the rest of the study