

Preview

Stitching up the Belt[n]arenes

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A synthetic strategy reported recently in the *Journal of the American Chemical Society* by Wang and coworkers, who used laser irradiation in the final key step of the synthesis, has led to the formation of highly strained belt[8]arene derivatives. This breakthrough could open doors to more controlled and precise syntheses of zigzag carbon nanotubes.

The age-old desire to prepare wholly unnatural products continues to spark the enthusiasm and fire the imaginations of chemists bent on developing efficient synthetic methodologies that will release chemistry from the shackles of thermodynamic control. As human beings, we have espoused a long and irresistible fascination with naturally occurring diamonds and graphite on account of their aesthetically pleasing structures and an ever-increasing number of applications. The total synthesis¹ of unnatural all-carbon compounds, including carbon nanotubes² (CNTs), in a precise manner remains a challenging goal. Single-walled CNTs display three different sidewall structures, referred to as the zigzag, armchair, and chiral forms. Whereas the armchair form exhibits metallic character, the zigzag one is semiconducting. The shortest segment of armchair CNTs, i.e., cycloparaphenylene (CPP), can be expressed (Figure 1A, left) as a compound with phenylene rings connected through their *para* positions. The synthesis of CPP, which was reported by Jasti, Bertozzi, and colleagues³ in 2008, led to rapid growth in the development of bottom-up approaches toward the precise syntheses¹ of structurally uniform CNTs. Another major contribution was made by Itami and coworkers⁴ in 2017 when they reported (Figure 1A, middle) the first syntheses of fully conjugated armchair hydrocarbon belts, leading to what is

tantamount to the π -extension of CPPs. The more rigid structures, exemplified by hydrocarbon belts (which exhibit belt-shaped constitutions consisting only of fused benzenoid rings), add yet another layer of complexity when it comes to their syntheses because of the increased ring strain compared with that of CPPs.

Despite these recent successes in preparing armchair hydrocarbon belts, members of the other major class of hydrocarbon belts with zigzag constitutions—namely the belt[n]arenes (Figure 1A, right)—have never been synthesized or observed experimentally, most likely because of their much higher ring-strain energy than that of their armchair counterparts. Most importantly, as the shortest segment of zigzag CNTs, belt[n]arenes could potentially serve (Figure 1C) as templates or seeds in the growth of uniform zigzag CNTs with well-defined structures and physical properties. Recently, in early 2020, Wang and coworkers⁵ proposed and executed a new synthetic strategy that led to the preparation of hydrocarbon belts that adopt truncated cone-like constitutions with fused alternating six-membered aromatic and seven-membered non-aromatic rings, producing the so-called belt[n]arene[n]tropilidenes. Starting from inexpensive and readily available resorcin[n]arenes, the authors were able to employ a ring-to-belt synthetic

transformation featuring exhaustive triflation, followed by consecutive vinylation and intramolecular olefin metathesis, to produce a series of the desired hydrocarbons. Even more recently, using a similar synthetic strategy, these same authors⁶ attempted the first synthesis of a substituted belt[8]arene and were successful to the extent that they could detect this compound by using mass (MALDI) spectrometry. The authors, whose work has just appeared in the *Journal of the American Chemical Society*,⁶ came up with the ingenious idea of taking advantage of the preorganized cone conformation and preinstalled phenolic hydroxyl groups of the readily available resorcin[4]arene. The possibility of stitching up all four “fjords” of resorcin[4]arene by intramolecular Friedel-Crafts alkylations was expected to produce the partially saturated octahydrobelt[8]arene, and it did in the event! Subsequent oxidative aromatization could potentially furnish the fully conjugated belt [8]arene with atomic precision.

Wang and colleagues commenced the implementation of their synthetic strategy by preparing the control hydrocarbon belt **5a** (Figure 1B) by exhaustive triflation, followed by a facile Suzuki coupling reaction and consecutive intramolecular Friedel-Crafts alkylations. The synthesis of the partially saturated belt **5a** encouraged the authors to pursue the preparation of octahydrobelt[8]arene **9b** with the opportunity for it to aromatize into the belt[8]arene upon oxidative dehydrogenation. With a slightly modified and optimized synthetic route (Figure 1B),

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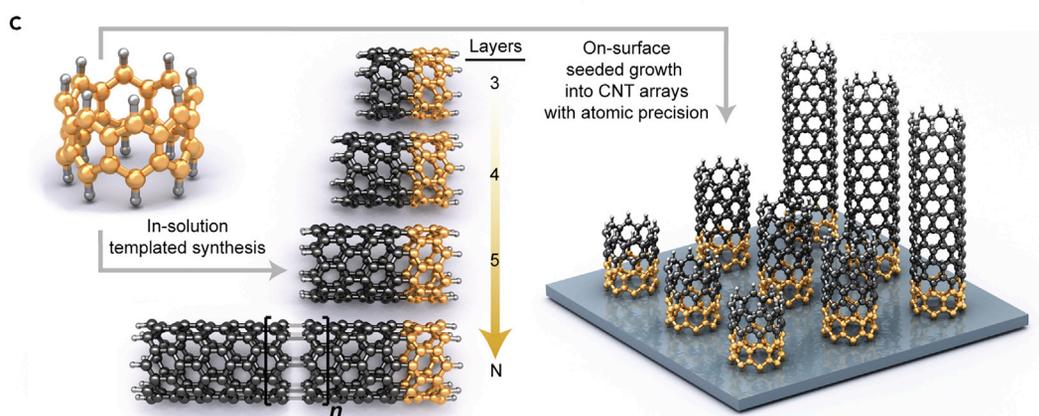
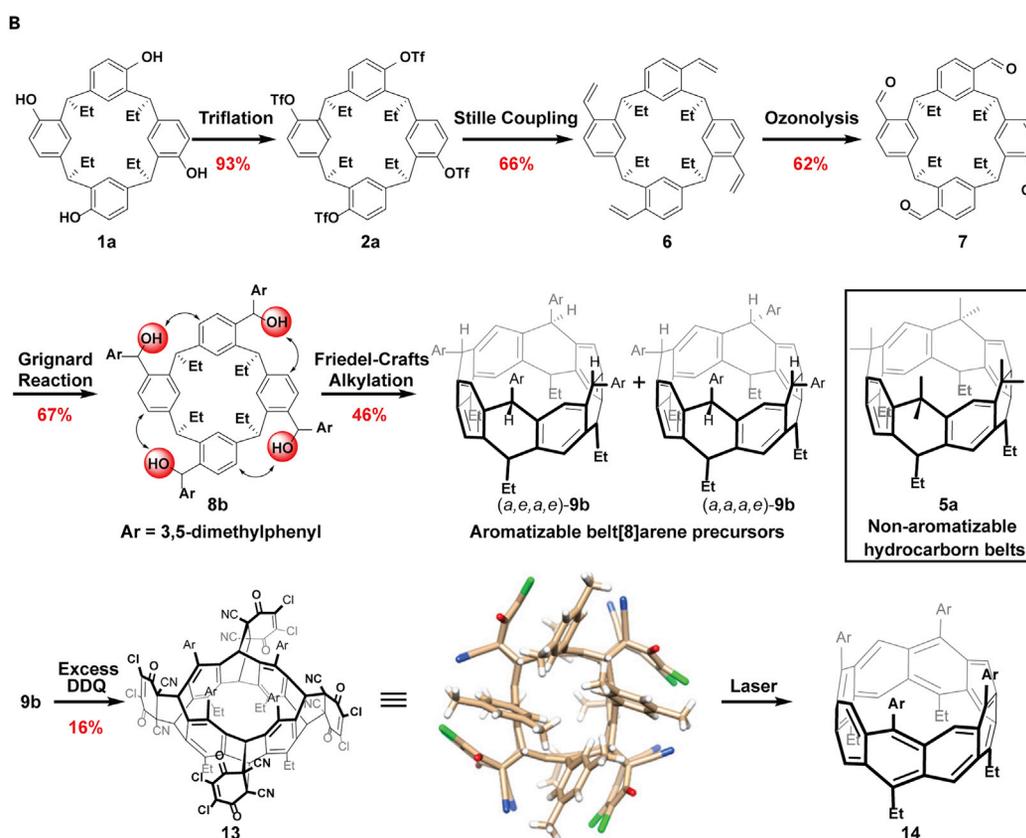
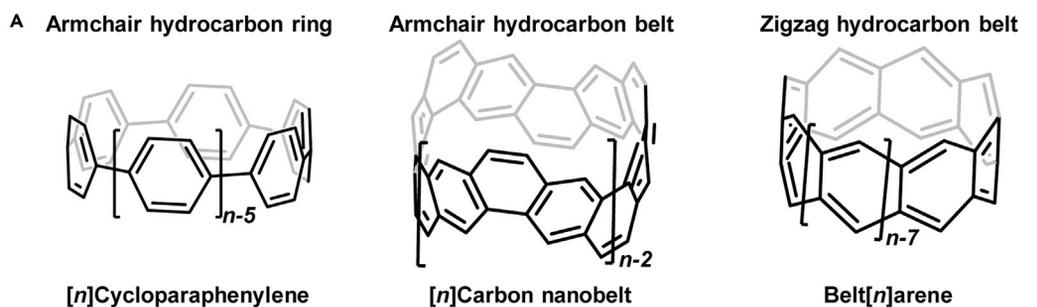


Figure 1. Synthetic Targets for Hydrocarbon Rings and Belts and Successful Synthesis and First Observation of the Octasubstituted (Ar, Et) Belt[8]arene Derivative 14 with Implications for Their Utility in the Seeded Growth of CNTs

(A) The structural formulas of the armchair hydrocarbon ring (left), the armchair hydrocarbon belt (middle), and the zigzag hydrocarbon belt (right).

(B) The detailed synthetic route toward the synthesis of the octasubstituted (Ar, Et) belt[8]arene derivative 14.

(C) Graphical illustrations displaying potential uses of zigzag belt[n]arenes in the precision synthesis of CNTs.

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starting from triflated resorcin[4]arene precursor **2a**, a Pd-catalyzed Stille coupling with vinylstannane afforded tetra-vinylated resorcin[4]arene **6**. Further ozonolysis, followed by the installment of an aryl (Ar) group, produced the corresponding macrocyclic tetraol **8b**. During the intramolecular Friedel-Crafts alkylations, the authors screened various acidic promoters extensively and concluded that Eaton's reagent (7.5 wt % phosphorus pentoxide solution in methanesulfonic acid) was the best one to promote the stitching-up reaction. This step produced (Figure 1B) a pair of diastereoisomers, (*a,e,a,e*)-**9b** and (*a,a,a,e*)-**9b**, as the major products in moderate yields after chromatographic separation. The structures of these diastereoisomers were confirmed by X-ray crystallography, revealing their rigid belt-shaped constitutions. As the last and also the most important step in this synthetic strategy, the authors carried out oxidative aromatization (Figure 1B) on the mixture of diastereoisomers by using different oxidants, of which 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was found to be the best option. In the event, Wang and coworkers⁶ employed an excess of DDQ in order to fulfill the complete oxidative aromatization, resulting in the formation of the belt[8]arene-DDQ₄ adduct **13**. It is impressive to have obtained belt **13**, even if the yield was only 16%, given that this relatively unstable adduct was generated from a series of oxidative aromatizations and Diels-Alder reactions in one pot. These observations support the effective DDQ-promoted aromatization of the distal cyclohexa-1,4-dehydrogenative diene rings. In order to obtain the fully conjugated belt[8]arene, the authors subjected adduct **13** to mild refluxing conditions or harsher (flash vacuum)

pyrolysis to promote retro-Diels-Alder reactions. Unfortunately, none of these methods led to the desired product. Finally and satisfyingly, the authors were able to complete the retro-Diels-Alder reactions on compound **13** under laser irradiation ($\lambda = 355 \text{ nm}$) and observed, for the first time, the formation of the fully conjugated hydrocarbon belt, the octasubstituted (Ar, Et) belt[8]arene **14** (*m/z* 928.5009), along with other belt [8]arene-DDQ adducts, as evidenced in the MALDI mass spectra. They found that belt[8]arene **14** could be produced as the major product upon fine-tuning of the laser intensity.

The present work, which constitutes the first synthesis and observation of the belt[8]arene derivative, represents a breakthrough in designing and synthesizing the simplest building blocks with extremely high ring-strain energies that are present in CNTs. It would appear that the authors drew their inspiration from macrocyclic chemistry and exercised their expertise in synthetic chemistry simply by exploiting the preorganization and pre-existing functional groups present in an easily accessible macrocycle, which they stitched up to afford the hydrocarbon belts by employing intramolecular Friedel-Crafts alkylations. Although the authors still have to go that extra mile and isolate the final substituted belt[8]arene as a crystalline product and perform detailed characterizations on it, their reported synthetic strategy does constitute progress toward the bottom-up construction (Figure 1C) of atomically precise nanostructures¹ and will hopefully encourage more chemists to join in the quest to advance carbon nanotechnology. In

addition, we anticipate that cutting-edge nanotechnology, such as atom manipulation⁷ using STM-AFM systems, will continue to progress rapidly and that new opportunities to complete the synthesis of these unstable, highly strained hydrocarbon belts will present themselves.

Turning the clock back over three decades, we pioneered^{8–12} the syntheses of belt[12]arene precursors in the late 1980s. We employed Diels-Alder reactions to synthesize a hexaepoxyoctacosahydro[12]cyclacene derivative,⁸ which we named kohnkene—after the graduate student, Franz Kohnke, who made it—in a highly efficient manner from the *syn*-isomer of 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene and 2,3,5,6-tetramethylene-7-oxabicyclo[2.2.1]heptane. Each time a new cyclohexene ring was formed during the macrocyclization process, which utilized 2 molar equivalents of both the bisdienophiles and the bisdienes, the cycloadditions were trebly diastereoselective. A sequence of (1) deoxygenation, (2) dehydration, and (3) partial hydrogenation reactions on kohnkene led to the isolation of the *D*_{6h} symmetrical dodecahydro[12]cyclacene derivative, which we called collarene^{9,10} and contained six benzene rings. In other words, in 1988 we got to within six benzene rings of belt[12]arene! It has been more than 30 years during which time little progress has been made in attaining this research goal. It is therefore with considerable pleasure that we find ourselves highlighting the recent work by Wang and coworkers,^{5,6} who, with their syntheses of the elusive belt[n]arenes, have made a significant contribution to the field of hydrocarbon belts.

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Preview

Programming Two-Dimensional Materials in Non-Euclidean Spaces

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Recently in *Nature Materials*, the Fu group reported a sphere diameter engineering (SDE) strategy for modulating the band gap of monolayer MoS₂, which exhibited high precision, reliability, uniformity, and flexibility with a tuning range of 360 meV. This work provides new ideas for engineering two-dimensional materials, commonly regarded as flatlands, in curved spaces.

Two-dimensional (2D) materials have attracted immense interest from both the laboratory and industry in the past decade because of their great potential in both fundamental sciences and diverse applications in flexible nanodevices and energy harvesting. Structurally, 2D materials exhibit two primary features: (1) highly ordered atoms arranged in plane, showing planar periodicity similar to that of bulk crystals; and (2) atomic-level thinness, giving considerable freedom to the out-of-plane deformation. Layered 2D mate-

rials also adopt dangling-bond-free surfaces, exerting weak forces to neighboring layers. Thanks to these structural characteristics, two special strategies have been developed for programming 2D materials with exotic properties. One is to stack 2D materials vertically with free tuning of the twist angle and the relative displacement between adjacent layers, creating new in-plane periodicity in the vertical heterostructures. Intriguing phenomena such as unconventional superconductivity,¹ novel direct optical band gaps,²

and chiral properties³ have been observed.

The other strategy is to engineer 2D materials in curved spaces rather than on flat surfaces. A curved space, also termed a non-Euclidean space, can be understood as a concave or convex surface on which the sum of interior angles of a triangle is no longer 180°. Even though 2D materials are often seen as “flatlands,” out-of-plane deformation can be easily introduced because of their atomic thinness and great freedom in the direction perpendicular to the lattice plane. Bending, folding, and crumpling have been applied to 2D materials. The curvature brought by these operations can break the

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