Carbon Nanobelts: Potential Precursors for the Controlled Preparation of Carbon Nanotubes

Reported by Joseph Forzano October 1, 2020

Background

Carbon nanorings (CNRs) and carbon nanobelts (CNBs) have been of significant interest to theoretical and synthetic chemists alike for over half a century. For the purpose of this seminar, these compounds are defined as fully conjugated macrocycles displaying a hoop-like three-dimensional structure and are characterized by radially oriented *p*-orbitals (Figure 1), high strain energies, and often high reactivities.[1] These properties alone originally inspired interest in the so-called nanohoops; however, they gained even greater attention with the discovery of single-walled carbon nanotubes (SWCNTs) in the early 1990s as potential building blocks for the controlled construction of these functional materials. Significant advances have been made with CNRs since Bertozzi's synthesis of cycloparaphenylenes in 2008,[2] but CNBs did not experience this same level of progress.[1] Nanobelts are ribbon-like nanohoops consisting of two or more non-intersecting continuous loops (Figure 2), and their fused-ring structures make hoop closure exceptionally challenging. Most CNBs are named according to the SWCNTs for which they make up a cross-section and can thus be classified into three broad categories: armchair, zigzag, and chiral belts.

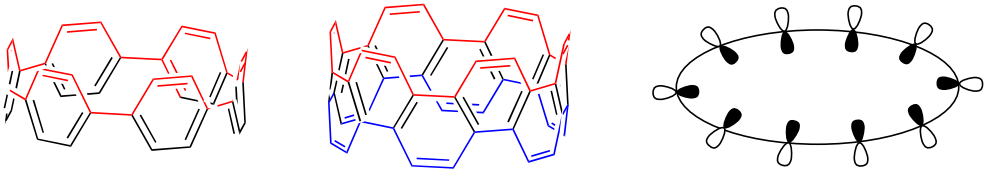


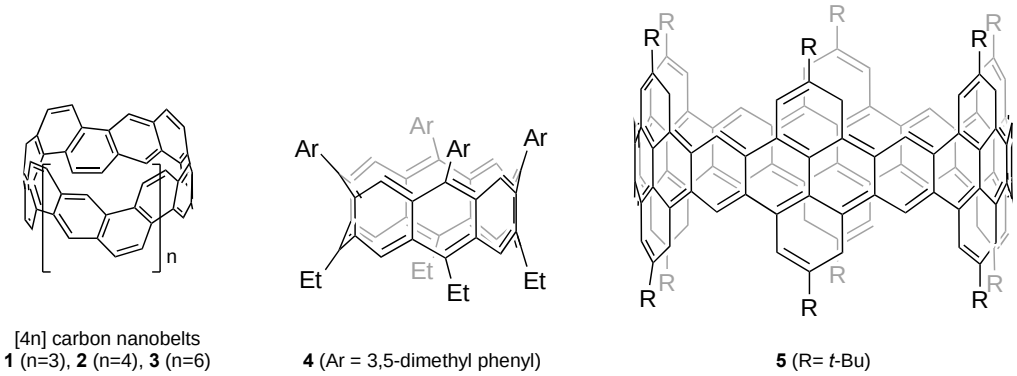
Figure 1 A carbon nanoring (left), a carbon nanobelt (center) and a schematic of the radially oriented *p*-orbitals of these structures (right).

Synthesis of CNBs

From initial studies in the late 1980s through the beginning of the century, most - ultimately unsuccessful - synthetic efforts used one of two strategies to achieve fully unsaturated belts: aromatization of a pre-constructed double-stranded macrocycle or closing of fjord regions with aryl-aryl coupling reactions.[1] Additionally, derivatizations of fullerenes and the incorporation of flexible rings provided related structures and allowed for characterization of various CNBs.[3,4] However, the isolated benzenoid CNBs remained elusive for nearly a decade.

At long last, Itami *et al*. reported the first successful synthesis and isolation of a [12] carbon armchair nanobelt **1** in 2017 using sequential Wittig reactions followed by a nickel(0)-mediated aryl-aryl

coupling reaction in 1% yield.[5] A subsequent publication in 2018 from the same group optimized the route used for the synthesis of **1** and successfully synthesized and isolated [16] and [24] ring CNBs (**2** and **3**, respectively), along with increasing the yield of **1.**[6] Since the publication of these seminal reports, several different methods for CNB synthesis have been reported. In 2019, the Miao group reported the synthesis of another armchair nanobelt and the first chiral nanobelt (not pictured) via the Scholl reaction, seeing a surprisingly small increase or even decrease in strain energy upon aromatization of the structure.[7] Earlier this year Wang *et al.* reported the first belt[*n*]arene **4** synthesis from simple starting materials via Friedel-Crafts alkylations followed by DDQ oxidation.[8] Most recently the Itami group reported another significant advance by constructing the first zigzag nanobelt **5** from iterative Diels–Alder reactions and deoxygenative aromatizations.[9]



[4n] carbon nanobelts
1 (n=3), **2** (n=4), **3** (n=6)

4 (Ar = 3,5-dimethyl phenyl)

5 (R= *t*-Bu)

Figure 2 Several of the CNBs successfully synthesized since 2017.

Outlook

SWCNTs from nature and made in labs often contain irregularities in diameter and wall structure, severely limiting their practical applications. Driven by a handful of research groups, progress toward the stepwise synthesis of consistent CNTs for practical applications has made significant strides through the development of methods for the synthesis of all three types of CNB. Future developments are expected with respect to generalizable synthetic routes for CNB synthesis, development of methodologies for controlled growth of CNBs into SWCNTs, and potential applications of isolated CNBs in areas such as optoelectronic device optimization and biological studies.

References

1. Robinovitz, M. *et al. Chem. Soc. Rev.* **2010**, *39* (8), 2879–2890.
2. Bertozzi, C. *et al. J. Am. Chem. Soc.* **2008**, *130* (52), 17646–17647.
3. Sawamura, M. *et al. J. Am. Chem. Soc.* **2003**, *125* (10), 2834–2835.
4. Gleiter, R. *et al. J. Am. Chem. Soc.* **2008**, *130* (21), 6716–6717.
5. Itami, K. *et al. Science (80).* **2017**, *356* (6334), 172–175.
6. Itami, K. *et al. J. Am. Chem. Soc.* **2018**, *140* (31), 10054–10059.
7. Miao, Q. *et al. CHEMPR* **2019**, *5*, 838–847.
8. Wang, M.-X. *et al. J. Am. Chem. Soc.* **2020**, *142* (10), 4576–4580.
9. Itami, K. *et al. ChemRxiv* **2020**. PRE-PRINT. DOI: 10.26434/chemrxiv.12324353.v2