Nanostructures

DOI: 10.1002/anie.201300625

Of Graphs and Graphenes: Molecular Design and Chemical Studies of Aromatic Compounds**

*Kim K. Baldridge and Jay S. Siegel**

aromaticity · computational chemistry · graphene · materials science · nanostructures

Dedicated to Kurt Mislow on the occasion of his 90th birthday

The recent passion of all things graphene has often focused on physics and materials aspects of this technologically important substance. However, graphene's ability to inspire novel molecular design defines an active research frontier uniquely suited to chemistry. Through the directed synthesis of polynuclear aromatic hydrocarbons (PAHs), related to graphene but of homogeneous molecular composition, we hone our ability to control structure and properties at the molecular level. Recently, a convergence of studies on novel aromatic compounds exemplifies the power and excitement of this area. Collectively, these studies further reveal a useful design principle for future work, which lies in the use of qualitative graph theory.[1]

Graphene has a hexagonal molecular graph akin to "chicken wire" (Figure 1 A).[2] Within the *graph* of graphene one finds *subgraphs* for a myriad of novel aromatic hydrocarbons, of which a small set of subgraphs (C3 and C6) can serve to demonstrate the art of molecular design by graph replacement.[3] Considering benzene as a "group element"[4] of six atoms that represent a graph vertex, one can then build symmetric C3 subgraphs within graphene, which evoke molecules such as neutral phenalenyl and triangulene radicals, as well as higher-order structures, simply by changing the length of the "ring fusion" *links* of the molecular graph.[5] Analogously, building symmetric C6 subgraphs yields coronene (i.e., [6]circulene; Figure 1 B) and kekulene (Figure 1 C), two archetypal polynuclear aromatic hydrocarbons at the heart of our understanding of benzenoid and hence graphenoid chemistry.[6]

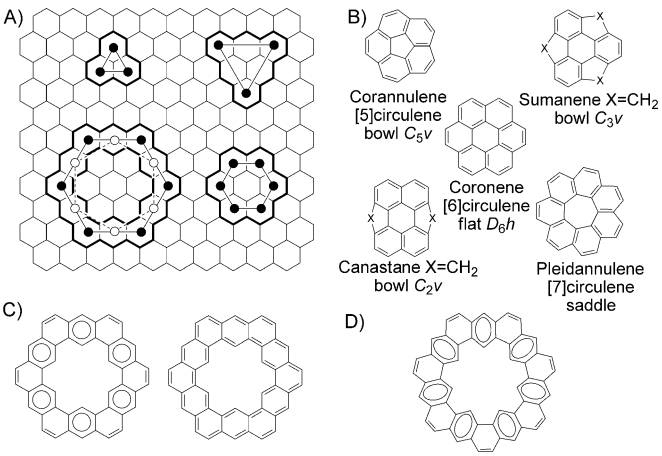

Figure 1. A) Graphene and subgraphs C3 and C6. B) Desymmetrization of coronene. C) Kekulene's structure ala Clar or as ring within ring. D) Septulene.

These elementary fragments of graphene become primary targets for chemical synthesis and tractable models for materials properties. A systematic approach to structural perturbation arises from deviations in ring size and atom type. Starting from coronene as an [*n*]circulene, one can envision perturbations of the hub as well as the rim rings. Changing the hub ring size by one conceptually changes coronene from [6]circulene to either [5]circulene (corannulene) or [7]circulene (pleiadannulene; Figure 1 B). Along with this change in hub ring size up and down comes an out-of-plane distortion to a bowl and saddle shape, respectively.[7] Note that changing the hub ring size also changes the order of the graph by changing the number of vertices as well as links.

Changing the rim ring size can occur in numerous ways, but to keep the illustration manageable, consider two symmetric representations: a) one changing rings along a diametric axis and b) one changing rings that constitute a three-fold symmetric grouping (Figure 1 B). In the former, contraction causes a curling of the sheet, like a canasta basket, whereas expansion induces a warping or twisting idealized as a helix. In the latter, contraction causes a bowling, as seen in sumanene and its heteroatom analogues (Figure 1 B), whereas expansion causes a puckering or rippling of the sheet. These distortions are basic perturbations to a flat sheet structure and can be transferred conceptually to other elementary fragments.

For kekulene as an archetypal [*n*]cycloannulene, a change in hub ring size changes the order of the cyclic graph, as exemplified in the synthesis of septulene by King and coworkers (Figures 1 C and D).[8] Septulene's computed saddle form, a minimum in a shallow well of the potential energy surface, undulates through pseudorotation and results in

[*] Prof. K. K. Baldridge, Prof. J. S. Siegel
Organic Chemistry Institute, University of Zurich
Winterthurerstrasse 190, 8057 Zurich (Switzerland)
E-mail: jss@oci.uzh.ch
Prof. J. S. Siegel
School of Pharmaceutical Science and Technology
Tianjin University, Tianjin (P.R. China)

[**] General funding from the Swiss NSF is acknowledged.

dynamic sevenfold symmetry; the specific bond lengths (experimental and computational) support a Clar electronic structure.[9]

Myśliwiec and Stępień recently synthesized chrysaoroles, an example of kekulene rim ring contraction and heteroatom replacement at three symmetry related sites (Figure 2A).[10] Consistent with the distortions observed from constriction of the rim of coronene to sumanene, chrysaorole also adopts a bowl-shaped geometry, with the added feature that the hub carbon atoms map to an [18]annulene.

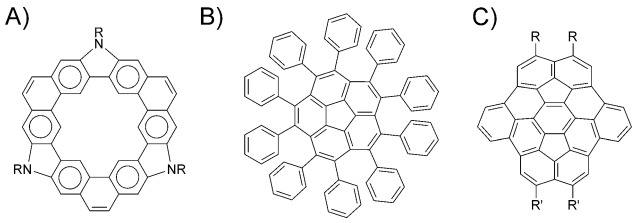

Figure 2. A) Decaphenylcorannulene. B) [6]Chrysaorole. C) Buckybowl.

Connecting arenes together by formation of new carbon–carbon bonds is a powerful Nobel-prize winning chemical methodology. Enhanced methods in this area include direct arylation of arylboronates with arene hydrocarbons by iridium insertion into an arene carbon–hydrogen bond. Recently, Scott, Itami, and co-workers have pushed this to a new level by perarylating corannulene (Figure 2B).[11] The steric congestion of the perarylation is evident from the very shallow bowl depth characteristic of persubstituted corannulenes, predicted by computation, and deduced from their disordered crystal structure.

Graph-based design of carbon material fragments need not be restricted to start from graphene. Fullerenes and carbon nanotubes serve equally well, as is evident from the wealth of chemistry from studies on corannulene and other C_{60} fragments. Very exciting are the elaborate orange-peel or origami-like strategies for preparing open networks and sewing them up.[12] Here, the methodology of Amsharov et al., using highly activated aluminum oxide and temperatures of approximately 400 °C shows promise.[13] Related work with highly Lewis-acidic organosilyl cations could also play an important role in this area.[14]

Less commonly observed are studies leading to unique fragments of higher-order fullerenes, such as C_{70}. Here too there have been recent advances. Wu and co-workers[15] have produced a deep bowl fragment of C_{70} and have shown its path to bowl inversion traverses a high-energy nonplanar transition state. Photoelectronic properties of these fragments mimic fullerene-based materials.

Carbon belts and tubes (Figure 3) are hotly pursued and one finds recent advances in this area by Jasti and co-workers,[16] followed quickly by Itami and co-workers.[17] More recently Müllen and co-workers, combined Jasti's method in tandem with a Scholl oxidation, and this work has resulted in cyclic arenes with coronene components.[18]

Modeling of structural dynamics and quantitative prediction of physiochemical properties plays an important role in

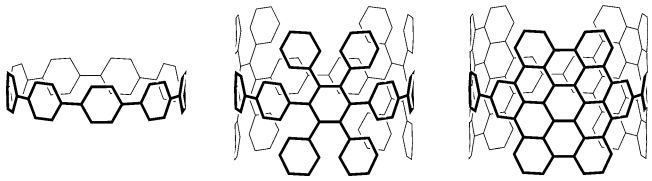

Figure 3. Cyclo-*p*-phenylene subgraphs from armchair nanotubes.

driving this field. Unfortunately, the field is plagued by post-rationalization instead of reliable prediction. This can be found egregiously in any claims that low-basis-set levels and computations lacking correlation (e.g., for dispersive interactions) perform "better" than cutting edge methods for polynuclear aromatic hydrocarbons. Such studies routinely set comparison of X-ray and QM bond lengths/bond angles as the critical criterion.[19] They erroneously neglect higher-order dynamic, electronic or photophysical properties in the analysis and thereby perpetrate a misconception of computational methods performance. Even top quality synthetic work cited herein,[10] accept such low-level methods as valid.

In contrast to the above abuses, serious use of QM methods can lead to greater insight regarding the prediction of molecular properties.[8,20] Greater vigilance is needed to stem the tide of poor quality computational data. Analogous to the criteria required to test the degree of confidence for reports of synthesized compounds (i.e., elemental analysis, MS, NMR, mp, etc.), requirements of "quality criteria" for the reporting of QM electronic structure data can help avoid fortuitous agreement from being taken as rigorous modeling.

Interest in the synthesis, study, and modeling of molecules representing elementary subgraphs of carbon allotropes continues to reveal chemical entities applicable to molecular devices be they (semi)conductors, photovoltaics, or luminophores. Now these molecules become the object of process chemistry and commercialization.[21] Taken together, molecular design, chemical synthesis, property elucidation and on-scale production, define a transitional research program with great potential for chemistry and society. Graph-based design of material analogues offers one systematic way to enter in this pursuit.

Received: January 24, 2013
Published online: April 16, 2013

[1] For a primer on graphs in chemistry, see: N. Trinajstić, *Chemical Graph Theory*, CRC, Boca Raton, **1992**.
[2] Consider a graph as a set of objects called *vertices* connected by *links* (e.g., an atom or cluster of atoms as *vertices* and bonds or ring fusions *links*).
[3] For a review of molecular graph replacement, see: Y. Sritana-Anant, T. J. Seiders, J. S. Siegel, *Top. Curr. Chem.* **1998**, *196*, 1–43.
[4] J. Loschmidt, *Konstitutionsformeln der Organischen Chemie in Graphischer Darstellung*, Wilhelm Engelmann, Leipzig, **1860**.
[5] Imagine the series of acenes as an acyclic graph with two benzene vertices and a single ring-fusion link.
[6] H. A. Staab, F. Diederich, *Chem. Ber.* **1983**, *116*, 3487–3503.

[7] a) Bowls to Saddles T. J. Seiders, J. S. Siegel, *Chem. Br.* **1994**, *30*, 313 – 316; b) Y. T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843 – 4867.
[8] B. Kumar, R. L. Viboh, M. C. Bonifacio, W. B. Thompson, J. C. Buttrick, B. C. Westlake, M.-S. Kim, R. W. Zoellner, S. A. Varganov, P. Mörschel, J. Teteruk, M. U. Schmidt, B. T. King, *Angew. Chem.* **2012**, *124*, 12967 – 12972; *Angew. Chem. Int. Ed.* **2012**, *51*, 12795 – 12800.
[9] E. Clar, *The Aromatic Sextet*, Wiley, New York, **1972**.
[10] D. Myśliwiec, M. Stępień, *Angew. Chem.* **2013**, *125*, 1757 – 1761; *Angew. Chem. Int. Ed.* **2013**, *52*, 1713 – 1717.
[11] Q. Zhang, K. Kawasumi, Y. Segawa, K. Itami, L. T. Scott, *J. Am. Chem. Soc.* **2012**, *134*, 15664 – 15667.
[12] a) L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere, *Science* **2002**, *295*, 1500 – 1503; b) G. Otero, G. Biddau, C. Sánchez-Sánchez, R. Caillard, M. F. López, C. Rogero, F. J. Palomares, N. Cabello, M. A. Basanta, J. Ortega, J. Méndez, A. M. Echavarren, R. Pérez, B. Gómez-Lor, J. A. Martín-Gago, *Nature* **2008**, *454*, 865 – 868.
[13] K. Y. Amsharov, M. A. Kabdulov, M. Jansen, *Angew. Chem.* **2012**, *124*, 4672 – 4675; *Angew. Chem. Int. Ed.* **2012**, *51*, 4594 – 4597.
[14] O. Allemann, P. Romanato, S. Duttwyler, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574 – 577.
[15] T.-C. Wu, M.-K. Chen, Y.-W. Lee, M.-Y. Kuo, Y.-T. Wu, *Angew. Chem.* **2013**, *125*, 1327 – 1331; *Angew. Chem. Int. Ed.* **2013**, *52*, 1289 – 1293.
[16] J. Xia, M. R. Golder, M. E. Foster, B. M. Wong, R. Jasti, *J. Am. Chem. Soc.* **2012**, *134*, 19709 – 19715.
[17] H. H. Omachi, Y. Y. Segawa, K. Itami, *Acc. Chem. Res.* **2012**, *45*, 1378 – 1389.
[18] T. Nishiuchi, X. Feng, V. Enkelmann, M. Wagner, K. Müllen, *Chem. Eur. J.* **2012**, *18*, 16621 – 16625.
[19] For an example, see: M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 5713 – 5716.
[20] L. Zoppi, J. S. Siegel, K. K. Baldridge, *WIREs Comput. Mol. Sci.* **2013**, *3*, 1 – 12.
[21] A. Butterfield, B. Gilomen, J. S. Siegel, *Org. Process Res. Dev.* **2012**, *16*, 664 – 676.

