Mechanochemical Transformation of Planar Polyarenes to Curved Fused-Ring Systems

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Electronic and redox-active materials are revolutionizing key areas such as energy storage – e.g. in the form of rechargeable batteries and supercapacitors – or CO_2 utilization and transformation. Among these functional materials, polyarenes and various forms of carbon polymers are of particular interest. The group of Professor Mihaiela Stuparu, from the Nanyang Technological University (Singapore), has been developing the chemistry and the applications of curved nanocarbons over the last decade (*Acc. Chem. Res.* **2021**, *54*, 2858–2870). "Corannulene is a fascinating bowl-shaped polycyclic aromatic hydrocarbon structure. It can be imagined as the smallest curved fragment of fullerene C_{60}," said Professor Stuparu. "It must be noted, however, that Barth and Lawton synthesized this molecule nearly two decades prior to the discovery of fullerene C_{60} (*J. Am. Chem. Soc.* **1966**, *88*, 380–381). Their solution-phase synthesis involved 17 steps and provided corannulene in <1% yield. After a period of dormancy, Scott's new synthesis of corannulene revived interest in this molecule and its multifaceted properties (*J. Am. Chem. Soc.* **1991**, *113*, 7082–7084). Scott's synthesis was based on a gas-phase technique. This technique is known as flash-vacuum pyrolysis (FVP) in which molecules are subjected to high temperatures (>1000 °C) under an inert atmosphere. Such high-energy conditions allow the planar precursor molecules to adopt unnatural conformations that can be trapped to access curved polyaromatic nuclei."

Professor Stuparu went on by explaining that since mechanochemistry also creates extraordinary reaction conditions through impact and shear forces, they reasoned that similar to FVP it may also prove to be a useful synthetic tool in accessing curved aromatic structures. Professor Stuparu further added: "The attraction of mechanochemistry lies in its simple operation, i.e., milling and grinding of solid reactants is expected to yield products in a fast and scalable manner. Our first efforts in this regard were focused on a corannulene–phenanthrene hybrid structure (*Angew. Chem. Int. Ed.* **2020**, *59*, 21620–21626) (Figure 1a). We noticed that mechanochemistry indeed led to faster reaction times and higher yields as compared to the solution-phase synthesis. Encouraged by these results, we planned to synthesize corannulene itself." Professor Stuparu explained that the idea was that under mechanochemical forces, the bay regions of a precursor molecule such as tetrabromomethylfluoranthene would come in close proximity to each other to react and generate two new six-membered rings (Figure 1b). The researchers found that although corannulene could be produced in this way, the yields remained low (<5%). Professor Stuparu added: "During the optimization efforts, we added tetrabutylammonium chloride (TBACl) merely as a salt to facilitate mixing between the reactants. This led to a marked enhancement in the yield to >65%. It is only upon scrutinizing the trace amounts of other molecules generated in the reaction that we realized that TBACl is likely to have participated in the reaction and resulted in a halide-exchange reaction before the formation of the new aromatic rings (Figure 1c)." This hypothesis was confirmed by the Stuparu group through mechanochemical preparation of tetrachloromethylfluoranthene and its efficient conversion into corannulene (Figure 1d).

Prof. Stuparu concluded: "To discover the halide-exchange reaction and formation of the phenanthrene nucleus from benzyl halide precursors was exciting, furthermore it has numerous potential applications for instance in the mechanochemical generation of helicenes. On the other hand, successful transformation of planar polyarenes into a curved geometry by creating new C–C bonds along the rim of the molecular structure opens up new possibilities of creating highly strained π-surfaces."

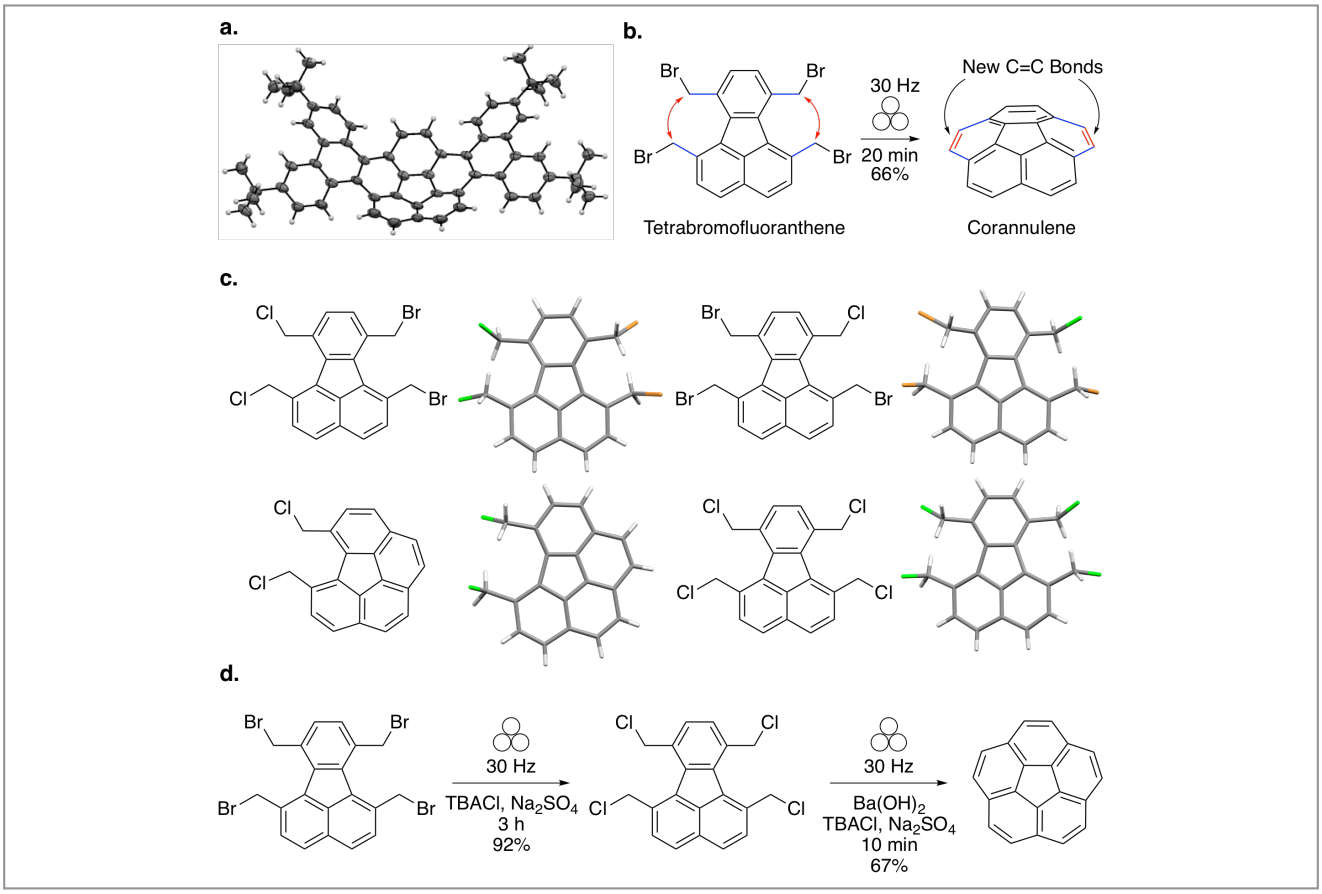
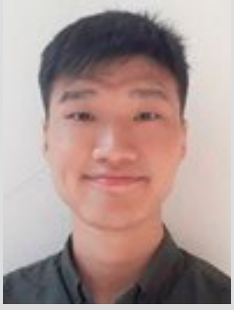


Figure 1 Mechanochemical synthesis of curved arenes. (a) X-ray crystal structure of the corannulene–phenanthrene hybrid structure. (b) Synthesis of corannulene from tetrabromomethylfluoranthene precursor. (c) Chemical and X-ray crystal structures of chlorinated compounds isolated from the corannulene synthesis. (d) The mechanochemical halide-exchange reaction and subsequent formation of corannulene from the tetrachloromethylfluoranthene precursor.

About the authors



T. Yong

Teoh Yong joined the research group of Prof. Mihaiela Stuparu as an undergraduate student at the Nanyang Technological University (Singapore), initially as a URECA student and then as a Final Year Project Student. It is during this time that he "discovered" corannulene. He continued working in the Stuparu group after finishing his bachelor's studies during which time he developed the mechanochemical synthesis of corannulene. He is currently a doctoral student in the research group of Professor Tomislav Friščić at McGill University (Canada).

Prof. F. García

Dr. Gábor Báti was born in 1989 in Budapest, Hungary. He received both B.Sc. (2012) and M.Sc. (2014) degrees in chemistry from Eötvös Loránd University (ELTE), Hungary, then pursued PhD studies in Nanyang Technological University (NTU), Singapore. Currently he is a Research Fellow at NTU in Professor Mihaiela Stuparu's lab, mainly focusing on the synthesis of curved polyaromatic systems.

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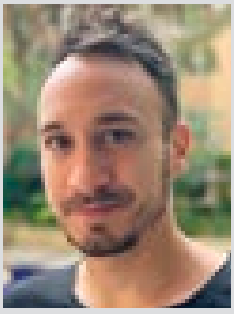

Dr. G. Báti

Prof. Felipe García's research group at the Nanyang Technological University (Singapore) is involved with developing complex and robust main group systems for technological and biological applications and mechanochemistry for the sustainable synthesis of compounds and materials.

Prof. M. Stuparu

Prof. Mihaiela Stuparu's research group is interested in developing new synthetic methodologies to curved polyarenes and studying their properties and potential applications. In this regard, the group has developed photochemical and mechanochemical methods for accessing non-planar nano-graphenes based on the corannulene motif.

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