Mechanochemical transformation of planar polyarenes to curved fused-ring systems

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The transformation of planar aromatic molecules into π-extended non-planar structures is a challenging task and has not been realized by mechanochemistry before. Here we report that mechanochemical forces can successfully transform a planar polyarene into a curved geometry by creating new C-C bonds along the rim of the molecular structure. In doing so, mechanochemistry does not require inert conditions or organic solvents and provide better yields within shorter reaction times. This is illustrated in a 20-minute synthesis of corannulene, a fragment of fullerene C₆₀, in 66% yield through ball milling of planar tetra-bromomethylfluoranthene precursor under ambient conditions. Traditional solution and gas-phase synthetic pathways do not compete with the practicality and efficiency offered by the mechanochemical synthesis, which now opens up a new reaction space for inducing curvature at a molecular level.
The synthesis of strained aromatic molecules from strain-free precursors is a challenging task. This requires the natural trigonal planar geometry of the sp²-hybridised carbon atoms to become non-planar. The angle strain associated with this pyramidalization needs to be overcome in any viable synthesis. This necessitates application of either high-energy reaction conditions or high-energy precursors. For instance, flash vacuum pyrolysis (FVP), in which molecules are subjected to high temperatures (500–1100 °C) in the gas-phase, is the most successful synthetic methodology to create non-planar molecules. In a landmark publication in 1991, Scott established the utility of FVP as a synthetic method that could bend diethylfluoranthene, a flat polyarene, into a bowl-shaped aromatic structure, corannulene. Scott reasoned that the high-energy conditions temporarily populate bent molecular geometries that would be inaccessible under normal circumstances. Only under such folded conformation, the two-carbon side chains could reach across the fluoranthene bay region to intramolecularly generate two new 6-membered rings. Ever since, a large family of molecular bowls have been produced through this fascinating method. A decade later the technique reached a new high in the chemical synthesis of fullerene C60. This feat of organic synthesis serves as an inspiration to explore new methods that can twist aromatic molecules and create new covalent bonds to lock the curved molecular geometry.

Mechanochemistry, the use of mechanical force to drive chemical reactions, promises sustainable, faster, scalable and efficient processes. In this regard, in the past few years, various synthetic techniques such as direct mechanocatalysis and liquid assisted grinding are developed. New possibilities for heating, cooling, and conducting gaseous mechanoochemical reactions are established. Furthermore, analytical techniques for in situ monitoring of the reactions are described. Along with these developments, the application of mechanochemistry for the synthesis of various polyarenes has also been increasing. So far, however, mechanochemistry is not known to transform planar aromatic molecules into non-planar structures. We reasoned that mechanochemistry, similar to FVP, creates extraordinary reaction conditions but through impact and shear forces. Such conditions maybe able to bend the molecules such as fluoranthene and allow them to react at the bay regions to form the curved fused-ring system. Unlike FVP, however, mechanochemistry offers no restrictions on the nature of precursors (flash vacuum pyrolysis requires the precursor to be able to sublime and withstand the sublimation conditions), a simpler experimental set-up, possible scalability, better yields, shorter times and operation under ambient conditions. Therefore, it might be a valuable method to access curved structures. To explore this hypothesis, we focused on tetrabromo-fluoranthene (1), as a precursor to corannulene synthesis. This allows for a direct comparison to be made not only with the gas-phase FVP but also the conventional solution-phase synthesis.

In this work, we show that mechanochemistry is indeed capable of inducing curvature at a molecular level. It is also a practically simple, mild, fast, high-yielding and a sustainable synthetic approach.

Results and discussion

Synthesis of planar polyarene precursor. Initially, we focused on the synthesis of precursor 1. The goal was to explore an environmentally friendly approach to access 1. For this, our investigations began with a key compound, 3,8-dimethylacenaphthenequinone 2, that can be procured from commercial sources. An aldol condensation of 2 leads to 3, followed by a Diels-Alder reaction to yield 1,6,7,10-tetramethylfluoranthene 4. Tetramethylfluoranthene 4 then undergoes benzylic bromination to form precursor 1.

The aldol condensation of 3,8-dimethylacenaphthenequinone with 3-pentanone was carried out under basic conditions (Fig. 2). Solution-based method requires 22 equiv of KOH dissolved in MeOH to attain a sufficiently high pH for the reaction. The excess of base must then be tediously neutralised using HCl to precipitate the product. Excessive acidification causes product 2 to irreversibly dimerise to 3a (Supplementary Fig. 1).

Mechanochemistry circumvents these issues as the reaction is complete within 15 min of ball milling using just 2.5 equiv of NaOH as the base, and MgSO₄ as the grinding auxiliary. The crude product requires no chromatographic purification. The reaction is easily scalable to 1 g with no notable difference in...
isolated yields. Investigations into the reaction conditions identify MgSO₄ as an essential grinding auxiliary, likely serving as both a dehydrating agent and a Lewis acid for the aldol condensation (Supplementary Table 1). NaOH can be replaced with a milder base such as K₂CO₃. The reaction progresses in this case too, albeit at a slower rate and requires two millings of 15 min each for completion (Supplementary Table 1). As a control, an un-milled reaction mixture with NaOH was stirred with a stir bar with no visible product formation observed after 30 min. This persists despite heating the reaction mixture to 50 °C. This contrast in reactivity suggests that ball milling is responsible for the mechanochemical activation of the reaction. Overall, ball milling makes the reaction greener and simplifies the workup by removing the laborious neutralisation step of excess NaOH, greatly reducing reaction time and generating cleaner products in higher yields.

In the next step, compound 3 undergoes an inverse electron demand Diels-Alder chelotropic elimination followed by a retro Diels-Alder reaction cascade to generate tetramethylfluoranthenes 4 (Fig. 3). Initial milling of compound 3 with MgSO₄ and norbornadiene at room temperature generates the dimer 3b only (Supplementary Fig. 1). This is likely due to the high activation energy required by the Diels-Alder reaction between norbornadiene and 3. This is verified by the successful Diels-Alder reaction of 3 with a more reactive dienophile, dimethylacetylene dicarboxylate (Supplementary Fig. 1 and Supplementary Table 2). Therefore, jars were heated to 95 °C during the milling process to attain the required activation energy. This change in milling conditions drives the reaction to completion within 2 h. In comparison, solution-phase synthesis requires stirring for 4 days at 140 °C to produce 65% of 4. It is important to note that snap-fit jars were used which allowed the norbornadiene to escape. If a screw-tight jar is used, the yield is halved due to high pressure inhibiting the chelotropic elimination of CO gas, which is part of the reaction cascade.

Mechanochemical benzylic bromination of 4 proved to be the most demanding step in this synthesis as ball milling strongly favours aromatic bromination over benzylic bromination, with no literature reported on mechanochemical Wohl–Ziegler bromination. Therefore, other advances in green chemistry were considered in favour of mechanochemistry for the synthesis of 1 (Fig. 4).

A user and environmentally friendly alternative is using ethyl acetate as the solvent⁵⁷. Although the mechanism of the reaction

is still unknown, ethyl acetate has been proven to be effective for benzylic bromination even in the absence of light⁵⁷. Although initial reflux in ethyl acetate only generates a complex mixture of mono and dibrominated products, the addition of azobisisobutyronitrile (AIBN) as a free-radical source resolves this, generating tetrabromomethylfluoranthenes within 3 h (Supplementary Table 3). The crude product can be subjected to the next reaction. However, to achieve better results, a pure product can be isolated at 78% yield by recrystallisation with ethyl acetate. In comparison, photochemical synthesis requires a light source, an excess of NBS, and provides 80% yield in 24 h of reaction time in toxic CCl₄⁵³.

**Fig. 3 Synthesis of 4.** The solution-phase reaction was reproduced using the procedure provided in Butterfield et al.⁵⁵.

**Fig. 4 Synthesis of precursor 1.** The reaction conditions for the solution-phase photochemical synthesis is adopted from Borchardt et al.⁵³.

**Inducing molecular curvature.** Having efficient access to precursor 1, we began to investigate the possibility of intramolecular formation of aromatic rings at the bay region of the fluoranthene nucleus. For this, we chose to employ basic conditions which is known to produce corannulene from precursor 1 in solution albeit with low yield.⁵⁴ In solid-phase too, only low yields of corannulene (2–5%) could be obtained upon milling of 1 with NaOH or NaO–Bu (Supplementary Table 4). We attributed these poor results to essentially a bi-phasic system in which the inorganic base and organic reactant did not interact with each other. To improve contact between reactants, we looked towards traditional phase-transfer agents such as tetrabutyrammonium chloride (TBACl). The hygroscopic nature of TBACl was observed to turn the crude reaction mixture into a gooey solid. We observed that 5 min of pre-milling of the precursor with TBACl followed by a 15 min of milling with barium hydroxide produced the best results and provided corannulene in 66% isolated yield. Without pre-milling step, the milling times of 10 and 20 min provided comparatively lower yields of 64 and 60%, respectively. In terms of total reaction time, the reaction with 5 min of pre-mill and 15 min of milling (yield = 66%) provides a comparison with the 20 min reaction (yield = 60%). It is reasonable to assume that a longer exposure of the reactants and the product to the strong basic conditions favour formation of side products and lowers corannulene yield. Finally, we observed that the reaction failed to produce any corannulene in the absence of a base (Supplementary Table 4).

To examine whether TBACl could be replaced with similar other salts, tetrabutyrammonium bromide (TBAB) and tetrabutyrammonium fluoride (TBAF) were used. However, this led to a drastic reduction in yield (5%) or a complete failure of reaction ( Supplementary Table 4). This suggested that simply a better mixing of solids was not the sole reason behind better yields in the presence of TBACl. To investigate whether TBACl
participated in the reaction, pre-mill stage solid was analysed (before addition of a base) and found to contain a fluoroanthene derivative 5 in which two bromine atoms were replaced by two chlorine atoms (Fig. 5). This result meant that TBACl was involved in the reaction. Intrigued by this, we began to examine whether byproducts could be isolated from corannulene synthesis. Fortunately, we isolated two trace compounds which were confirmed to be compounds 6 and 7 through X-ray crystallography (Fig. 5). Overall, therefore, it appears that during the reaction, the nucleophilic chloride anions displace the bromine atoms from precursor 1. A base is necessary for the reaction, and the more robust and more electronegative chlorine atoms would stabilise the benzylic carbanions more efficiently. Therefore, it is reasonable to assume that besides improving mixing of solids, TBACl acts as a chlorinating agent and the reaction mechanism involves anionic intermediates.

The finding that chlorinated compounds were involved in the reaction arose an interesting possibility: can tetrachloromethylfluoranthene (8) serve as a precursor for corannulene synthesis? To answer this, we employed the knowledge gained thus far to prepare 8 through subjecting tetrabromomethylfluoranthene to a mecanochemical halide-exchange reaction with the help of TBACl (Fig. 6). This reaction produced 8 in an isolated yield of 92%. Precursor 8 was then subjected to the ball milling reaction under identical conditions as in the case of 1 and produced the best yield of 67% of corannulene. TBACl was, however, still required for a successful reaction indicating that the mixing of solids was also critical to the success of the reaction (Supplementary Table 4). Furthermore, since chloride precursor 8 adds an additional step to the synthesis, the bromide precursor 1 still represents an optimum route to corannulene synthesis. In comparison to the solid-phase synthesis, FVP at 1000 °C provides 18%53 while Sygula’s solution-phase synthesis gives an isolated yield of 14% of corannulene from precursor 154.

**Mechanistic aspects.** In terms of reaction mechanism, based on the formation of compounds 5–7 during synthesis, we assume that bromine atoms are first replaced with chlorine atoms. Subsequently, benzylic protons are deprotonated since the reaction does not work in the absence of a base. The support for this notion comes from the work of Kharasch who established coupling of benzyl halides in the presence of a strong base58. Later work in the area by Dubios and Gingras showed that intramolecular ring formation through carbenoid coupling could yield phenanthrene and [5]-helicene structures beginning with benzyl halide precursors59. While the exact reaction mechanism for such processes still remains unknown, the proposed pathways include nucleophilic substitution, electrocyclic reactions, carbone formation by an-elimination of HCl and radical-mediation (Fig. 7). It is difficult to differentiate between these pathways as they lead to the same product.

**Absorption characteristics.** In UV-Vis spectroscopy (Fig. 8), compound 3 displays three broad absorption bands at 230, 261 and 334 nm. Upon Diels-Alder reaction, which forms the fluoranthene nucleus (4), a bathochromic shift of 34 nm is observed due to extension in π-conjugation. Fluoranthenes absorption is known to be highly complex with a number of independent electronic transitions60. This can be observed in the case of halide derivatives 1 and 8 with absorption extending into the blue region of the electromagnetic spectrum. The halide substitution pattern does not alter the absorption characteristics due to a methylene spacer, which interrupts the electronic conjugation between the halides and the aromatic nucleus. Formation of the first aromatic ring in the bay region of fluoranthene, however, results in loss of molecular planarity and a blue shift of ~25 nm is observed for compound 7. Formation of a strained bowl upon second ring-closure results in a further loss in planarity and a further blue
shift of 57 nm. The absorption spectrum of corannulene matches well with the previous literature reports.61,62.

Comparison with solution-phase synthesis. Finally, a comparison can be made with an optimised solution-phase synthesis of corannulene55 which employs the high-energy octabrominated precursor 9 (Fig. 9 and Supplementary Fig. 2)63. The excessive bromination in 10 means that an additional debromination step is required to obtain corannulene. Compared to this optimized synthesis of corannulene, the present synthesis, beginning with dimethylnaphthenequinone, improves overall yield by 17%, reduces overall reaction time from a few days to a few hours, and reduces the amounts of the reagents required (Supplementary Fig. 2). Finally, it eliminates the need for the environmentally harmful solvents such as chlorobenzene from corannulene synthesis.

In summary, mechanochemistry offers a promising alternative to conventional gas-phase and solution-based synthetic methods in inducing molecular curvature. With the help of corannulene, it can be demonstrated that the solid-phase synthesis is practically simple. It can be carried out under ambient conditions and requires a shorter reaction time while producing a higher yield. Unlike FVP, it does not require a volatile precursor or high-energy conditions. Unlike solution-phase synthesis, it does not require a high-energy precursor or solvents. Overall, therefore, given the potential of scalability and the challenges in developing high-yielding sustainable synthesis of curved fused-ring systems, mechanochemistry appears to be a worthy alternative to the traditional solution and gas-phase chemistries.

Methods

Synthesis of 3. 1.0 g 3,8-Dimethylnaphthenequinone (4.76 mmol), 476 mg NaOH (11.9 mmol), 3-pentanone (9.52 mmol, 0.8 g), MgSO4 (19.04 mmol, 2.6 g) and a 15 mm φ stainless steel ball (13.55 g) were added to a 30 mL stainless steel jar. The jar was tightly sealed using paraflm and milled at 30 Hz for 15 min. The resulting powder was scraped from the jar, dispersed in 10 mL of acetone and filtered. The filtered cake was washed twice with 10 mL of acetone and the filtrate was evaporated to yield 3 (1.2 g, 90% yield).1H NMR (400 MHz, CDCl3): δ 7.76 (d, J = 8.3 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.36 (dd, J = 14.4, 8.3 Hz, 2H), 2.90 − 2.75 (m, 4H), 2.61 (s, 3H), 2.15 (s, 3H), 1.68 − 1.61 (m, 3H).13C NMR (100 MHz, CDCl3): δ 210.97, 170.65, 139.26, 139.12, 133.36, 131.89, 131.00, 130.92, 130.87, 130.79, 130.78, 130.73, 128.34, 128.06, 125.82, 86.19, 48.82, 22.23, 19.87, 11.21, 10.34. HRMS (EI) calcd for C19H18O2 (M+) 278.1307, found 278.1311.

Synthesis of 4. 100 mg of 3 (0.36 mmol), 294 µL norbornadiene (2.88 mmol), 131 mg trimethylbenzylammonium chloride (0.72 mmol), 68 µL acetic anhydride (0.72 mmol) and 600 mg of MgSO4 were loaded into a 15 mL stainless steel jar...
(10 mm Teflon ring) with a 10 mm Ø stainless steel ball (4.02 g). The jar is heated to 95 °C and milled at 30 Hz for 2 h, with 20 min break in between. The crude mixture is scrapped from the jar and purified using the procedures provided in Butterfield et al.\textsuperscript{16}.  

Column chromatography was performed (eluent: from 100% hexane to hexane:DCM 30:1) to obtain pure corannulene as a white powder (28 mg, 66% yield).

1H NMR (400 MHz, CDCl₃): δ 8.2 Hz, 2H), 7.62 (s, 2H), 5.06 (d, J = 8.6 Hz, 2H), 7.62 (s, 2H), 5.06 (d, J = 10.4 Hz, 8H). 13C NMR (100 MHz, CDCl₃): δ 138.73, 133.97, 133.66, 133.22, 132.45, 132.28, 132.17, 132.07, 129.47, 128.19, 45.55, 45.32. HRMS (EI) calcd for C₂₀H₁₄Br₄ (M⁺) 395.9822, found 395.9832.

Synthesis of corannulene from precursor 8. 43 mg of tetrachloromethylfluoranthene (0.11 mmol), 250 mg of tetrabutylammonium chloride (0.9 mmol), 250 mg of sodium sulphate dehydrate and 150 mg of barium hydroxide octahydrate (0.5 mmol) were loaded into a two sets of 15 mL zirconia jars with a 10 mm Ø zirconia ball (3.08 g) and milled at 30 Hz for 10 min. The crude mixture was suspended in DCM and dry loaded onto silica gel. Column chromatography was performed (eluent: from 100% hexane to hexane:DCM 30:1) to obtain pure corannulene as a white powder (18 mg, 67% yield).

### Data availability

All data supporting the findings of this study are available within the article and Supplementary information files, and also are available from the corresponding author upon reasonable request. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2085614 (corannulene), CCDC 2085628 (compound 5), CCDC 2085612 (compound 6), CCDC 2085613 (compound 7) and CCDC 2085611 (compound 8). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: 20 January 2021; Accepted: 4 August 2021; Published online: 31 August 2021

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Acknowledgements
Financial support from the Ministry of Education Singapore under the A*STAR Tier 1 (2019-T1-002-066) (RG106/19) (2018-T1-001-176) (RG18/18); Agency for Science, Technology and Research (A*STAR)-AMR IREG A1883c0006 and A1783c003; and NTU 04NS00017C2303 is gratefully acknowledged.

Author contributions
M.C.S. conceived the idea of the project and designed the synthesis. M.C.S. and F.G. supervised the progress of the project. Y.T. and G.B. carried out the experimental work and contributed equally. M.C.S. prepared the manuscript and revised it while all the authors commented on the manuscript.
Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-25495-6.

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Peer review information Nature Communications thanks Evelina Colacino and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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