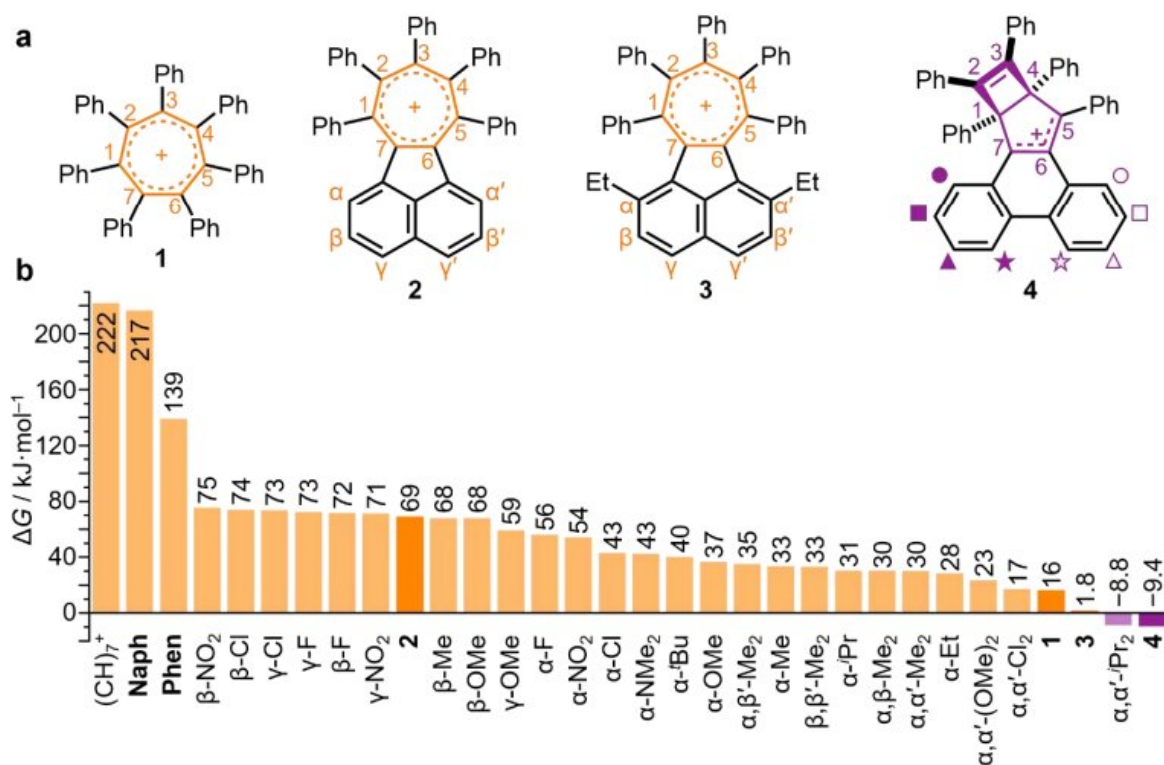


Scientists twist chemical bonds beyond their limits

March 6 2023



Predicted Effects of Periphery Overcrowding. (a) Cations 1–4 synthesized in this work. (b) Calculated Gibbs energy differences (ΔG) between tropylium and Dewar tropylium forms of $(\text{CH})_7^+$, Naph, Phen, 1–4 and a series of derivatives of 2 ($\omega\text{B97XD} / 6\text{-311G} / \text{CH}_2\text{Cl}_2$). The substituent positions indicated in panel (b) correspond to the positions of 2 labeled in panel (a). Positive values (orange bars) indicate an energetically favorable tropylium isomer, while negative values (purple bars) denote a bias toward the Dewar tropylium. For asymmetrical substitution patterns that break the C_2 symmetry, the lower energy of the two possible Dewar tropylium isomers has been used to estimate ΔG . Credit:

Rupturing Aromaticity by Periphery Overcrowding. Pre-print: https://assets.researchsquare.com/files/rs-1347057/v1_covered.pdf?c=1646753973

A group of scientists from Durham University and University of York have twisted molecules to their breaking point in order to challenge the understanding of chemical bonds.

The researchers explored how far the chemical bonding in an aromatic ring can be twisted before its aromatic bonding breaks.

They achieved this by making overcrowded [aromatic rings](#). Rather than [benzene](#), they used tropylium, which shares electrons around a ring of seven [carbon atoms](#).

Each of these carbon atoms can be functionalized, and having seven attachment points in the ring, rather than the six carbon atoms of benzene, allowed the researchers to cram more groups around the edge of the aromatic ring, causing more strain.

The researchers found that low levels of overcrowding made the ring twist, but without breaking its aromatic bonding.

By adding progressively larger groups around the edge of the ring, the team twisted the ring further, eventually causing the aromatic bonding to break.

The [electrons](#) no longer circle the seven carbon atoms and instead, the ring pinches across its middle to form two smaller flat rings.

Surprisingly, the researchers found there is a balance point, where the ring jumps back and forth between aromatic structure and the two

smaller rings. One molecule made in this study spends 90% of its time as the pinched structure and 10% of its time as a larger aromatic ring.

Full study results have been published in the journal *Nature Chemistry*.

Reflecting on the study results, Dr. Paul McGonigal of University of York, said, "In these overcrowded [molecules](#), strain and aromatic bonding are delicately balanced. The structure, properties, and potential applications of a material are ultimately determined by this balance.

"The [precise control](#) over the twisting of our molecules is unprecedented.

"We were not only able to twist an aromatic molecule up to the maximum amount of strain it can tolerate, but also to discover what happens when we push beyond that limit. We hope this investigation is a step towards us being able to more routinely turn aromatic bonding 'off' and 'on' in a controlled manner."

Project lead investigator, Promeet Saha of Durham University, said, "The reversible pinching and reopening of an [aromatic ring](#) are truly remarkable.

"Aromatic bonding is such a powerful stabilizing force that we usually think of it being a constant presence. However, our findings demonstrate that it can be surprisingly dynamic."

Chemical bonding in aromatic molecules is key to the structure, stability and function of chemicals such as drugs and plastics.

More information: Paul McGonigal, Rupturing aromaticity by periphery overcrowding, *Nature Chemistry* (2023). [DOI: 10.1038/s41557-023-01149-6](#).

www.nature.com/articles/s41557-023-01149-6

Provided by Durham University

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