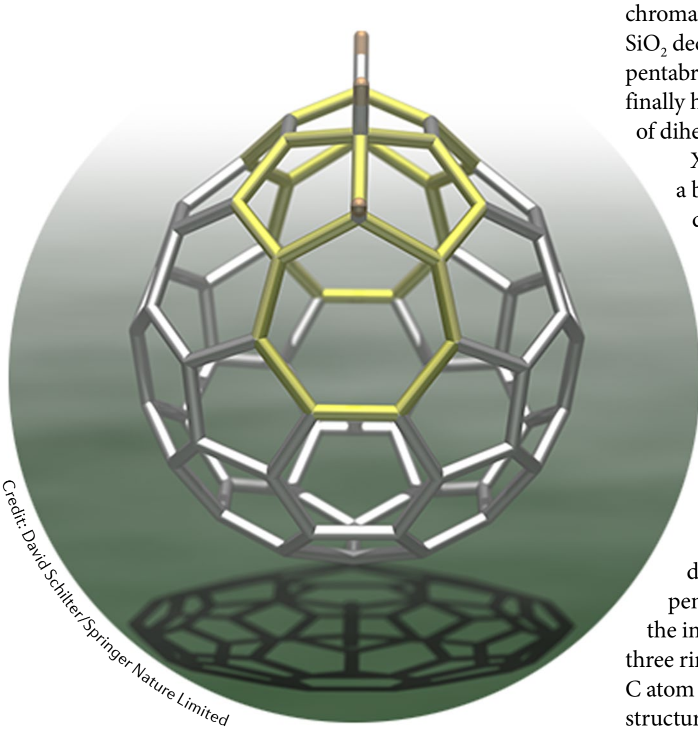
Nature Reviews Chemistry | https://doi.org/10.1038/s41570-019-0093-3 | Published online 29 March 2019

FULLERENES

It's hip to be heptagonal

> I dream of synthesizing a pristine fullerene that violates the isolated pentagon rule

The iconic molecular football C_{60} comprises 12 pentagons separated by 20 hexagons. It is the pentagons, which alone would make a dodecahedron, that impart positive curvature because the hexagons, being the building blocks of graphene, do not contribute to curvature. In contrast, heptagons are saddle points that impart negative curvature, something not conducive to forming fullerenes. Indeed, heptagon-containing closed structures such as chlorofullerene hept-$C_{68}Cl_6$ are rare. The unique structural effects of heptagon motifs motivated Qianyan Zhang, Shun-Liu Deng, Su-Yuan Xie and colleagues to perform combustion at low pressures to see if the motifs could be found in stable molecules. Writing in *Journal of the American Chemical Society*, the team now describes dihept-$C_{66}H_4$, the smallest hydrofullerene with two heptagons.



Credit: David Schilter/Springer Nature Limited

Although the first fullerenes were prepared using arc discharge of graphite, low-pressure hydrocarbon combustion is a more controllable and scalable method that gives soot containing many fullerenes and hydrogenated derivatives. This family of products, which a decade ago was limited to molecules obeying the 'isolated pentagon rule', continues to grow in diversity. Zhang, Deng, Xie and co-workers combusted a C_6H_6/C_2H_2 mixture in O_2 at 15–20 Torr — a pressure and O:C ratio low enough to favour the formation of new carbonaceous molecules instead of complete combustion. "An early experiment afforded traces of dihept-$C_{66}H_4$ and a mass spectrum but no unambiguous structure," recalls Xie. However, with some optimization, and after extracting their soot with toluene and performing multiple rounds of chromatography (on reverse-phase SiO_2 decorated with pyrene or pentabromobenzyl groups), they finally had macroscopic quantities of dihept-$C_{66}H_4$.

X-ray diffraction from a black single crystal of dihept-$C_{66}H_4$ revealed it to have a closed C_{2v}-symmetric structure distinct from other derivatives such as endohedrally functionalized fullerene $Sc_2@C_{66}$ and chlorofullerene $C_{66}Cl_6$. To the team's delight, dihept-$C_{66}H_4$ featured two heptagons, each of which is fused to a separate pair of doubly hydrogenated fused pentagons (shaded in yellow in the image). At the centre of these three rings is an sp^3-hybridized C atom that protrudes from the structure to accommodate the saddle-shaped seven-membered ring. Thus, the presence of the two negatively curved seven-membered rings is possible because each is fused to two five-membered rings that ensure net positive curvature and a closed structure, the bottom half of which is similar to C_{60}.

Compared with the all-sp^2-hybridized parent fullerene dihept-C_{66}, hydrofullerene dihept-$C_{66}H_4$ has a larger electronic bandgap due to the four sp^3-hybridized C atoms interrupting the π-system. "I dream of synthesizing a pristine fullerene that violates the isolated pentagon rule," says Xie. Dihept-C_{66} would be one such species, but the team predicts other viable C_{66} isomers with lower energies and larger bandgaps (combustion usually favours thermodynamically stable or metastable products). Xie is nevertheless satisfied with his team's preparation of hydrofullerene dihept-$C_{66}H_4$, noting that "any new species isolated from carbon soots helps us understand the mechanism by which carbon-based materials form in flames." Furthermore, negatively curved carbon allotropes such as heptagon-containing schwarzite networks are topical because they could serve as porous materials in supercapacitors and Li-ion batteries. We lack a good method to prepare such allotropes, so finding heptagon-containing species in combustion soot is encouraging as it suggests that negatively curved carbonaceous materials are more accessible than was previously thought.

David Schilter

ORIGINAL ARTICLE Tian, H.-R. et al. An unconventional hydrofullerene $C_{66}H_4$ with symmetric heptagons retrieved in low-pressure combustion. *J. Am. Chem. Soc.* https://doi.org/10.1021/jacs.9b01638 (2019)