

# Gas phase synthesis of [5]-helicene

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During the last decades, helicenes — ortho-fused polycyclic aromatic hydrocarbons (PAHs), in which benzene building blocks are annulated at an angle of 60° to form helically-shaped molecules — have received considerable attention from the organic and physical chemistry and material science communities due to their unique features in optics (chiroptical activity, nonlinear optics and circular polarization) and chiral sensing (chemical sensors) along with exceptional properties in organocatalysis and distinctive molecular structures. Considering the molecular structure of helicenes, the backbone twists in opposite directions due to the steric hindrance between the terminal rings. Helicenes are distinguished for their chirality despite missing asymmetric carbon atoms with the chirality developing from the handedness of the helix. Clockwise and counterclockwise helices are non-superimposable as the result of their axial chirality with a left- and right-handed helices being defined by minus (M) and plus (P).

Here, we reveal a versatile route to form helicenes via a directed, vinylacetylene mediated gas phase chemistry. In contrast to the traditional routes following solution chemistry and often ionic reaction intermediates, the innovative gas phase synthesis encompasses low-barrier reactions through targeted, stepwise ring expansion mechanisms involving free radical reaction intermediates. We reveal the gas phase chemistry synthesizing [5]-helicene along with atomic hydrogen via the bimolecular reaction of the [4]-helicenyl radical with vinylacetylene. The energies and molecular parameters of the local minima and transition states involved in the reaction were computed at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory with a chemical accuracy of 3–6 kJ/mol for the relative energies and 0.01–0.02 Å for bond lengths as well as 1–2° for bond angles.

The facile route to synthesize [5]-helicene through the reaction of the [4]-helicenyl radical with vinylacetylene represents a versatile pathway that could in principle be extended to higher helicenes. Our mechanistic studies reveal that the key step of the reaction is a low-barrier benzannulation through a resonance-stabilized free radical intermediate that leads to the helicene. In circumstellar environments, starting from [4]-helicene, propagation via hydrogen loss by photodissociation followed by reaction with vinylacetylene provides an exceptional route to [5]-helicene and eventually to [6]-helicene thus supplying a directed, stepwise synthesis of racemic, helically-shaped three-dimensional nanostructures via elementary neutral-neutral reactions.

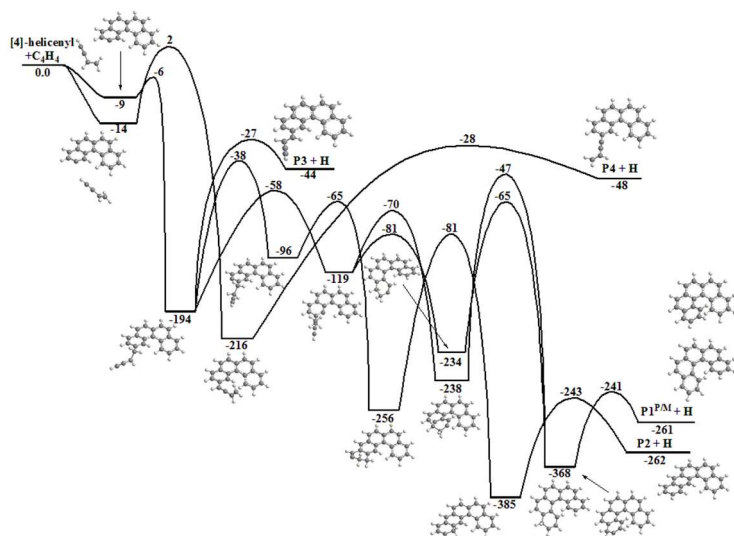


Fig.1 Potential energy surface (PES) for the [4]-helicenyl reaction with vinylacetylene. This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory for the channels leading to [5]-helicene P1 and benzo[a]tetraphene P2. The relative energies are given in kJ/mol.