CONTRACTIVE ANNULATION – A NEW STRATEGY FOR THE SYNTHESIS OF SMALL STRAINED CYCLOPHANES

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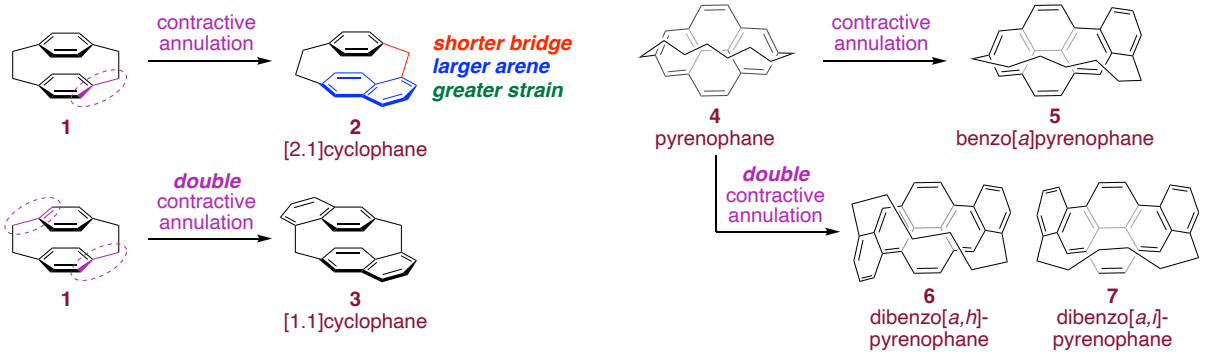
Contractive annulation was recently developed in our group as a new strategy for the synthesis of small, strained cyclophanes. The crux of the strategy is that a bridge atom is used in the π-extension of an aromatic ring in an existing cyclophane. As such, the growth of the aromatic system is necessarily accompanied by the contraction of the bridge. This brings with it an increase in molecular strain. A key feature of contractive annulation is that aromatic stabilization energy is used to counterbalance the increase in strain energy.

Contractive annulation was first used successfully in the synthesis of [2.1]naphthalenophane **2** from [2.2]paracyclophane (**1**).[1] It was subsequently demonstrated that it could be applied in a two-directional fashion in the synthesis of [1.1]naphthalenophane **3**.[2] Opportunities abound for the further development of the contractive annulation strategy, using not only [2.2]paracyclophane (**1**) as a starting material, but also other cyclophanes such as the [*n*](2,7)pyrenophanes, e.g. [8](2,7)pyrenophane (**4**). Single contractive annulation of **4** would lead to benzopyrenophane **5** and double contractive annulation would afford dibenzopyrenophanes **6** and **7**. Progress toward the achievement of these objectives will be presented.



*Single and double contractive annulation of [2.2]paracyclophane (**1**) and [8](2,7)pyrenophane (**4**)*

References

1. Biswas, S.; Qiu, C. S.; Dawe, L. N; Zhao, Y.; Bodwell, G. J. *Angew. Chem. Int. Ed.*, **2019**, *58*, 9166–9170; *Angew. Chem.* **2019**, *131*, 9264–9268.
2. Biswas, S.; Tabasi, Z. A.; Dawe, L. N.; Zhao, Y.; Bodwell G. J. *Org. Lett*. **2022**, *24*, 5009–5013.