Molecular Mis-Shapes, Mistakes and Misfits

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Abstract: This seminar introduces two unusual examples of strain-induced rearrangements, (1) the rapid and reversible enantiomerization of sp^3-C stereochemistry in rigid tricyclic carbon cages,[1–3] and (2) the 'ruptured aromaticity' and resulting aromatic-to-nonaromatic equilibrium of overcrowded tropyliums.[4–6]

Firstly, the sp^3-carbon stereochemistry of barbaralanes is inverted through strain-assisted Cope rearrangements, emulating the low-barrier configurational dynamics typical for sp^3-nitrogen inversion or conformational isomerism. This dynamic enantiomerization can be stopped, restarted, or slowed by external reagents, while the configuration of the cage is controlled by neighbouring, fixed stereogenic centres. As part of a phosphoramidite–olefin ligand (Figure 1a), the fluxional cage acts as a conduit to transmit stereochemical information from the ligand while also transferring its dynamic properties to chiral-at-metal coordination environments, influencing catalysis, ion pairing and ligand exchange energetics.

Secondly, the strain energy of an aromatic system is incremented beyond its aromatic stabilization energy, causing it to rearrange and aromaticity to be ruptured. Increasing steric bulk around the periphery of π-extended tropylium rings leads them to deviate from planarity. Upon further increasing the strain, however, the aromatic π-electron delocalization of the system is broken, forming a nonaromatic, bicyclic analogue, 'Dewar tropylium'. By counterbalancing strain against aromatic stabilization energy, the aromatic and nonaromatic isomers exist in rapid equilibrium with one another (Figure 1b).

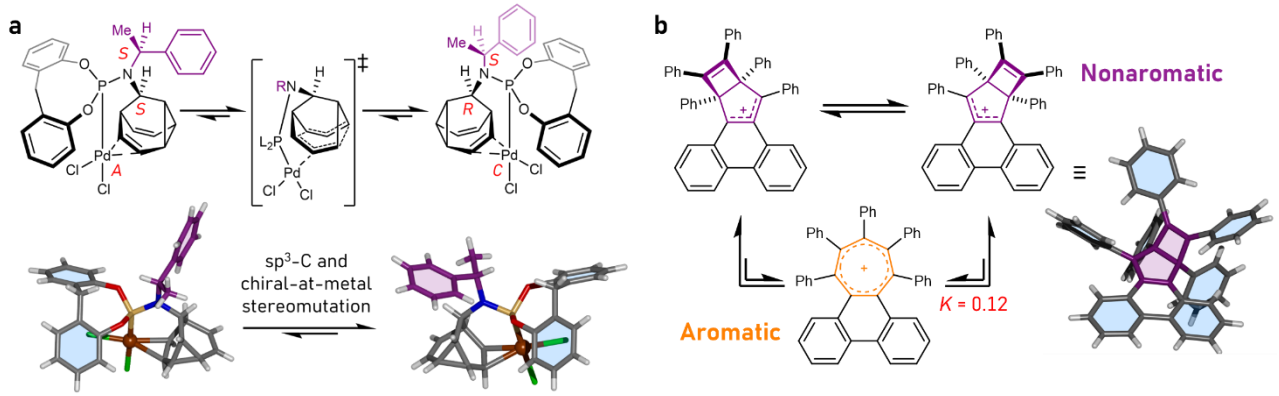

Figure 1. (a) Fluxional rearrangement of 9-substituted barbaralanes lead to global inversion of sp^3-carbon-centred stereochemistry of the triyclic cage, which can be used to transmit stereochemical information to coordinated chiral-at-metal centres. (b) The peripheral overcrowding of an 6π-electron tropylium ring causes strain energy to exceed aromatic stabilisation energy, causing the aromatic ring to collapse reversibly to a nonaromatic 'Dewar tropylium'.

1 **Shapeshifting Molecules: The Story so Far and the Shape of Things to Come**, Bismillah, A. N.; Chapin, B. M.; Hussein, B. A.; McGonigal, P. R. *Chem. Sci.* **2020**, *11*, 324–332.

2 **Shape-Selective Crystallisation of Fluxional Carbon Cages** Bismillah, A. N.; Sturala, J.; Chapin, B. M.; Yufit, D. S.; Hodgkinson, P.; McGonigal, P. R. *Chem. Sci.* **2018**, *9*, 8631–8636.

3 **Control of Dynamic sp^3-C Stereochemistry**, Bismillah, A. N.; Johnson, T. G.; Hussein, B. A.; Turley, A. T.; Saha, P. K.; Wong, H. C.; Aguilar, J. A.; Yufit, D. S.; McGonigal, P. R. *Nature Chem.* **2023**, *in press*, DOI: 10.1038/s41557-023-01156-7.

4 **Excited-State Aromatic Interactions in the Aggregation-Induced Emission of Molecular Rotors**, Sturala, J.; Etherington, M. K.; Bismillah, A. N.; Higginbotham, H. F.; Trewby, W. J.; Aguilar, J. A.; Bromley, E. H. C.; Avestro, A.-J.; Monkman, A. P.; McGonigal, P. R. *J. Am. Chem. Soc.* **2017**, *139*, 17882–17889.

5 **Extended Conjugation Attenuates the Quenching of Aggregation-Induced Emitters by Photocyclization Pathways**, Turley, A. T.; Saha, P. K.; Danos, A.; Bismillah, A. N.; Monkman, A. P.; Yufit, D. S.; Curchod, B. F. E.; Etherington, M. K.; McGonigal, P. R. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202193.

6 **Rupturing Aromaticity by Periphery Overcrowding**, Saha, P. K.; Mallick, A.; Turley, A. T.; Bismillah, A. N.; Danos, A.; Monkman, A. P.; Avestro, A.-J.; Yufit, D. S.; McGonigal, P. R. *Nature Chem.* **2023**, *in press* DOI: 10.1038/s41557-023-01149-6.