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Intramolecular Pancake Bonding in Helical Structures

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Invited for the cover of this issue is the collaborative group of Miklos Kertesz from Georgetown University, USA, and Masayoshi Nakano from Osaka University, Japan. The image depicts head-to-tail covalent-like through-space pi–pi bonding between radicaloid terminal groups in pi-conjugated helical molecules. Read the full text of the article at 10.1002/chem.201700999.

What is the most significant result of this study?

We show that diradicaloid helical conjugated molecules can display strong through-space bonding interactions between the two ends of the molecule. These interactions are analogous to pi-stacking pancake bonding widely observed for dimers and other aggregates of stable pi-conjugated radicals. We show that these multicenter interactions can have a significant stabilizing effect, but they depend in subtle ways on the specific overlap and relative orientations of the radical carrying subunits.

What was the inspiration for this research?

It is well known since the discovery of helicenes 60 years ago that the pi-electrons overlap through the space of the van der Waals gap from one helical turn to the next. This interaction is generally repulsive and reflects the steric crowding associated with the close approach of closed shells. What if the units that come in close contact in a helicene-like structure have radicaloid character? Numerous examples exist displaying strong pi–pi stacking attractive interaction between pi-conjugated radicals. Our two groups have been interested in diradicals for some time, and in this work we decided to look for conjugated helical systems with a diradical character. We were also inspired by the discovery by Juricek et al. of cethrene, a helical diradicaloid analogue of zethrene. The advantage of working with computational modeling is that one can investigate this unique effect varying the sizes and composition providing a list of the best candidates for synthesis.

What other topics are you working on in this collaboration?

We would like to find further examples of through-space covalent-like pancake bonds in helical pi-conjugated molecules. A potentially relevant application can be to compare the diradical states that possess such bonds with their charged closed shell counterparts that do not have such bonds which correspond to an extended geometry of the molecule. Altering geometry and size by changing the charge state of a molecule is a realization of a molecular actuator, a miniature motor part driven by the electrochemical environment. In addition, these types of molecules will have attracted much attention from the viewpoint of open-shell singlet systems bearing tunable through-bond and through-space intermediate diradical characters, which are expected to be a new class of highly-efficient nonlinear optical and magneto-optical molecules.