

Poster Presentation

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Cooperativity in the Reaction of 9-Methylantracene With a 1,4-Dithiin Molecule

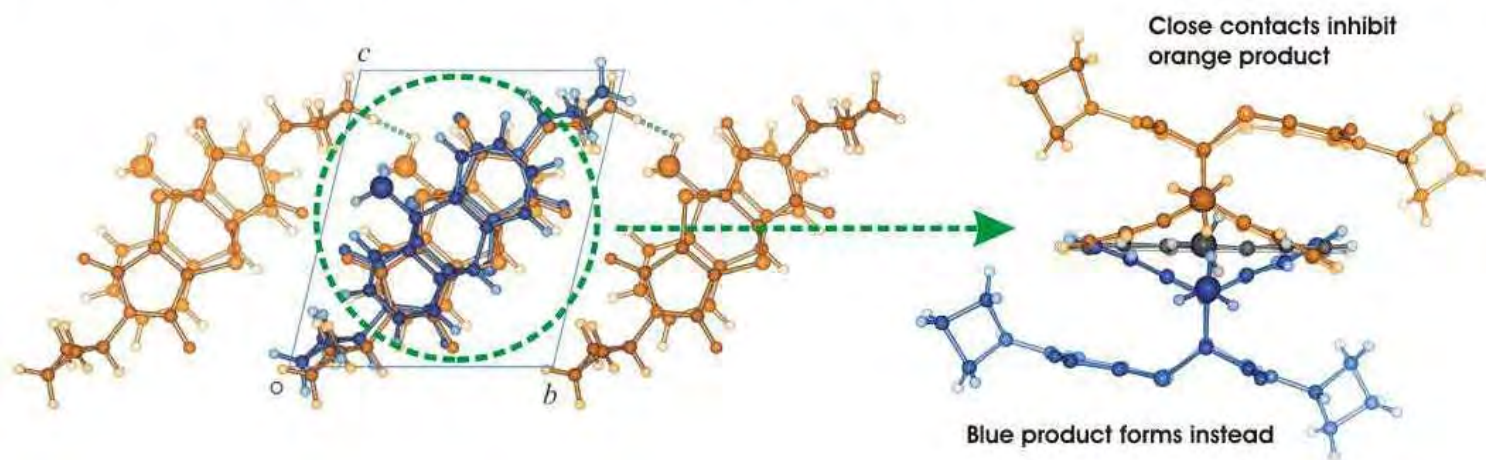
S. Khorasani¹, M. Fernandes¹

¹Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

Solid-state chemistry involves the manipulation of molecules and materials through photochemical, thermal, or mechanical reaction methods. Single-crystal-to-single-crystal (SCSC) reactions are rare, but offer the opportunity to study reaction mechanisms and molecular motions in the solid state at the atomic level using single crystal X-ray diffraction. This allows the effect of the surrounding molecules, and hence the reaction cavity, on the reacting molecules to be examined which may ultimately lead to postcrystallization methods for creating new materials or reaction products that cannot easily be obtained via solution. SCSC reactions involving two different molecules are relatively uncommon. A convenient system that allows the study of such reactions is the [4+2] Diels-Alder reaction of 1,4-dithiintetracarboxylic type compounds with anthracene derivatives. In the work reported here, electron donor to acceptor interactions between 9-Methylantracene and bis(N-cyclobutylimino)-1,4-dithiin lead to the formation of chiral charge transfer (CT) crystals [1]. These undergo a topochemical thermal SCSC [4 + 2] Diels-Alder reaction in the solid state. CT crystals were reacted at 40 °C, their structures determined by X-ray diffraction at various degrees of conversion, and examined using Hirshfeld surfaces and lattice energy calculations to find evidence of reaction cooperativity and feedback mechanisms. In this case, a maximum reaction conversion of around 96% was obtained indicating that the reaction is non-random within the charge transfer stacks, with close contacts between product molecules in the reacted crystal also providing some evidence for reaction cooperativity along the b axis perpendicular to the CT stacking axis.

[1] S. Khorasani, M.A. Fernandes, *Cryst. Growth Des.*, 2013, 13, 5499–5505

Product molecules in reacting crystal dynamically influence reaction pathways



Keywords: solid-state reaction, single-crystal-to-single-crystal, topochemistry