

MS36 Crystallography in solid state reactions and catalysis

Chairs: Fernando Lahoz, Krešo Bučar

MS36-O1 Designing single-crystal-to-single-crystal Diels–Alder reactions: the role of nonbonded interactions

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Electron donor/acceptor (EDA) interactions influence the way in which pairs of dithiin and anthracene molecules assemble, forming heteromolecular crystals of charge-transfer (CT) complexes that can potentially react in the solid state.

Typically the crystal structures consist of stacks of alternating electron donor and acceptor molecules in a 1:1 ratio. These crystals can then undergo a thermally induced solid-state (SS) Diels – Alder reaction in a single-crystal-to-single-crystal (SCSC) fashion^{1–3}, with the dithiin molecules as the dienophiles and anthracenes as the diene (see Figure 1; R = allyl, cyclobutyl or phenyl; X = Br or Me). Examination of close contacts in one such crystal, AD:9BrA (R = allyl, X = Br), indicates that the diene can theoretically react with the dienophile above or below it within a stack as the reaction distances are less than 3.5 Å in both directions.

A single crystal was selected and allowed to react at 30 °C, analyzed at various states of conversion by single-crystal X-ray diffraction, and was found to react by approximately 10% every 6 days, with the reaction occurring in a single direction along the CT stack axis. The solid-state reaction creates a void space which leads to a molecular conformational change within the crystal. The reaction occurs topochemically when fewer than 28% or more than 80% of the molecules have reacted, with minimal motion during the reaction. In the conversion range of 28 – 80%, the reaction occurs in an almost topotactic manner with significant molecular motion and associated crystal deterioration.

Consequently, the single crystal shows significant signs of deterioration after approximately 28% conversion but remained intact upon further reaction and was found to anneal as 100% conversion was approached, leading to the formation of new intermolecular interactions not present in the starting crystal.

In this paper we discuss the central role of the nonbonded interactions (which differ according to the substituents on the dithiin and anthracene molecules) in determining the nature of the reaction cavity, the direction in which and the extent to which the reaction occurs.

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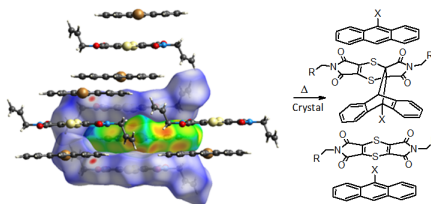


Figure 1. Packing in the crystal structure of AD:9BrA (bis (N-allylimino)-1,4-dithiin: 9-bromoanthracene). The Diels–Alder product forms in the reaction cavity initially in a topochemical fashion, influenced by intermolecular interactions.

Keywords: solid-state reaction, Diels–Alder, topochemical, reaction cavity, charge-transfer complex, molecular recognition