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Feedback mechanisms in single-crystal-to-single-crystal solid-state reactions

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Reactions in single crystals offer an opportunity to study the movement of atoms and molecules during the reaction process at the atomic level through X-ray diffraction techniques. However, examples of single-crystal-to-single-crystal (SCSC) reactions are relatively uncommon as the reaction process often leads to complete crystal disintegration. Even more unusual are SCSC reactions involving two different molecules. The main reason for this is the lack of co-crystals with suitably orientated reactant molecules. A useful way around this problem is to use charge transfer (CT) interactions to pre-align the molecules of interest in the solid-state so as to allow a solid-state reaction to occur. In this case, the CT interactions usually lead to a structure composed of stacks in which the acceptor and donor molecules alternate. In the case of charge transfer complexes made of 1,4-dithiintetracarboxylic type compounds and anthracene derivatives, it is usually possible to carry out [2+4] Diels-Alder cycloaddition reactions in the solid-state, in which the former act as dienophiles and the later as dienes. Modification of substituents on either the acceptor or donor molecule also has an effect on the course of the reaction in a single crystal.

Several concepts have been proposed to explain how molecular reactions occur in the solid state with those of relevance to SCSC reactions having been reviewed in detail.[1] Of relevance to this work are the topochemical principle, the concept of a reaction cavity, and the identification of possible reaction affecting feedback mechanisms. Solid-state reactions where the structure of the product is determined by minimal motion from the coordinates of the starting materials are said to have occurred topochemically. However, very few reactions occur in this way resulting in interesting solid-state chemistry. Here we present examples of solid-state reactions in which interactions between reactant molecules, or between product molecules and reactant molecules influence the course of the reaction. One of these is the reaction of 9-methylanthracene with bis(N-cyclobutylimino)-1,4-dithiin where the results show that steric effects between product molecules and reactant molecules during the SCSC reaction influence the formation of products along the b axis of the structure, resulting in a more ordered structure than initially suggested by X-ray crystal structure analysis (see Figure). [2] Other examples showing significant crystal rebuilding after reaction will also be presented. [3]

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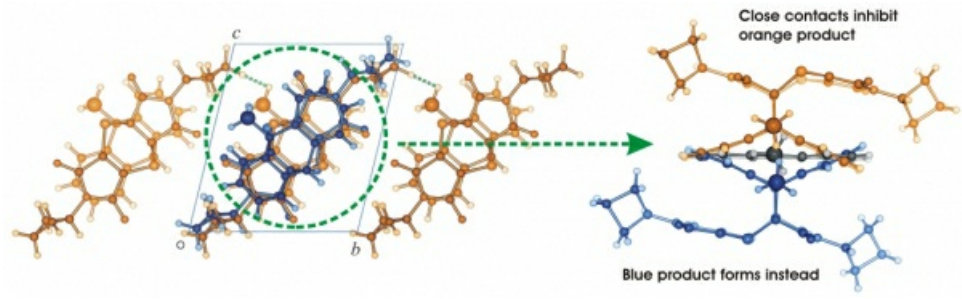

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