Poster

Influencing the reaction pathway in solid-state Diels-Alder cycloaddition using a vinyl substituent

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The use of solid-state reactions as a crystal engineering tool in material design has gained traction over the years as chemists continue to pursue greener ways of making chemical compounds. The absence of solvent use in this method is not the only advantage, these reactions have also been found to result in higher product yields with excellent regio- and stereo selectivity in comparison to conventional methods [1-4]. The improved stereoselectivity is a result of the topochemical control, where the crystal lattice of the starting material influences the arrangement of neighbouring molecules, therefore influencing the reactivity as the molecular motions are restricted.[5]

In this study, we follow the Diels-Alder reaction of bis(*N*-propylimino)-1,4-dithiin as the electron acceptor and 9-vinylanthracene as electron donor in a charge-transfer crystal, to investigate the influence of the vinyl substituent on the direction of the reaction. The CT crystalises in the monoclinic *Cc* space group with stacks of alternating acceptor and the donor, of similar distances between the reacting atoms both up and down the stack (Fig. 1). The anthracene moiety in 9-vinylanthacene is planar, and the vinyl at the 9-position is rotated at an angle (19.3°) from the plane. A single crystal of the CT was carefully selected and reacted in a warm water bath at 40°C at 2-hour intervals with 16% conversion after 16 hours. At this point the reaction appears ordered, with the donor seemingly preferring to react on the anthracene face opposite the vinyl, *via* site **B**. Defects in the appearance of the crystal become more prominent after 30% conversion as the crystal reacts. The reaction progresses and soon changes in the orientation of one of the propyl groups, from a *trans* position with respect to each other to a *cis* position are noted. After 48hours of reaction at 60°C, 100% conversion is achieved with the crystal structure adapting to the triclinic *P*-1 space group.

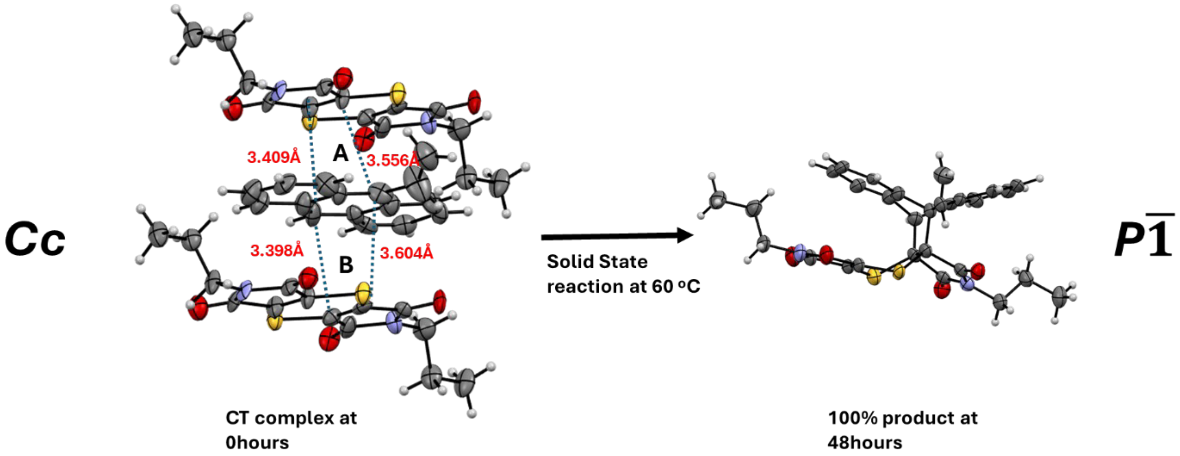

Figure 1. The compounds crystallise in a CT complex of 1:1 ratio between the donor and the acceptor, containing two reaction sites of similar distance apart. The SCSC thermal Diels-Alder reaction favours the downward pathway *via* site B to yield a cycloadduct product initially.

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