



## Short communication

## Quantitative regio-selective Diels–Alder reaction of an unsymmetrical 1,4-dithiin and anthracene through heterogeneous solid state conversion

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## ABSTRACT

The solid state, Diels–Alder reaction of an unsymmetrical 1,4-dithiin and anthracene produced an adduct regioselectively via a charge-transfer complex prearranged to undergo a transformation among a constitutional isomeric mixture generated in the reaction solution. The heterogeneous solid state conversion allowed the reaction to proceed in almost quantitative yield.

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Solid state reactions have attracted considerable attention on account of their enhanced stereo-selectivity and high product crystallinity under solvent free conditions [1–5]. In solid state reactions, the stereo-chemical structures and reactivity are controlled by the crystal lattices, fixed distance and orientation between the reaction centers, free spaces surrounding the reactant molecules, and reaction cavities [6,7]. Although a higher activation energy is required to initiate the chemical process in the solid state than in the solution state [8], it is believed that a practically useful solid state reaction can be expanded by exploiting intermolecular interactions, such as charge-transfer (CT), hydrophobic,  $\pi$ – $\pi$  interaction and/or hydrogen bonding for the crystal lattice design [9].

In our previous paper, it was reported that a mono-phase single-crystal-to-single-crystal (SC-to-SC) Diels–Alder reaction between bis(*N*-methylimino)-1,4-dithiin and anthracene proceeded homogeneously in quantitative yield without any collapse of the crystal lattice during the entire conversion due to the flexibility of the 1,4-dithiin ring [9]. This was attributed to anisotropic heterogeneous propagation in the heteromolecular CT crystal, which resulted in a quantitative product formation in the solid state reaction. This paper expands the mono-phase solid state conversion to obtain

a regio-selective product using an unsymmetrical 1,4-dithiin molecule as an electron acceptor that improved solid state reaction yield and more importantly produced a regio-selective Diels–Alder adduct.

The unsymmetrical 1,4-dithiin (**2**) was synthesized by the cyclization and purified by a cyclization reaction of a 1:1 mixture (mole ratio) of methyl succinamic acid and propyl succinamic acid using a reported method [10]. The reaction produced three products containing bis(*N*-methylimino), bis(*N*-propylimino), and bis(*N*-methyl, *N'*-propylimino)-1,4-dithiin, (**2**), (**3**) and (**4**), respectively, which were separated by chromatography. Methyl and propyl groups were introduced into each imino moiety, in order to induce different steric effect during the crystallization and reaction process.

The Diels–Alder reaction between unsymmetrical 1,4-dithiin (**2**) and anthracene can generate constitutional isomers (**4**) and (**5**), as shown in Fig. 1.

The cycloaddition reaction of (**2**) with anthracene occurs readily in solution thermally via the 1:1 electron donor/acceptor (EDA) complex [11]. The EDA complex of unsymmetrical 1,4-dithiin (**2**) and anthracene was formed by mixing dichloromethane solutions of dithiin and anthracene in a 1:1 mole ratio. UV–vis absorption spectra of the mixture solution showed that the CT band absorbed between 420 nm and 580 nm ( $\lambda_{\max}$ : 488 nm) where neither anthracene nor dithiin absorb, as shown in Fig. 2 [12–14].

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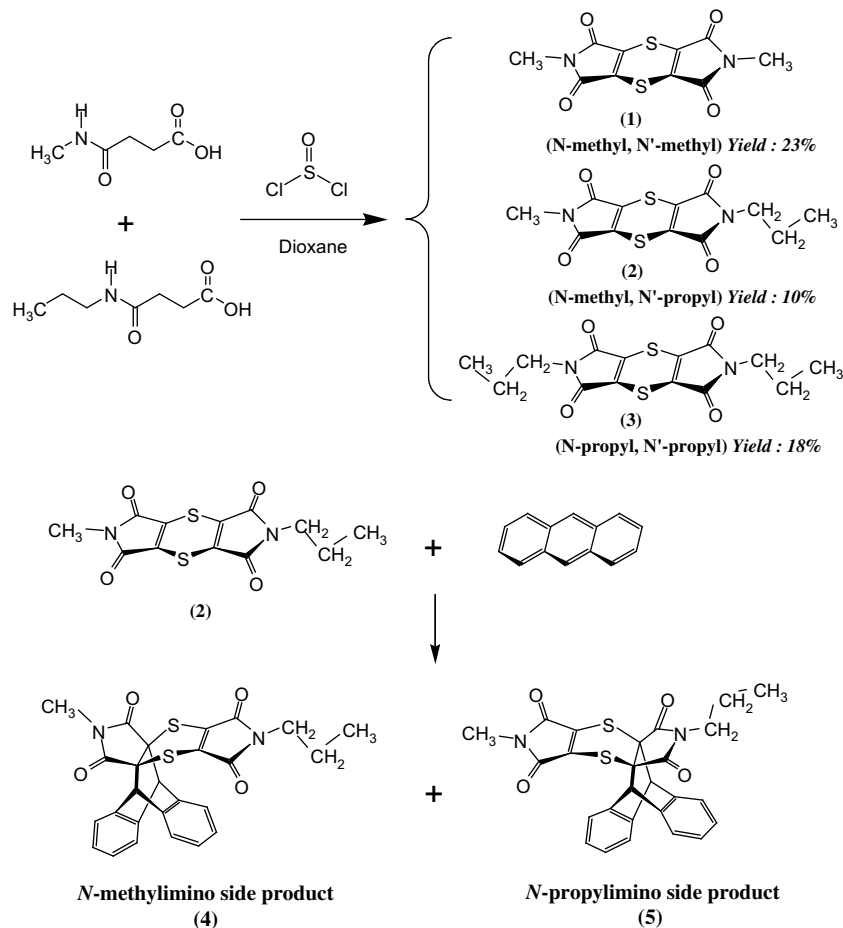


Fig. 1. Synthesis of the unsymmetrical-dithiin and their Diels-Alder reaction with anthracene.

Bis(*N*-methyl, *N'*-propylimino)-1,4-dithiin (**2**) and anthracene form an EDA complex in solution that further reacts thermally to yield a mixture of regioisomers (**4** and **5**) of the Diels-Alder cycloadducts as shown in Fig. 1. In a solution state reaction, the formation ratio of two isomeric products, (**4**) and (**5**) was observed at a 3:1 mole ratio by <sup>1</sup>H NMR spectroscopy. The results indicate that the double bond of the *N*-methylimino group in dithiin reacts more easily with anthracene than with the *N*-propylimino group probably due to the enhanced steric hindrance of the propyl group (Fig. 3).

On the other hand, a single crystal of the EDA complex of 1,4-dithiin and anthracene was grown as a transparent dark brown

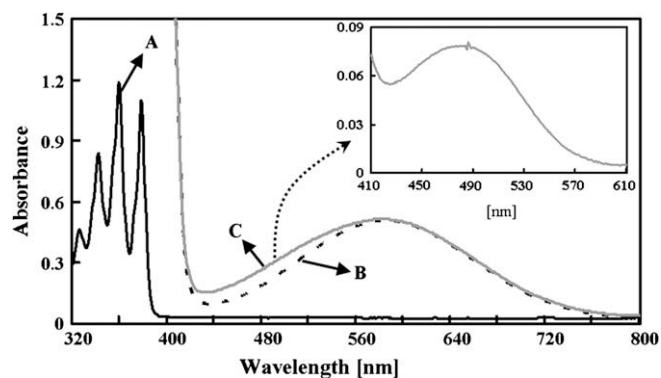


Fig. 2. Absorption spectrum of a dichloromethane solution of anthracene (A) unsymmetrical 1,4-dithiin (B), and their mixture (C). The in-set spectrum shows the EDA complex absorption band of 1,4-dithiin and anthracene.

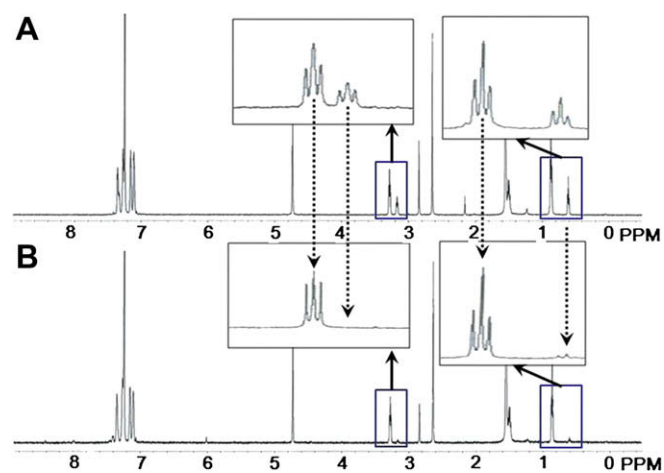


Fig. 3. <sup>1</sup>H NMR spectra of the solution state products mixture (A), and solid state reaction product (B) without any purification process.

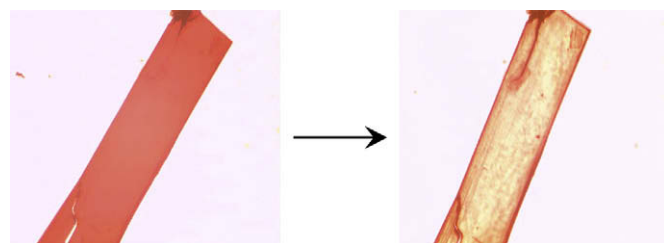


Fig. 4. Optical microscopy image of the solid state reaction phenomena.

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