Diels-Alder Topochemistry via Charge-Transfer Crystals ; Artificial Crystal with Modified Lattice Structure from Monophasic Solid State Reaction

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Introduction

Almost all functionalities of organic materials for electronics and photonics are induced by π-π electron oriented intermolecular interactions.[1] Intermolecular interactions including π-π interactions, coupling of molecular transition dipole, and characterization of molecular stacking are very significant with respect to special functionalities in the solid state. Dye molecular have a large π-conjugated planar structure and are thus valuable candidates for organic functional materials.[2] Moreover, the stacking structure of dye molecule in the solid state can also control the reactivity and selectivity for the solid state reaction.[3] In other words, the crystal lattice of the starting dye material controls the relative orientation of the neighboring reactant dye molecules, and thus their reactivity, since molecular motion is restricted in the solid state as compared to solution-phase reactions.[4, 5]

It was indeed succeeded in obtaining a series of reactive crystalline EDA complexes and described a *thermal* single crystal-to-single crystal reaction[6] between the *heteromolecular* system, bis(alkylimino)-1,4-dithiin and anthracene.[7] In this report, we describe the detailed mechanistic study of the solid-state reaction by exploiting the model of a nucleation and growth mechanism which could prove the anisotropic heterogeneous propagation during the single-crystal-to-single-crystal transformation.

Results and Discussion
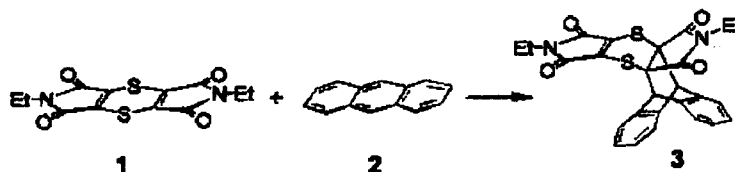
Scheme 1

It was known that the *bis*(*N*-alkylimino)-1,4-dithiin (acceptor) form 1:1 charge-transfer (CT) complex with anthracene (donor) in solution phase, and the resulting CT complex could be grown as single crystal in dichlomethane solution, successfully (**Scheme 1**) X-ray crystallography revealed the packing of the cofacially oriented 1,4-dithiin and anthracene in infinite alternate stacks along the crystallographic **a**-axis (**Fig. 1A**). Such a stacking was facilitated by the planar structure of the dithiin with the two ethyl groups in *trans* configuration (see **Fig. 1A**). The donor/acceptor stacks were linked to each other along the crystallographic **b**-axis through hydrogen-bonding contacts between the carbonyl group of the 1,4-dithiin and the hydrogen in 9-position of the anthracene (**Fig. 1B**).[8] Moreover, the ethylene groups of the 1,4-dithiin approach the centers of the anthracenes above and below the 1,4-dithiin with a distance of $d = 3.34$ Å.
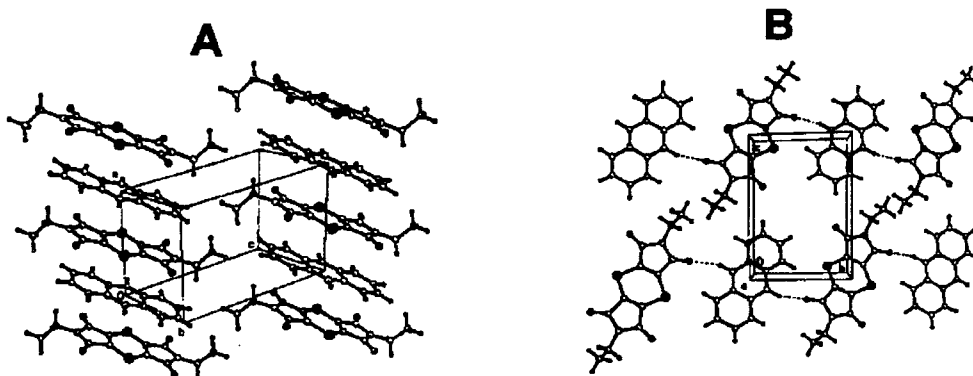

Fig. 1. Crystal structure of the CT complex of 1,4-dithiin and anthracene showing (A) alternate donor/acceptor stacks and (B) hydrogen bonding between anthracene and 1,4-dithiin.

This cofacial orientation of 1,4-dithiin and anthracene in close distance represents an ideal arrangement for solid-state Diels-Alder cycloadditions in the charge-transfer crystal. In benzene solution, bis(N-ethylimino)-1,4-dithiin (1) reacts with anthracene (2) to form the Diels-Alder product 3 (see Scheme 1). This reaction has been shown to occur via the formation of the 1:1 charge-transfer (CT) complex of 1 and 2. Similarly, the CT crystals of the acceptor 1 and the donor 2 reacted slowly at room temperature within 2 months to give the same product (3). Concomitantly, the brown color of the crystal changed to yellow uniformly throughout the entire crystal.
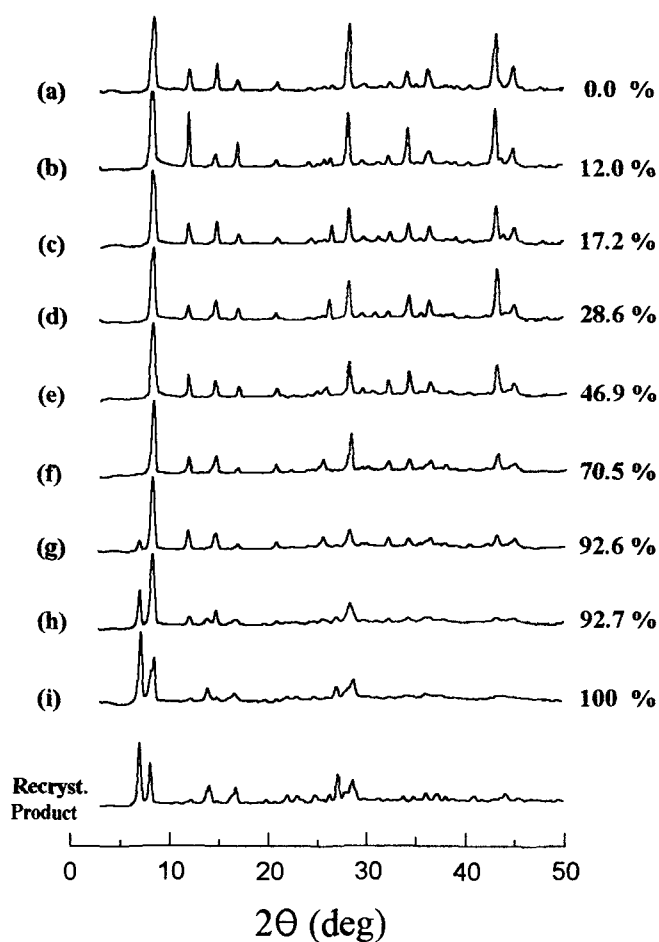

Fig. 2. Temporal evolution of the power diffraction diagram of the dithiin/anthracene complex.

The X-ray single crystal analysis and powder X-ray diffraction study was carried out to confirm the topochemical Single-Crystal-to-Single-Crystal transformation. The powder X-ray diffraction study revealed clearly *no formation of any new crystalline or amorphous phase* during the reaction (**Fig. 2**) until more than 70 % conversion. Thus, it is confirmed that the solid-state reaction did not diminish the quality of the single crystals of the complex even after 70 % converted stage. The X-ray diffraction patterns exhibited only limited changes in the position/intensity of the peaks to indicate merely small (continuous) lattice distortions accompanied by relatively minor structural changes up to 70 % conversion. After the 70 % converted stage, new peaks start to appear and grow with the conversion increased (see **Fig. 2g-2i**). Interestingly, this new diffraction pattern is very similar with the pattern of the recrystallized product crystal in which the packing structure of the product are significantly different with the that of the reactant. It was confirmed with comparison of the X-ray crystal analysis of the reactant and partially converted crystal and recrystallized product, respectively (*vide supra*).

The single-crystal X-ray structure analyses were carried out at various degrees of conversion to monitor the changes in the crystal lattice parameters and atomic movements in the reactant lattice during formation of the Diels-Alder cycloadduct. The solid-state cycloaddition caused slight changes in the cell parameters on going from the reactant to the product lattice.
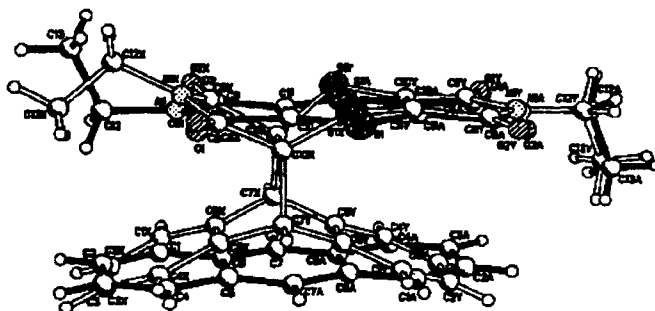

Fig. 3. Changes of the atomic positions during the solid-state cycloaddition reaction (black bonds : reactants ; white bonds : cycloadduct).

Typically, **Fig. 3** demonstrates the molecular changes on going from the reactant (black bonds) to the cycloadduct (white bonds). Both structures were extracted from the same X-ray data as a superposition of the crystallographically ordered starting material and the product (which was reproducibly oriented within the reactant crystal lattice without affecting the crystallographic positions of the reactant molecules).

The crystal structure of the cycloaddition product obtained from the solid-state reaction was compared with that obtained from the solution-phase reaction (**Fig. 4**). Thus, the solid-state product showed a crystal packing very similar to the original anthracene/1,4-dithiin cocrystal with the infinite alternate arrangement of anthracene and 1,4-dithiin moieties. In contrast, the crystal structure of the cycloaddition product from a solution-phase reaction showed a dimeric packing with two cycloaddition products oriented in opposite directions, leading to a 1,4-dithiin/anthracene/anthracene/1,4-dithiin sequence.
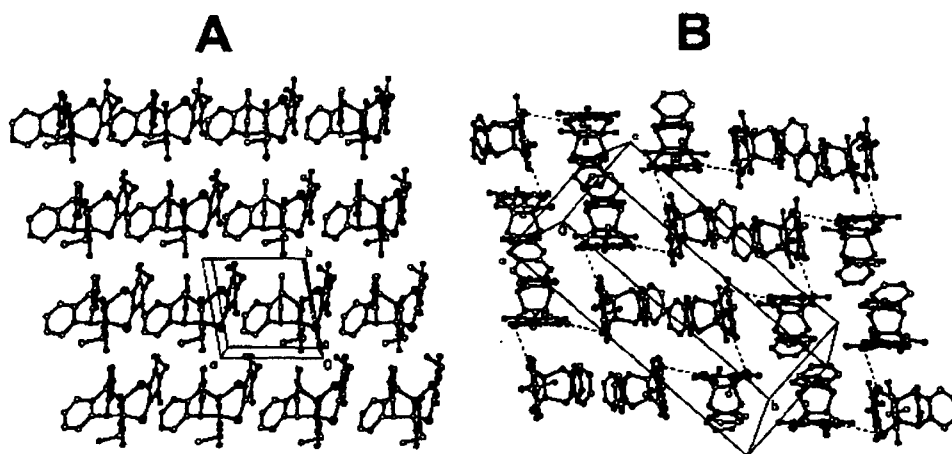

Fig. 4. Crystal packing of the two modifications of the cycloaddition product obtained from (A) the solid-state (B) the solution-phase reaction.

Conclusion

Crystal engineering by the judicious choice/design of Dye molecules; the donor (anthracene) and acceptor (dithiin), permits the solid-state transformation to be achieved *within the same crystal lattice* and allows the progressive crystalline change to be precisely monitored by X-ray diffraction methods to high conversions. Such a monophasic transformation allows *permanent* and *predictable* lattice control sufficient to assemble the cycloaddition product in anti-thermodynamic crystalline form. The latter represents a new kind of topochemical matrix (template) synthesis (predetermined by the reagent packing) and opens the interesting possibility of assembling materials non-adiabatically to form artificial crystals with modified properties.

References and Notes

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8. Thus, the observed H---O distance of d = 2.46 Å, which is significantly shorter than the sum of the van-der-Waals radii of hydrogen and oxygen (d_{vdw} = 2.72 Å), clearly reveals such interactions.