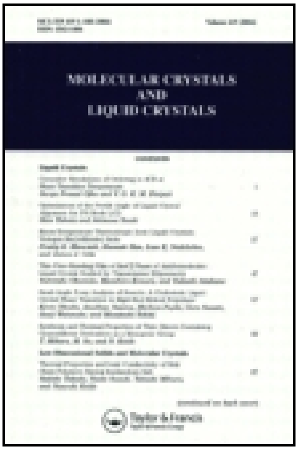

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Kaleidoscopic Photochemical Behavior of Unsymmetric Diolefin Crystals

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KALEIDOSCOPIC PHOTOCHEMICAL BEHAVIOR OF UNSYMMETRIC DIOLEFIN CRYSTALS

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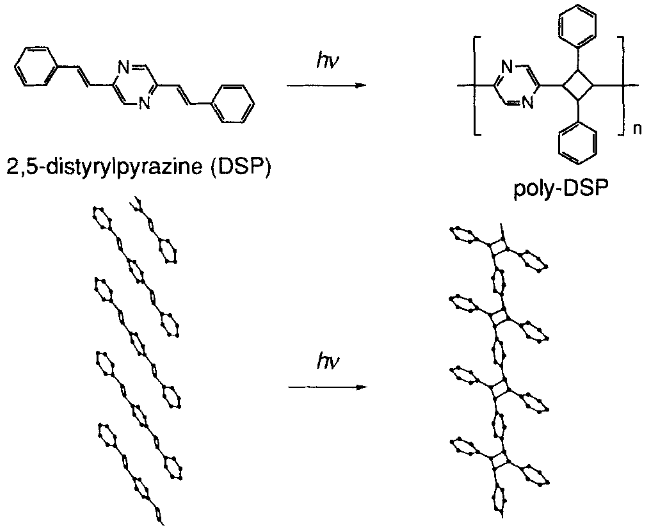
Abstract Various types of topochemical [2+2] photocycloaddition behaviors are described focusing on the recent results of a series of alkyl pyridylethenylcinnamate derivatives. Highly stereoregular polymerization and "absolute" asymmetric synthesis were achieved by using crystal-lattice controlled [2+2] photocycloadditions. Product control by employing co-crystallization of solvent molecules and a low temperature photoirradiation technique is demonstrated in the topochemical photoreactions of diolefin molecules. A methodology for the synthesis of highly strained compounds, [2.2]paracyclophane derivatives, in the crystalline state is also described.

Keywords: Topochemical reaction, Photochemistry, Diolefin compounds, Photopolymerization, [2.2]paracyclophane, Asymmetric synthesis

INTRODUCTION

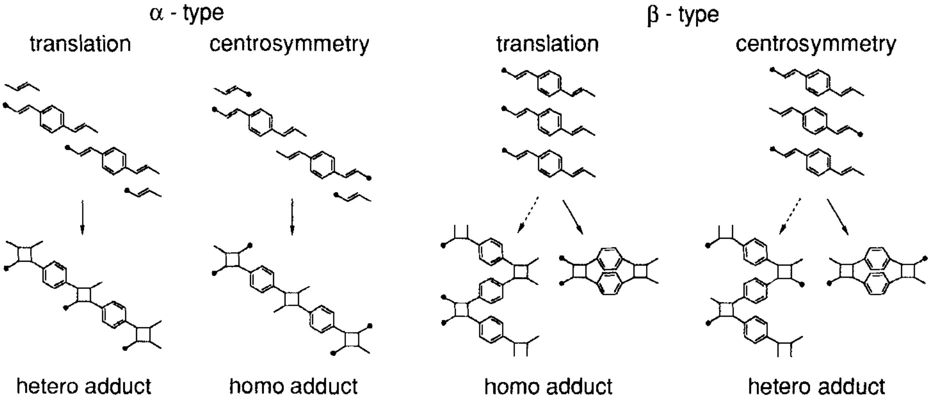
A reaction that proceeds in the crystalline state is called a crystal-lattice controlled reaction or a topochemical reaction. Based on crystallographic results of crystal-lattice controlled [2+2] photochemical reactions, Schmidt and co-workers established the topochemical concept in which the nature of the crystal structure determines the photoreactivity of the crystal, such that the reaction occurs with a minimum movement of the components.[1] Furthermore, they demonstrated the correlation between the crystal structure of starting compounds and the molecular structure of their photoproducts, and proposed an empirical rule on a geometrical criteria for the [2+2] topochemical photoreaction; the reacting double bonds of the molecules must be located within about 4.2 Å and aligned more or less parallel to each other.

The first clear-cut example of the crystal-lattice controlled polymerization was the [2+2] photopolymerization of 2,5-distyrylpyrazine (DSP) crystal prepared by recrystallization from the benzene solution (Scheme 1).[2] On the polymerization of DSP into poly-DSP, not only the correlation between the product and the starting crystal structure but also that between the unit cells of starting and resulting crystals was demonstrated for the first time in an organic reaction; the polymerization of DSP crystal proceeds with retention of the space group of the crystal (Pbca).[3] After the finding of the polymerization of DSP crystals, a great number of symmetric[4] and unsymmetric[5] diolefin crystals have been found to be photoreactive.



SCHEME 1

Photoreactive diolefin crystals are roughly classified into two types of crystal packing modes: in the α-type packing, monomers are superimposed with displacement by about half a molecule in the direction of the long molecular axis, and in β-type packing, without displacement. Furthermore, in the case of unsymmetric diolefin crystals, each packing of the α- and β-types is further classified into translation- and centrosymmetry-type packings. Corresponding to the molecular arrangements of these diolefin crystals, four types of photoproducts (α- and β-type, and homo- and hetero-type adducts) could be expected to be formed based on the topochemical principle (Scheme 2).[1] All the possible types of crystals and photoproducts have now been attained, except for the high molecular weight polymers having a zigzag type of main chain structure arising from β-type crystals.

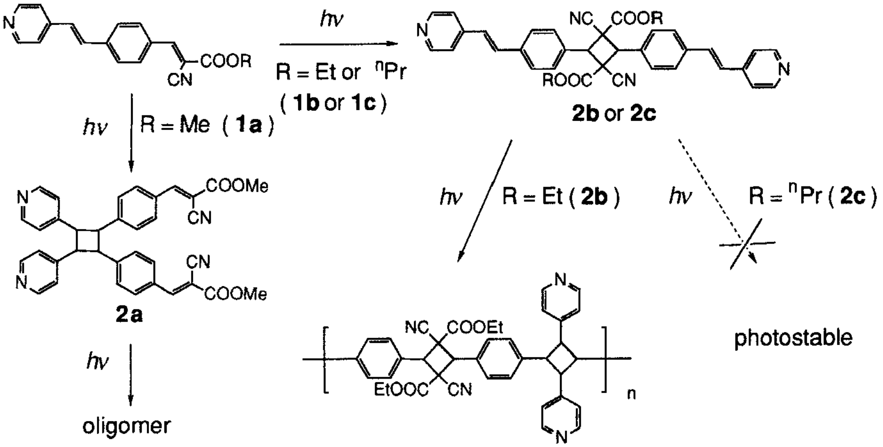


SCHEME 2

In the present article, recent topics on the crystal-lattice controlled [2+2] photocycloaddition of unsymmetric diolefin crystals are reviewed, involving product control by mixed crystal formation, regio- and stereoselectivities, and effect of irradiation temperature.

PHOTOCHEMICAL REACTIONS OF ALKYL α-CYANO-4-[2-(4-PYRIDYL)-ETHENYL]CINNAMATE CRYSTALS

A slight change in the chemical structure of diolefin compounds causes a drastic variation in the packing arrangement of the molecules and in the topochemical photoreaction mode. For example, alkyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate crystals show a wide variety of photochemical behaviors, as summarized in Scheme 3.[6-8] Methyl ester **1a** was photodimerized at the pyridyl side olefins to give the β-homo-type dimer **2a**, and finally oligomers on further photoirradiation. Ethyl **1b** and propyl **1c** esters have similar crystal structures, and give the same type (α-homo) of dimers **2b** and **2c** via a reaction at the ester side olefins. Although the propyl ester dimer **2c** is photostable and the reaction terminates at this stage, the ethyl ester dimer **2b** is photoreactive to give a polymer through an α-homo addition of pyridyl side olefins. These behaviors were well-interpreted by X-ray crystallographic analyses. Such a diverseness of the topochemical reaction is a characteristic feature that stands in contrast with ordinary chemical reactions in solution. At the present time, not only the topochemical products but also the crystal structures are hardly predictable from the molecular structures of the components. However, concerning the design of reactions, controlling the topochemical product becomes possible to some extent by using several techniques.



SCHEME 3

Enhancement of Topochemical Polymerizability by Complex Formation with Solvent Molecules[8]

Based on an X-ray crystallographic study, the double bonds in the photostable dimer **2c** were confirmed to be unfavorably located for photoreaction (Figure 1a). Moreover, since the repeating unit in α-type linear polymers is about 7.5 Å, according to a molecular modeling evaluation, the stacks in the starting crystals are preferred to have a similar length of the repeating unit (L). However, L (5.932 Å) is apparently shorter than this range in the crystal of **2c**. To overcome these difficulties, a better result would be expected by detaching the center of the gravities of the dimers from each other; in this case, the distance between the double bonds will become shorter to give a suitable structure for the polymerization as well as the photoreaction. Complexation of some kinds of spacers into these crystals may be effective for this purpose.

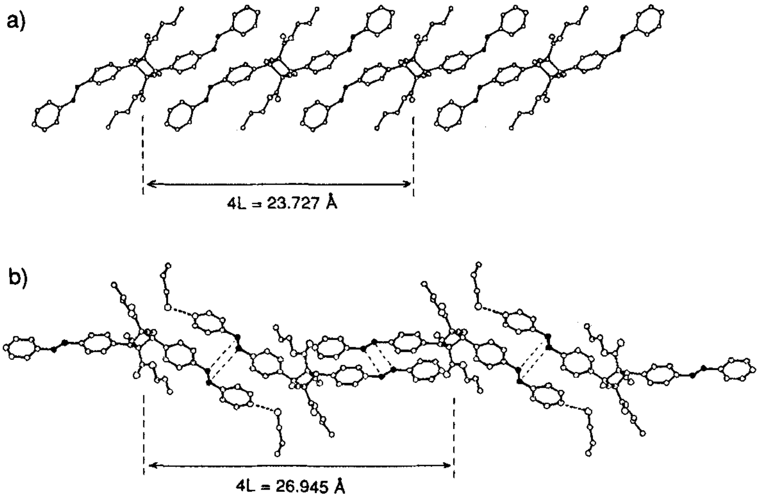
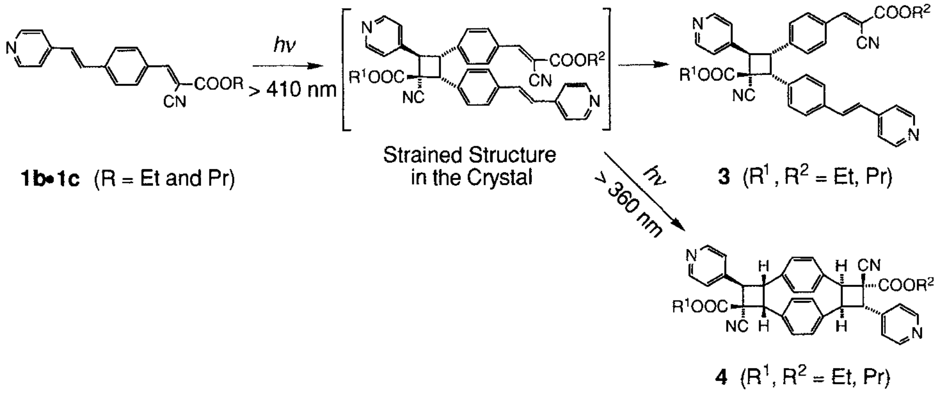


FIGURE 1 Molecular arrangements of a) **2c** and b) **2c•PrOH** viewed perpendicular to the direction of the polymer chain with the length of the repeating unit of the dimer (4L).

Recrystallization of dimer **2c** from 1-propanol afforded the mixed crystal **2c•PrOH**, which contains solvent molecules in a 1:1 molar ratio. **2c•PrOH** became photoreactive and gave the polymer ($\overline{Mn}$ = 3,000) having the same type of structure as the ethyl ester polymer. As shown in Figure 1b, the 1-propanol molecule in **2c•PrOH** is hydrogen-bonded with the pyridine nitrogen atom in the dimer. Consequently, two reactant dimer molecules were separated from each other to a suitable distance (L = 6.736 Å) and two reactive sites were contracted to a normal photoreactive range. Furthermore, it was found that the complex prepared from ethanol solution, which contains two molar equivalents of the solvent molecules, underwent photoreaction to give a higher molecular weight polymer ($\overline{Mn}$ = 12,000).

Formation of a Highly Strained [2.2]Paracyclophane Derivative from the Mixed Crystal of Ethyl and Propyl Esters

As already mentioned, ethyl **1b** and propyl **1c** esters have similar crystal structures, so the mixed crystal of these monomers was prepared in order to attempt a topochemical copolymerization.[9] However, the X-ray powder diffraction pattern suggests that the mixed crystal **1b•1c** has a crystal structure that is very different from the original ones. On photoirradiation with a cut-off filter ($\lambda > 410$ nm), which was used so that only the monomer was excited, not the α-homo-type adducts but the β-hetero-type dimer **3** was isolated. Furthermore, with light of shorter wavelength ($\lambda > 360$ nm), a [2.2]paracyclophane derivative **4** was formed in almost quantitative yield (Scheme 4).[10] Formation of such a highly strained compound is reasonably interpreted in terms of the crystal structure of **1b•1c**. As shown in Figure 2, two molecules make a β-centrosymmetry-type molecular pair, which comes into contact with the other molecular pair in an almost perpendicular fashion at the van der Waals distances. Thus, after the first cycloaddition



SCHEME 4

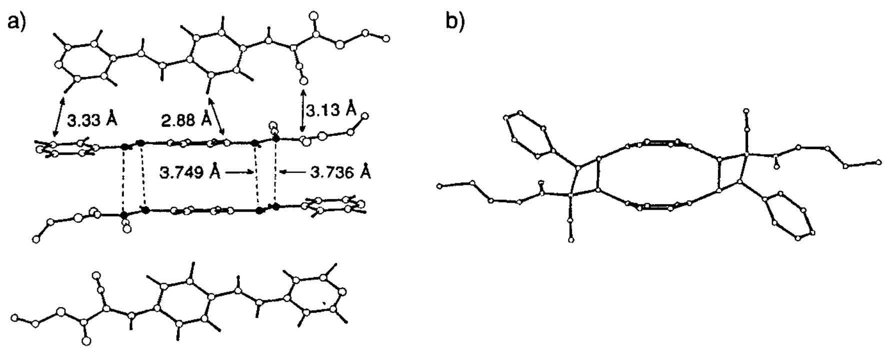


FIGURE 2 a) A crystal structure of mixed crystal **1b•1c** and b) molecular structure of [2.2]paracyclophane **4**.

between two molecules, the residual olefins in monocyclic dimer **3** would be forced to stay within a photoreactive distance by virtue of a repulsion with the neighboring molecules.

PHOTOCHEMICAL REACTIONS OF ALKYL α-CYANO-4-[2-(2-PYRIDYL)-ETHENYL]CINNAMATE CRYSTALS

A Highly Stereoregular Polymerization via Topochemical Photoreaction[11]

Methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamates (**5a**, **5b**), which are regioisomers of **1a** and **1b**, are also highly photoreactive in the crystalline state.[12] In these crystals, of which the crystal structures are similar to each other (in both crystals, space group is $P\bar{1}$), molecules are arranged in a β-centrosymmetry-type packing (Figure 3). Consequently, on photoirradiation with a cut-off filter ($\lambda > 410$ nm), β-hetero-type dimers **6a** and **6b** were formed in almost quantitative yield (Scheme 5). This result was in accord with the prediction based on topochemical considerations.

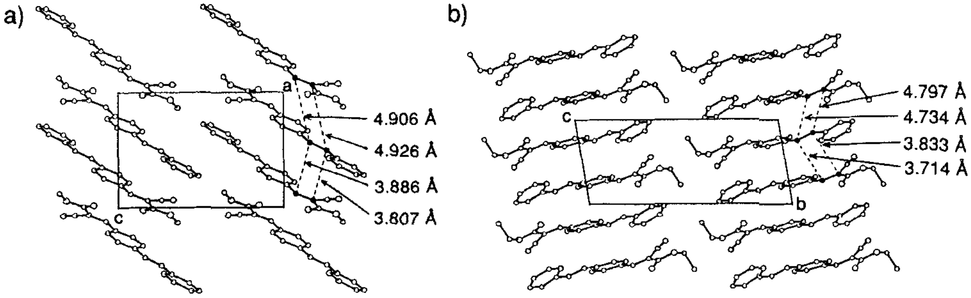
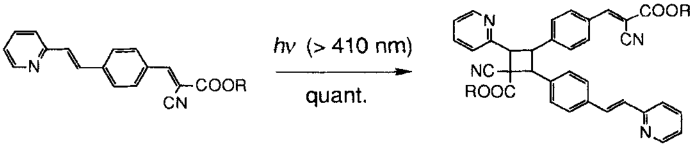


FIGURE 3 Crystal structures of a) **5a** viewed along the b-axis and b) **5b** viewed along the a-axis.



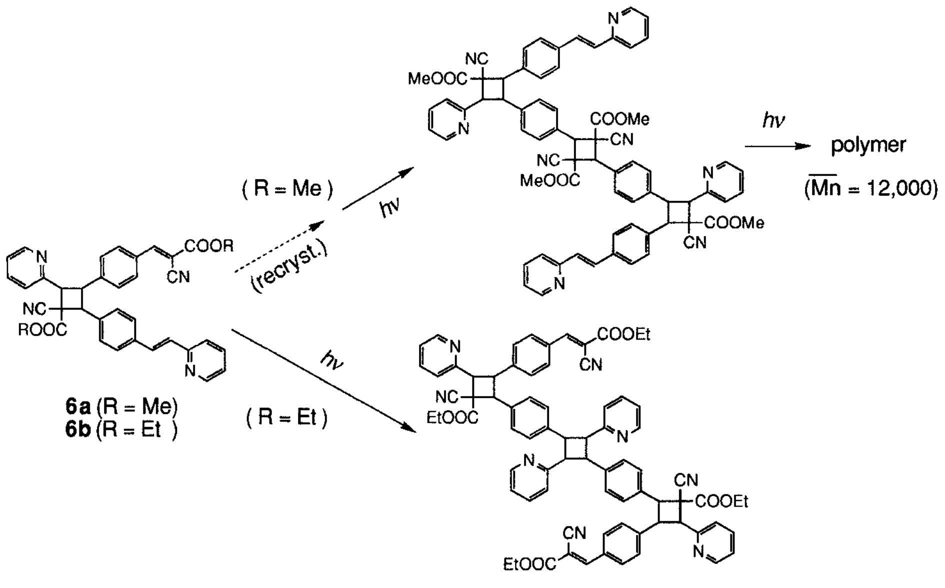
5a (R = Me)
5b (R = Et)

6a (R = Me)
6b (R = Et)

SCHEME 5

An interesting observation was that the crystallinity of as-prepared **6b** increased as the photoirradiation temperature increased; as-prepared **6b** obtained at 70 °C showed a high crystallinity whereas amorphous product was formed at about 2 °C or below.

Dimer crystals **6a** and **6b**, prepared by recrystallization, are also highly photoreactive, and gave α-homo-type tetramers arising from the addition of ester side olefins for **6a** and pyridyl side olefins for **6b** (Scheme 6). The crystal structures of the dimers reasonably elucidate the photoreactions (Figure 4).



SCHEME 6

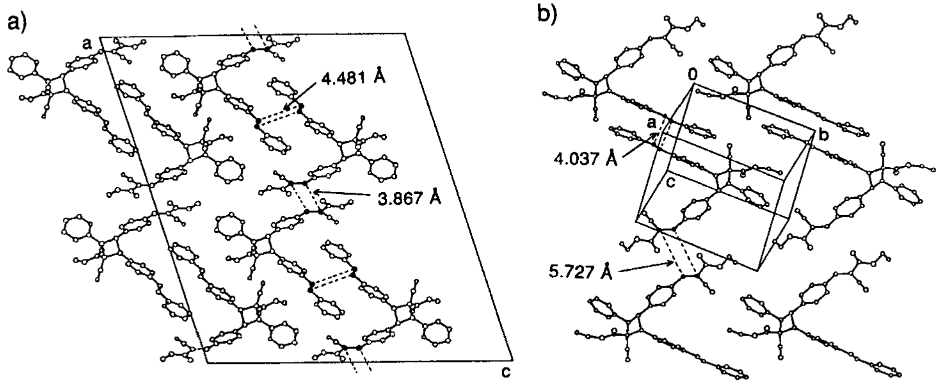


FIGURE 4 Crystal structures of a) **6a** viewed along the b-axis and b) **6b**.

The highly crystalline as-prepared **6b** obtained by a high temperature experiment also afforded the tetramer in a relatively high yield, but as-prepared **6a** was amorphous, and a definite product including the tetramer was not isolated on further irradiation. Likewise, there is a characteristic difference of photochemical reactivities between **5a** and **5b**: on photoirradiation, the tetramer was not detectable in photoproducts derived directly from **5a**, but small amounts of the tetramer and octamer were formed directly from crystal

5b. This difference is understood from the correlation of crystal structures between the monomers and the dimers. The crystal structure of recrystallized **6a** (space group: A2/a) is quite different from that of monomer **5a** ($P\bar{1}$), whereas **5b** and **6b** are similar to each other (in both crystals the space group is $P\bar{1}$).

On further irradiation for 28 h at -40 °C, recrystallized dimer **6a** was converted into highly crystalline polymer ($\overline{\mathrm{Mn}}$ = 12,000). On the basis of the geometry of the two pyridyl side olefins of **6a**, the polymer should have a very unique repeating unit containing 8 original molecules in which three types of cyclobutane structures are incorporated in a sequence of $[\alpha\beta\varepsilon\beta\alpha\beta^{-1}\varepsilon\beta^{-1}]$, where β and β^{-1} are enantiomeric to each other and ε is a stereoisomer of the α-type cyclobutane (Figure 5).[13]

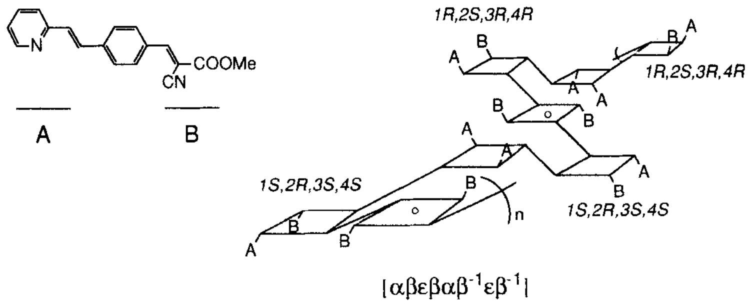
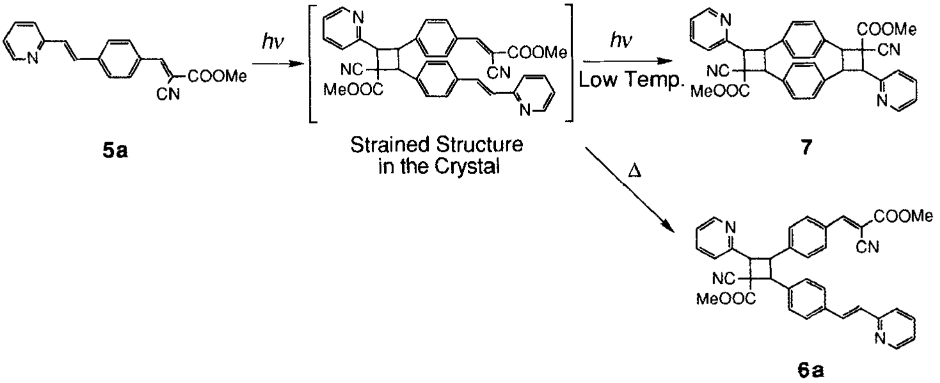


FIGURE 5 Polymer structures derived from crystal **6a**. Phenylene rings are omitted as a matter of convenience. A and B correspond to 2-pyridyl and -(CN)COOR, respectively.

Temperature Dependence of the Topochemical Reaction

The study of temperature effects on topochemical reactions is a useful tool in understanding molecular dynamics in the course of photoreaction of organic crystals, as well as for visualizing a possibility of formation of well-defined products.[14] On the basis of these considerations, a low temperature photoreaction of methyl ester **5a** was conducted. On photoirradiation with λ > 300 nm at -78 °C, the reaction proceeded cleanly to give the



SCHEME 7

[2.2]paracyclophane derivative **7** (65% yield) together with β-hetero-type dimer **6a** (7% yield) (Scheme 7).[11] However, [2.2]paracyclophane could not be obtained from ethyl ester **5b** under the similar conditions.

The formation of [2.2]paracyclophane **7** can be explained as follows: In the case of normal β-type crystals such as **5a**, molecular motion after the first cycloaddition can not be suppressed at high temperature. In that case, the unreacted olefinic pair moves beyond the distance suitable for reaction in order to release the strained bond angle. At a low temperature, however, the motion of the two chains would be "frozen" to some extent, with the retention of a favorable distance for the intramolecular cycloaddition.[15]

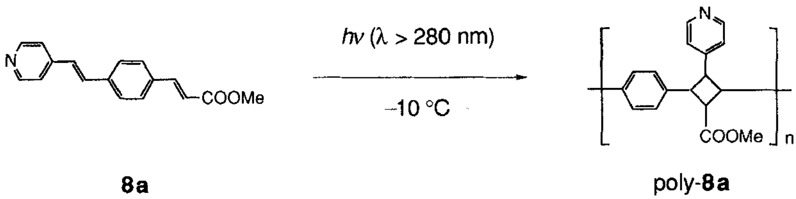
By contrast, in the photoreaction of mixed crystal **1b•1c**, the [2.2]paracyclophane derivative **4** was formed quantitatively even at room temperature, as mentioned. This is owing to quite a unique β-type molecular packing (Figure 2).

Recently, such a product control technique by a steric compression in the solid state was extended to the photoreaction of the propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]-cinnamate crystal[16] at a low temperature to result in formation of the same type of [2.2]paracyclophane.[17] This result demonstrated the generality of the present synthetic method of forming highly strained [2.2]paracyclophane derivatives from β-type crystals using low temperature photoirradiation.

PHOTOCHEMICAL REACTIONS OF ALKYL 4-[2-(4-PYRIDYL)ETHENYL]-CINNAMATE CRYSTALS

Polymerization of Methyl Ester and Reversible Photochemical Process of the Resulting Polymer

Crystals of **8a**, which corresponds to the decyano derivative of **1a**, were highly photoreactive and gave high molecular weight polymer (poly-**8a**) crystals in quantitative yield (Scheme 8, Figure 6a).[6,18] By an X-ray crystallographic analysis of the starting monomer, it was confirmed that the monomers are arranged in an α-translation-type packing, and that the photopolymerization proceeds through a typical topochemical [2+2] cycloaddition in a similar manner to DSP.



SCHEME 8

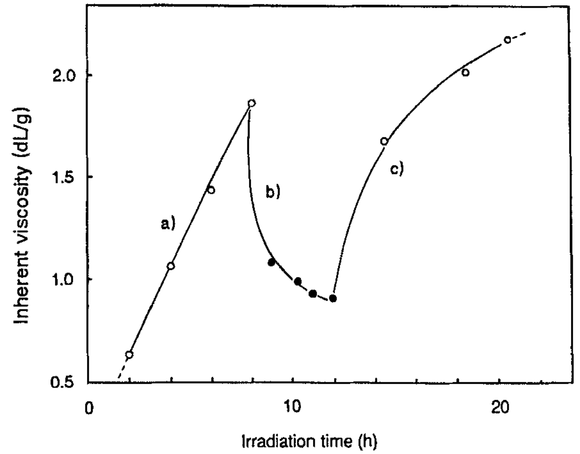


FIGURE 6 Plot of the irradiation time versus the inherent viscosity for the reversible photochemical process of the polymer derived from **8a** crystals. Photoirradiation was carried out at -10 °C with $\lambda > 280$ nm for a) and c), and at 2 °C with $\lambda = 254$ nm for b).

Although the molecular weight of the final polymer, obtained by photoirradiation at room temperature, was not very high (inherent viscosity (η_{inh}) = 0.82 dL/g), it gradually increased with decreasing irradiation temperature, attaining an inherent viscosity of 1.86 dL/g after irradiation at -10 °C. In addition, the crystallinity of the final polymer gradually increased as the irradiation temperature decreased.

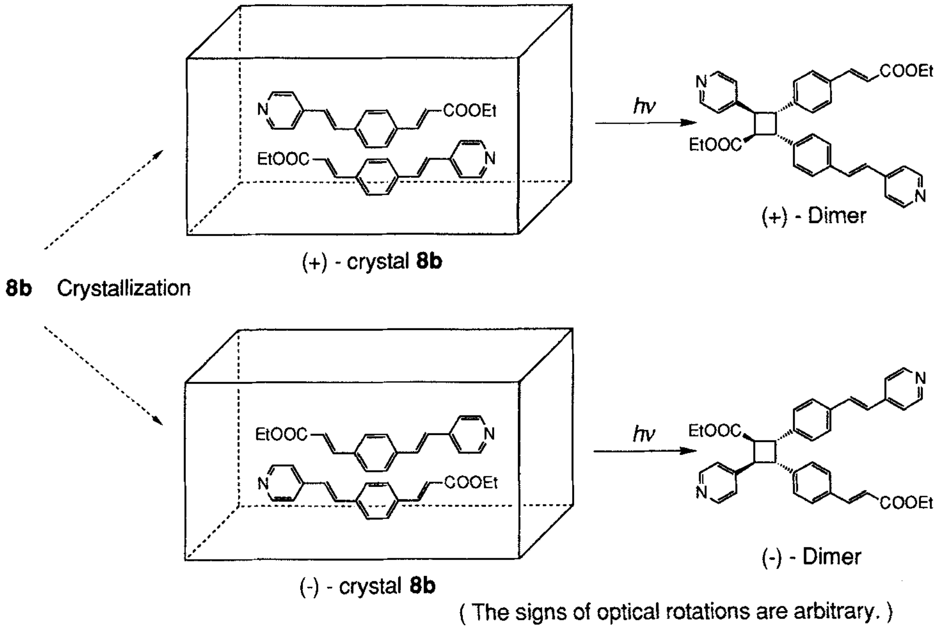
When an as-prepared poly-**8a** (η_{inh} = 1.86 dL/g) was irradiated in the crystalline state with a low-pressure mercury lamp (λ = 254 nm), a considerable decrease in the inherent viscosity was observed (Figure 6b). Further photoirradiation under the same conditions as that of the first polymerization ($\lambda > 280$ nm) gave a high molecular weight polymer again (η_{inh} = 2.17 dL/g, Figure 6c). Throughout the process, ^{1}H NMR and X-ray diffraction patterns were almost identical, and a drastic change in crystallinity was never observed. This implies a reversible process between topochemically controlled formation and cleavage of cyclobutane rings by wavelength-switching, and the present result provides the first example of photochemically induced topochemical polymerization-depolymerization in a crystal lattice.

"Absolute" Asymmetric [2+2] Photoreaction

The achievement of an asymmetric synthesis starting from an achiral compound in the absence of any external chiral reagents has long been an intriguing challenge to chemists. Several attempts to use the chiral environment of crystals as a sole chiral source have been made to achieve asymmetric syntheses.

Among those approaches, a successful asymmetric synthesis with quantitative enantiomeric yield has been performed for the first time by Addadi *et al.* by using the topochemical photopolymerization of unsymmetric diolefin crystals.[19] Scheffer *et al.*[20] and Toda *et al.*[21] have reported asymmetric unimolecular photoreactions involving the di-π-methane and Norrish type-II reactions of chiral crystals.

Recently, we have found that ethyl ester **8b** gave an optically active dimer through the topochemical [2+2] photocycloaddition (ee > 90%, Scheme 9).[18,22] The asymmetric induction is explained by the formation of a chiral arrangement of achiral molecules **8b** (space group: $P2_12_12_1$), followed by a successive topochemical photoreaction.



(The signs of optical rotations are arbitrary.)

SCHEME 9

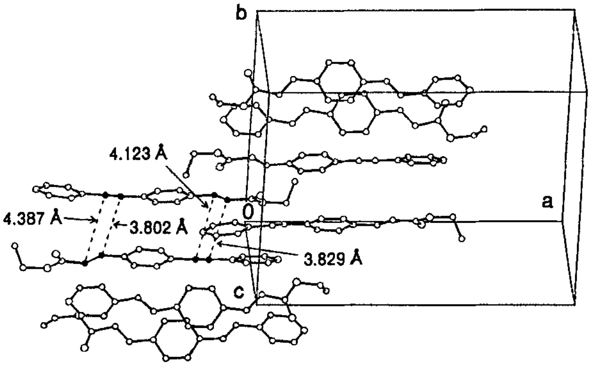


FIGURE 7 Crystal structure of **8b**.

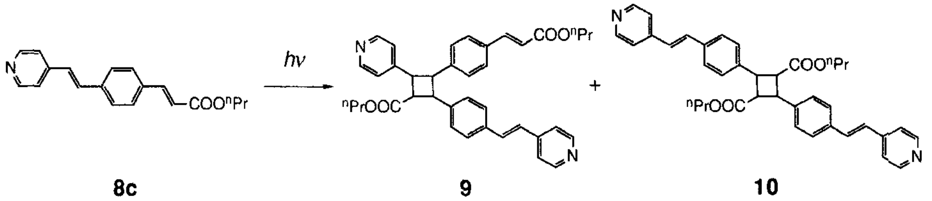
In the crystal of **8b**, there are two crystallographically independent molecules, which form a molecular pair in a β-type arrangement in which no stack for the polymerization exists (Figure 7). Thus the formation of a β-hetero-type dimer through the photoreaction is readily interpreted from the crystal structure. Furthermore, it should be noted that a cyclobutane ring having the same absolute configuration is generated by the addition of either of the two pairs of facing double bonds because of the "cisoid form" of molecule **8b**. In addition, since every molecular pair is related only by the 2_1 screw axis, enantiomerically homogeneous adducts are anticipated to arise from the topochemical photoreaction of one single crystal.

An interesting observation was that a large quantity of crystals **8b** having the same chirality was afforded by seeding. Moreover, crystals **8b** obtained from each recrystallizing batch without seeding, always gave one or the other enantiomeric dimer in excess. Such growth of chiral crystals may be termed "amplification of asymmetry."

In terms of an intermolecular [2+2] photoreaction system, the present result has aroused wide interest because of its extension to asymmetric synthesis by using β-packing crystals with quantitative enantiomeric excess.

Two Types of Dimer Formation from Crystals of Propyl Ester

Propyl ester **8c** was less reactive than both **8a** and **8b**, but upon photoirradiation gave two types of dimers; a β-hetero-type **9** and a homo-type dimer **10** (Scheme 10).[18] At room temperature, the ratio of the products (**9** : **10**) was approximately 3 : 1. Although the final product was amorphous, this unusual behavior can be explained reasonably in terms of the crystal structure of **8c**.



SCHEME 10

Crystal **8c** has 16 molecules in the unit cell, and there are two independent molecules in the asymmetric unit. Of great interest is the fact that the molecules form two different types of molecular stacks (Figure 8); in stack A, the molecules are superimposed to form β-type packing, while in stack B, the molecules are displaced by about half a molecule in the direction of the molecular long axis. From the molecular arrangement in stack A, formation of the β-hetero-type dimer **9** is quite reasonable. The intermolecular

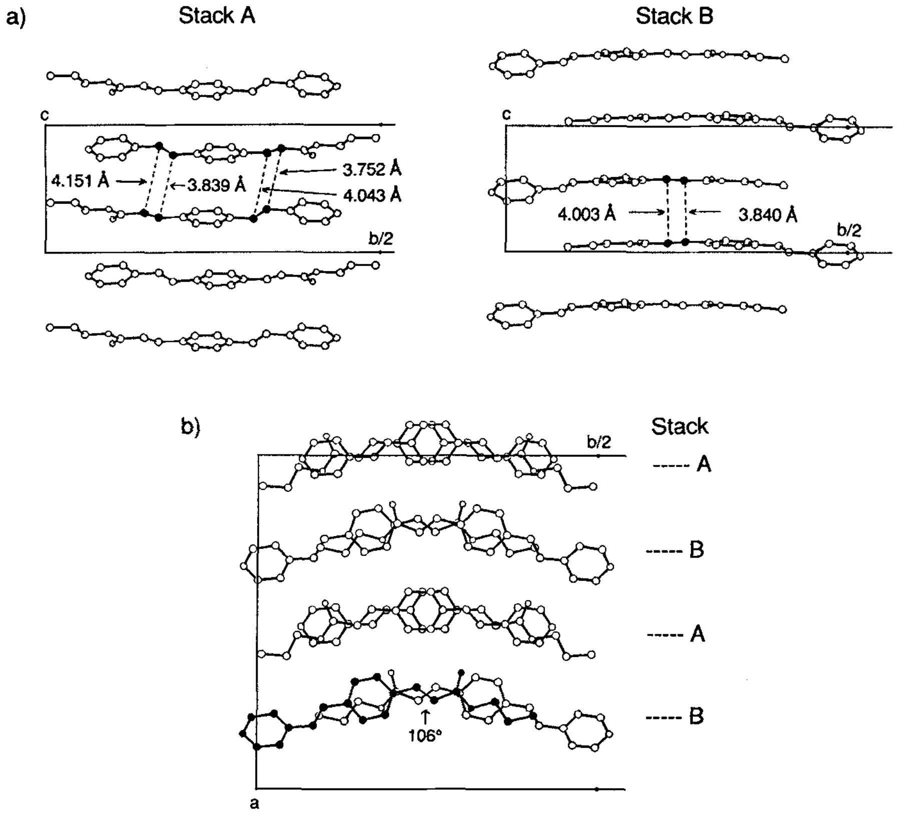


FIGURE 8 Crystal structure of **8c**, viewed along a) the a-axis and b) the c-axis.

distances between the two facing double bonds of the molecules in stack B are also within a photoreactive distance. However, the orientation of the olefinic pair is not topochemically favorable for [2+2] cycloaddition; the two double bonds are distorted by 106° (or 74°) (Figure 8b).[23] Accordingly, although the number of molecules in both stacks is the same, **10** was formed relatively in low yield.

CONCLUSION

The "kaleidoscopic" topochemical behaviors of alkyl pyridylethenylcinnamate derivatives have been thoroughly studied and are well understood in terms of X-ray crystallographic analyses. Topochemical reactions clearly depart from typical solution chemistry; the crystal-lattice control has played a pivotal role in the synthesis of highly strained [2.2]paracyclophane derivatives, highly stereoregular polymerization and the "absolute" asymmetric synthesis described herein. However, these examples represent only a subset of the topochemically reactive crystals that exhibit a wide variety of characteristic photochemical behaviors.

On the other hand, the difficulty of predicting the topochemical reaction course based on the molecular structure of the starting materials was also described. In the context of this discussion, a serious attempt should be made to provide a logical format for the treatment of structurally related crystal systems so that the relationship between molecular structure and the topochemical products can be established. Progress in the field of computational methodology and crystal engineering is valuable for this endeavor. Thus, the regioselectivities of topochemical photodimerizations have been explained on the basis of the computational calculations.[24]

Even in their imperfect present state of development, topochemical reactions provide an efficient tool for the construction of unique molecular structures, which in some instances may be difficult. More activity in this area will demonstrate the usefulness of this fascinating aspect of topochemical reactions.

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13. At the pyridyl side of **6a**, a possibility to give a δ-type cyclobutane (stereoisomer of β-type) cannot be excluded. Thus, the structure of the repeating unit of the resulting polymer may be not $[\alpha\beta\varepsilon\beta\alpha\beta^{-1}\varepsilon\beta^{-1}]$ but $[\alpha\beta\delta\beta\alpha\beta^{-1}\delta\beta^{-1}]$.
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