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"Kaleidoscopic" Photoreaction Behavior of Alkyl 4-[2-(4-Pyridyl)ethenyl]cinnamate Crystals: A Crystalline Linear High Polymer from the Methyl Ester, an "Absolute" Asymmetric Reaction of the Ethyl Ester, and Two Types of Dimer Formation from the Propyl Ester

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Abstract: The photochemical behavior of methyl, ethyl, and propyl 4-[2-(4-pyridyl)ethenyl]cinnamate (**1a**, **1b**, and **1c**) crystals was investigated mainly on the basis of X-ray crystallographic analysis. Methyl ester **1a** gave a highly crystalline linear polymer (η_{inh} = 1.9 dL/g) through a typical [2+2] topochemical photopolymerization. Furthermore, a reversible photochemical process was demonstrated for the first time in organic crystals, which depended on the wavelength of the irradiating light. Ethyl ester **1b** formed a chiral crystal of β-type packing, and afforded an optically active dimer (**2b**) upon photoirradiation of a single crystal of **1b** in high enantiomeric yield (>90%). The asymmetric induction could be explained by the formation of a chiral arrangement of prochiral molecules (**1b**), followed by a successive topochemical photoreaction. A large quantity of crystals **1b** was obtained by seeding with a trace amount of seed crystals **1b**, which gave a dimer of the same optical rotation as that of the dimer obtained from the seed crystals ("amplification of asymmetry"). Crystals of **1b**, which were obtained from each recrystallizing batch without seeding, always gave either of enantiomeric dimers in excess; the resulting enantiomer was mostly (−)-**2b**. This result affords significant information concerning the exploitation of a new route of "absolute" asymmetric synthesis through a topochemical process. The crystal structure of propyl ester **1c** is unusual such that each unit cell contains sixteen molecules of **1c**, comprising two types of molecular stacks. Upon photoirradiation, crystals of **1c** gave a homo- and a hetero-type dimer that were predicted from molecular arrangement in two types of stacks in the crystal of **1c**.

Introduction

Some recent studies concerning topochemical photoreaction have focused on (in addition to the correlation between crystal structure and photochemical behavior) topochemical induction, which is directly related to the crystallization process of those olefin crystals.

For example, an asymmetric synthesis of chiral dimers and oligomers has been accomplished by Addadi et al. through a process of crystallization of an achiral monomer in a chiral crystal, followed by a topochemical photopolymerization.[1] Furthermore, Scheffer et al.[2] and Toda et al.[3] have reported asymmetric synthesis in unimolecular transformation using the chiral-crystal environment. However, achieving the desired type of crystal structure in any given case is very difficult because the factors that control the crystal packing are not yet well understood; these examples of asymmetric synthesis with quantitative enantiomeric yield are very rare at the present stage.[4]

In a series of topochemical [2+2] photoreactions of unsymmetric diolefin crystals, it has been revealed on several occasions that only a slight change in recrystallizing solvents results in a drastic variation of crystal structure, as is the case for a slight change in the chemical structure of these diolefin compounds.[5] The variation in chemical behavior can be rationalized in almost all of the cases by topochemical principles and a knowledge of the crystal structure.[6]

In this paper, "kaleidoscopic" photochemical behavior depending on the chemical structure of alkyl 4-[2-(4-pyridyl)ethenyl]cinnamate (**1**) crystals was mechanistically and crystallographically investigated, involving the formation of a highly crystalline linear polymer, an "absolute" asymmetric photoreaction of a chiral crystal, and two types of dimer formation from a single crystal having two types of molecular arrangements.

Results and Discussion

Polymerization of 1a and Reversible Photochemical Process of Poly-1a. Crystals of **1a** were highly photoreactive and gave high molecular weight polymer (poly-**1a** crystals in quantitative yield (Scheme I, Figure 1a). By X-ray crystallography of the starting monomer and an NMR analysis of the polymer, it was confirmed that the photopolymerization proceeded through a typical topochemical [2+2] cycloaddition.[7]

Although the molecular weight of the final polymer, which was obtained by photoirradiation at room temperature, was not very high (η_{inh} = 0.82 dL/g), it gradually increased with decreasing irradiation temperature, attaining an inherent viscosity of 1.86 upon irradiation at −10 °C. In addition, the crystallinity of the final polymer gradually increased as the irradiation temperature decreased. The temperature dependence of the reaction indicates that a relatively large thermal motion of the reacting molecules is undesirable for the crystal-lattice-controlled reaction process to proceed.

On the other hand, when an as-prepared poly-**1a** (η_{inh} = 1.86 dL/g) was irradiated in the crystalline state with a low-pressure mercury lamp (254 nm), a considerable decrease of the inherent viscosity was observed (Figure 1b). The depolymerized polymer did not show any appreciable change in its ^{1}H NMR pattern from that of original polymer, except for the appearance of a weak signal due to terminal olefin, suggesting that depolymerization proceeded by a cleavage of the cyclobutane ring. Furthermore, the X-ray diffraction pattern was little altered, suggesting that the depolymerization proceeded under crystal-lattice control, although the crystallinity of the polymer slightly decreased during depolymerization. Only a few articles have been reported on the crystalline-state depolymerization of the polymer derived from diolefin crystals. For example, the polymer of 2,5-distyrylpyrazine (poly-DSP) is thermally depolymerized to the oligomer in the crystalline state.[8] However, the present result provides the first

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[1] Addadi, L.; van Mil, J.; Lahav, M. *J. Am. Chem. Soc.* **1982**, *104*, 3422 and references cited therein.

[2] Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648.

[3] Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, M.; Toda, F. *J. Am. Chem. Soc.* **1989**, *111*, 697.

[4] Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

[5] (a) Hasegawa, M. *Pure Appl. Chem.* **1986**, *58*, 1179. (b) Hasegawa, M.; Saigo, K.; Kato, S.; Harashina, H. *ACS Symp. Ser.* **1987**, *337*, 44.

[6] Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

[7] The photopolymerization of crystal of **1a** was reported in a previous communication: Hasegawa, M.; Harashina, H.; Kato, S.; Saigo, K. *Macromolecules* **1986**, *19*, 1276.

Scheme I

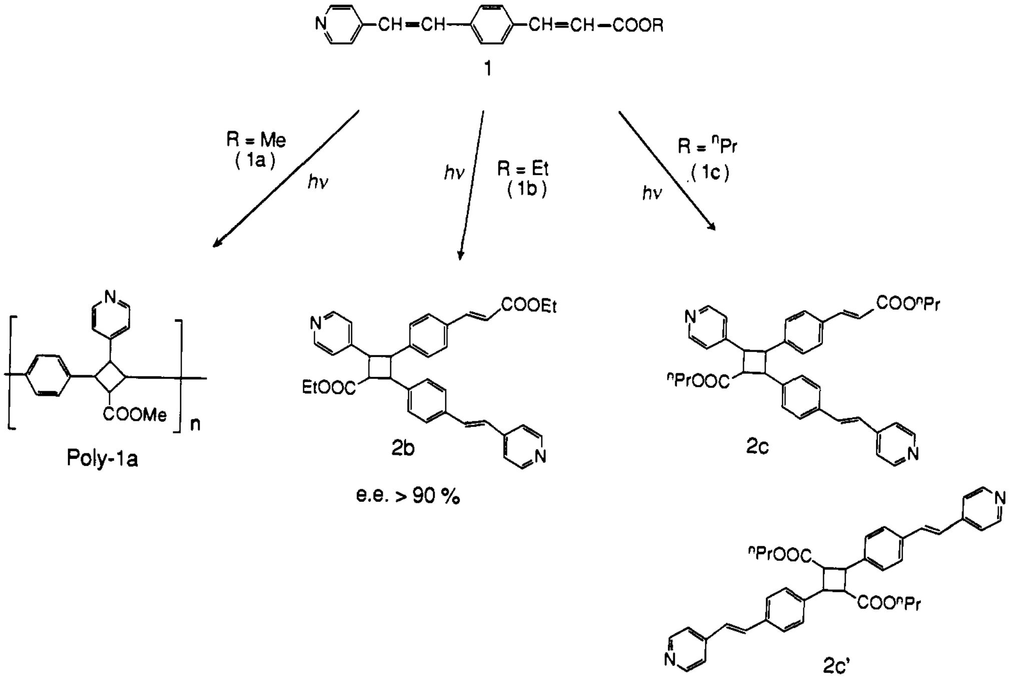

Table I. Results of the Seeding and Photoirradiation of **1b**

	seed crystals		crystals obtained by seeding				
run no.	sign of optical rotation of dimer	quantity used for seeding (mg)	quantity obtained by seeding (mg)	irradiation time^a (h)	chemical yield of dimer (%)	$[\alpha]_D{}^b$ (deg)	optical purity^c (%)
1	+	6.7	240	10	63	+72	(+)92
2	+	3.5	389	10	67		(+)92
3	−	2.8	190	7	45	−75	(−)95
4	−	5.0	199	6	42		(−)94

^{a}Irradiated at −40 °C, employing a cut-off filter (>365 nm). ^{b}c 1.0 in CH_2Cl_2. ^{c}Determined by HPLC on an optically active solid phase.

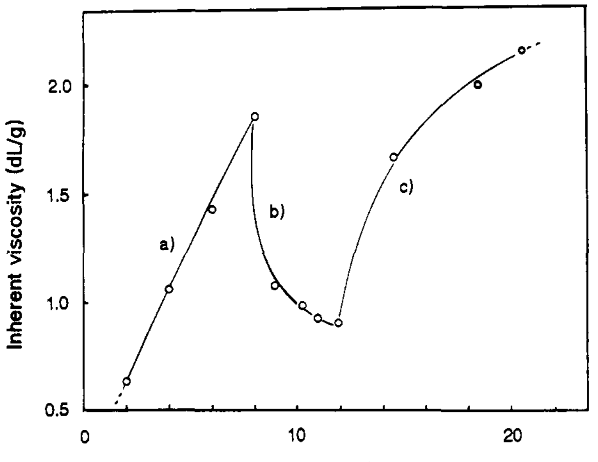

Figure 1. Irradiation time versus the inherent viscosity for the reversible photochemical process of the polymer derived from **1a** crystals. Photoirradiation was carried out at −10 °C with $\lambda \geq 280$ nm for (a) and (c), and at 2 °C with $\lambda = 254$ nm for (b). The inherent viscosity of monomer **1a** is 0.05 dL/g.

example of photochemically induced topochemical depolymerization.

When the depolymerized product was then photoirradiated under the same conditions as that of the first polymerization, polymerization occurred again, resulting in a high molecular weight polymer ($\eta_{inh} = 2.17$ dL/g) without any reduction of the crystallinity or any change of X-ray diffraction pattern (Figure 1c). The ^1H NMR spectrum of the polymer was almost identical with that of the polymer obtained by the first polymerization, implying a reversible process between topochemically controlled cyclobutane formation and cleavage.

Absolute Asymmetric Photodimerization in Crystal of 1b.[9] Compound **1b** was also highly photoreactive in the crystalline state and was converted by [2+2] cycloaddition into dimer **2b** (Scheme I). Upon photoirradiation with $\lambda \geq 365$ nm at −40 °C, **2b** was obtained in about 70% yield, whereas with $\lambda \geq 320$ nm at room temperature the topochemical process seriously deteriorated, resulting in indefinable oligomers. The cyclobutane structure of **2b**, which was confirmed by ^1H NMR and MS spectroscopy, coincided with the structure predicted from the crystal structure of **1b** on the basis of topochemical considerations.

It was proved by a CD measurement that dimer **2b**, obtained by photoirradiation of a single crystal of **1b**, was optically active. The asymmetric induction was reasonably interpreted from the crystal structure of **1b**, as is discussed later. Although the crystals of **1b** gradually became amorphous as the photoreaction proceeded, the enantiomeric excess for **2b** was always more than 90%. The enantiomeric excess of **2b** was quantitative during the initial stage of the photoreaction (up to about 12% of conversion), but gradually decreased to some extent with the reaction time. Such a reduction in the enantiomeric excess is considered to be due to a certain distortion of the crystal lattice caused by an accumulated strain during the photoreaction.

Furthermore, we succeeded in obtaining a large quantity of crystals of **1b**, which have the same chirality as crystals of **1b** that were used as seed during recrystallization from ethanol. Such growth of a chiral crystal may be described as "amplification of asymmetry" by seeding. Both results concerning seeding and photoreaction of **1b** are summarized in Table I. By seeding with

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(8) Hasegawa, M.; Nakanishi, H.; Yurugi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2113.

(9) Hasegawa, M.; Chung, C.-M.; Muro, N.; Maekawa, Y. *J. Am. Chem. Soc.* **1990**, *112*, 5676.

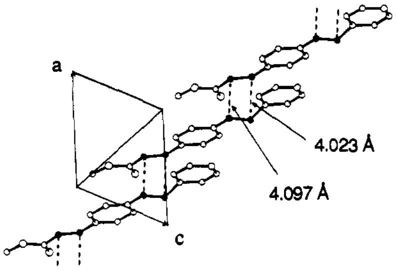

Figure 2. Crystal structure of **1a**, viewed along the *b* axis.

3–7 mg of crystals, about 200–400 mg of crystals were obtained. In all runs carried out in this experiment, dimer **2b**, obtained by photoreaction of both the seed crystals and of the crystals produced by the seeding, had the same sign of optical rotation.

Experiments were also carried out without the addition of chiral seed crystals during the recrystallization of **1b** from ethanol. Of great interest, the crystals of **1b** obtained by ordinary recrystallization afforded (−)-**2b** 15 out of 17 times in high enantiomeric excess (85–100%) upon photoirradiation for 1 h. Therefore, from the present result, it can be concluded that the seeding of chiral crystals is not necessary for the amplification of asymmetry, but only for obtaining chiral crystals of the intended optical rotation. Such a significant one sided generation of chirality may be induced by a trace amount of one of the enantiomers or some other chiral nucleating agent in our laboratory.

A differential scanning thermogram of **1b** showed two endothermic peaks at 112 and at 120 °C. The crystal (designated as form α), which gave the optically active dimer **2b** by irradiation, when annealed at 112 °C for 5 min and then slowly cooled to 40 °C, melted at 120 °C and showed only one DSC peak. This result implies that a metastable crystal (form α) is transformed by a melting process into a stable one (form β), which was not obtained by recrystallization from solvent. Crystals of form β were photostable. These two dimorphs showed remarkably different infrared spectra and powder diffraction patterns.

Two Types of Dimer Formation from Crystal of 1c. Crystal **1c** was less reactive than both **1a** and **1b**, but by photoirradiation gave two types of dimers: a hetero-type (**2c**) and a homo-type dimer (**2c′**) (Scheme I). At room temperature, the ratio of the two dimers produced (**2c**:**2c′**) was approximately 3:1. Although the final product was amorphous, the structures of dimers **2c** and **2c′** can be reasonably explained in terms of the crystal structure of **1c**.

Crystallographic Interpretation of Photochemical Behaviors. The molecular structures and atomic numbering systems of **1a**, **1b**, and **1c** are shown in the supplementary material. The benzene and pyridine rings and ethylene groups of the molecules of the monomers are planar within experimental errors. In the pyridyl side of **1a**, the ethylenic plane rotates 5.3° about C(4)–C(13) from the benzene ring, and the pyridine ring rotates 8.2° about C(14)–C(15) from the ethylenic plane in the same direction; the molecule of **1a** is very similar in structure and planarity to other common diolefinic compounds (for example, methyl 4-[2-(2-pyrazyl)ethenyl]cinnamate[10]). In contrast to molecule **1a**, the molecular structures of **1b** and **1c** are in a "cisoid form". Furthermore, **1b** has a tortuous molecular structure; in the pyridyl side, the rotations of the ethylenic plane about C(4)–C(14) from the benzene ring and of the pyridine ring about C(15)–C(16) from the ethylenic plane are 21.3° and 14.4°, respectively, in the opposite direction; these values are similar to those of the second molecule in the asymmetric unit of **1b**. In the case of a molecule of **1c**, the benzene and pyridyl rings rotate 5–15° from the ethylenic plane in the pyridyl side.[11]

The molecules of **1a**, related to each other by a [101] translation, make a molecular stack (see Figure 2); the molecules are displaced along the molecular long axis by about half a molecule, which is defined as α-translation-type packing. Although no particularly short intermolecular contact was found, it is obvious that the pyridine ring and the carbonyl oxygen atom of one molecule approach the benzene rings of two neighboring molecules, respectively.

The intermolecular distances between the ethylenic double bonds of the stacked molecules are 4.023 and 4.097 Å, which are within the limits that allow topochemical [2+2] cycloaddition. It is conclusive that the polymer chain grows linearly along the [101] direction. Although a linear polymer formed from one polymerization stack is chiral, a polymer of the opposite chirality should be formed from another stack that is related to the former stack by a glide plane, thus resulting in a racemic polymer.

In the crystal structure of **1b**,[12] there are two crystallographically independent molecules, which make a molecular pair and are arranged according to β-type packing; no stack for the formation of polymer exists (Figure 3). The intermolecular distances of the two facing double bonds in each molecular pair are approximately within the normal photoreactive distances (3.802 and 4.387 Å for one pair of facing double bonds, and 3.829 and 4.123 Å for the other). Thus, the generation of a β-hetero-type dimer (**2b**) as the main product of photoreaction between two molecules unrelated by symmetry is fairly consistent with the crystal structure of **1b**.

It should be noted that a cyclobutane having the same configuration is generated by the addition of either of the two pairs of facing double bonds, because of the cisoid form of molecule **1b**. Furthermore, the molecular pairs are related by a 2_1 screw axis to each other, thus, an enantiomer (**2b**) should be generated in large excess by the topochemical photoreaction of one single crystal. As is summarized in Scheme II, the prochiral molecules **1b** crystallized into the chiral crystal, and afforded an optically active dimer (**2b**) upon photoirradiation. The chirality of **2b** is due only to the chiral environment of the crystal, and not to any influence of other chiral source. Thus, the dimerization of **1b** can be defined as being an absolute asymmetric reaction.

In a solid-state intermolecular photoreaction system, Addadi et al. succeeded in execution of an asymmetric synthesis using a molecular arrangement of the α-translation-type.[1] The present result extends asymmetric synthesis to a β-packing crystal with the production of a quantitative enantiomeric excess, accompanied by an amplification of asymmetry.

Crystals of **1c** have 16 molecules in the unit cell, and there are two independent molecules in the asymmetric unit. Of great interest is the fact that the two independent molecules form two different types of molecular stacks, as shown in Figure 4; in stack A, the molecules are superimposed along the *c* axis to form β-type packing; in stack B, the molecules are displaced by about half a molecule in the direction of the molecular long axis, resulting in α-type packing along the *c* axis. The molecules in each stack are related to the nearest-neighbor molecules by the glide plane. The intramolecular distances between two facing double bonds in stack A are 3.752 and 4.043 Å for one olefinic pair, and 3.839 and 4.151 Å for the other; both olefinic pairs are favorable for [2+2] cycloaddition according to the proposed distance criteria.[6] On the basis of the molecular arrangement in stack A, the formation of the β-hetero-type dimer **2c** upon photoirradiation is quite reasonable. The intermolecular 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 rotated by 106° (or 74°) with respect to each other (Figure 4).[13] Although the number of molecules in both stacks is the same, the low ratio of **2c′** in the resulting dimers is due to the unfavorable geometry for [2+2] reaction. The formation of dimer **2c′**, in spite of the large angle between the two

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(10) Hasegawa, M.; Aoyama, M.; Maekawa, Y.; Ohashi, Y. *Macromolecules* **1989**, *22*, 1568.

(11) In all the monomers, the rotations of the benzene rings and carbonyl groups from the ester side ethylenic plane are relatively small (within 7.5°).

(12) Of the two crystal systems of **1b**, crystallographic study of the crystal of form α was carried out.

(13) The twisted angle between the double bonds was calculated by a downward projection of one double bond perpendicularly to the plane containing the other double bond and atoms connected to this double bond.

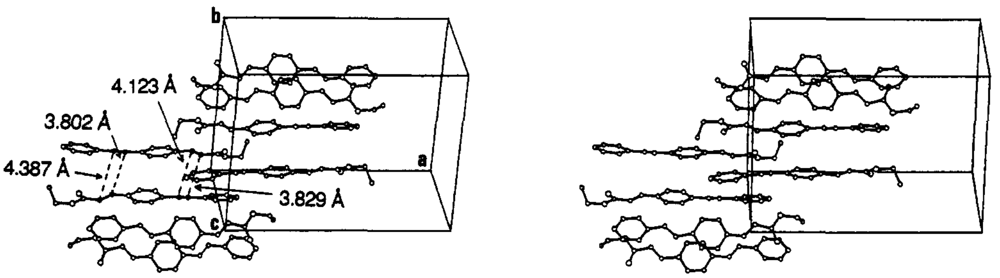


Figure 3. Stereoview of the unit cell packing arrangement in **1b**.

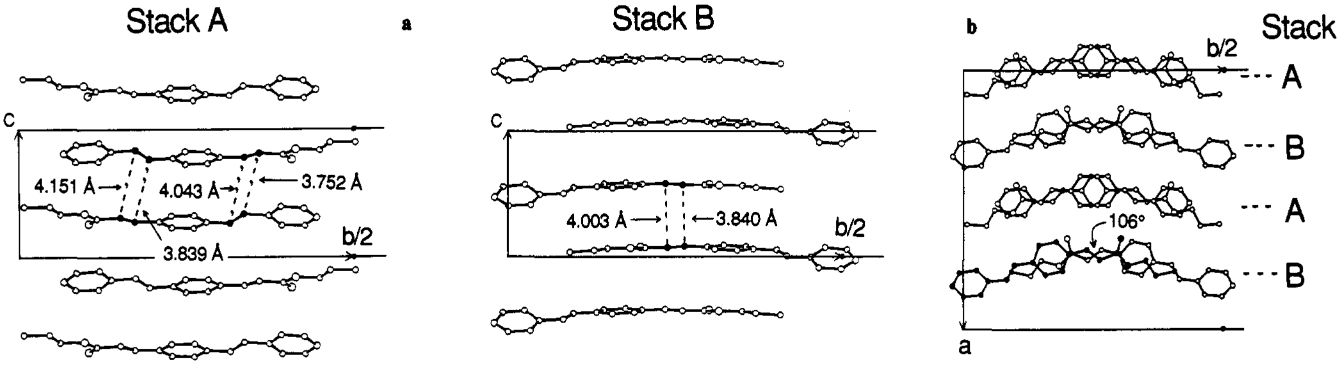
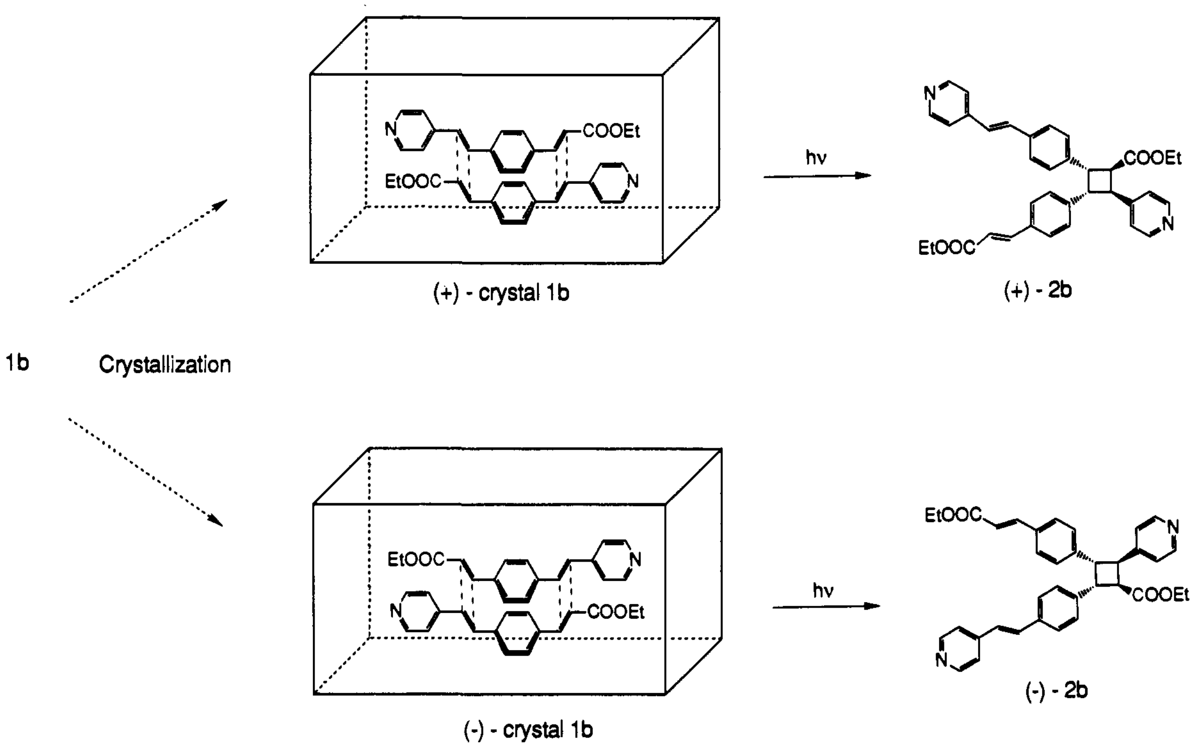


Figure 4. Crystal structure of **1c**, viewed (a) along the *a* axis and (b) along the *c* axis.

Scheme II



(The signs of optical rotations are arbitrary.)

double bonds, is anomalous. A few articles have reported that, in olefin crystals, the reactive double bonds are arranged skew to each other and yet react upon photoirradiation, as exemplified by 7-methoxycoumarin (skewed angle, 65°).[14] In the case of the formation of **2c′**, the monomer molecule might rotate during photoirradiation such that a smaller angle is achieved. It is nevertheless surprising that such as "large" molecule as **1c**, which should be less movable than a smaller one in the solid state, reacts in spite of the large skewed angle of the double bonds in stack B.

Conclusions

A slight change in the chemical structure of diolefin compounds caused a drastic variation in the packing arrangement of the molecules and in the topochemical photoreaction mode. Compound **1a** upon crystallization formed an α-type packing crystal, affording a linear high polymer upon photoirradiation. Crystalline poly-**1a** could undergo a depolymerization reversibly. This result is the first demonstration of the topochemical reversibility of

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[14] Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1985**, *50*, 2337.

[15] Ichimura, K.; Watanabe, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1420.

photoreaction between polymerization and depolymerization. **1b** formed a novel chiral crystal of β-type packing; an optically active dimer (**2b**) was obtained in high yield (>90%) upon photoirradiation. In this reaction, the sole asymmetric influence was due to the asymmetric environment of the crystal. This result is very significant from the view point of designing a β-packing chiral crystal for the accomplishment of asymmetric synthesis. In addition, a one-sided generation of chirality was confirmed without any intentional seeding of the chiral crystals. Crystal **1c** consists of α- and β-type molecular packing arrangements, and on photoirradiation gave two dimers (**2c** and **2c′**, respectively). In the α-packing stack, although two reactive olefins are oriented seriously skew with respect to each other, photodimerization occurs.

Experimental Section

Measurements. ^{1}H NMR spectra were obtained on a JEOL JMR GX 400 spectrometer with tetramethylsilane as an internal standard with the resolution of 0.5 Hz. Infrared spectra were recorded by a JASCO IR-810 spectrophotometer. Differential scanning calorimeter (DSC) curves were recorded on a Shimadzu DSC-50 calorimeter under a nitrogen stream for about 5 mg of the sample. The X-ray powder diffraction was measured on Rigaku Rotaflex RU-200 X-ray diffractometer ($\lambda = 1.541\,84$ Å). The melting points were recorded using a Laboratory Devices MEL-TEMP and were uncorrected. The inherent viscosities were measured at 30 °C at a concentration of 0.3 g/dL in *m*-cresol.

Synthsis of Monomers. 4-[2-(4-Pyridyl)ethenyl]benzaldehyde (**3**) was prepared by a reaction between terephthalaldehyde and γ-picoline according to a previously reported method.[15] To a solution of **3** (0.03 mol) in pyridine (50 mL) were added malonic acid (0.06 mol) and piperidine (2 mL); the solution was refluxed for 3 h. After cooling to room temperature, the resulting solution was poured into water. The precipitate, mainly 4-[2-(4-pyridyl)ethenyl]cinnamic acid (**4**), was collected by filtration and washed by water. Drying under reduced pressure gave a 93% yield of **4**.

To a suspension of **4** (0.04 mol) in methanol (1 L) and ethylene dichloride (1 L) was added concentrated sulfuric acid (10 mL); the mixture was refluxed for 8 h to give a homogeneous solution. After cooling to room temperature, the solution was neutralized with a 1 M aqueous sodium hydroxide solution. Evaporation of methanol (ca. 500 mL) was followed by washing with 3 L of water. Successive evaporation of ethylene dichloride and purification by column chromatography (silica gel, methylene dichloride) gave a 61% yield of **1a**. Crystals **1a** were obtained by recrystallization from methanol.

1b and **1c** were synthesized and recrystallized in a similar manner by using the corresponding alcohols. The chemical yields of **1b** and **1c** were 55 and 71%, respectively.

1a: mp 147–149 °C; IR(KBr) 1720, 1630, 1310, 1170, 980, 830 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.59 (m, 2 H), 7.70 (d, 1 H, $J = 16$ Hz), 7.60–7.36 (m, 7 H), 7.29 (d, 1 H, $J = 16$ Hz), 7.07 (d, 1 H, $J = 16$ Hz), 3.82 (s, 3 H).

1b. 1b is dimorphic. Form α: mp 107–115 °C (ethanol); IR(KBr) 1700, 1600, 1310, 1180, 970, 825 cm^{-1}. Form β: mp 118–121 °C (melt); IR(KBr) 1710, 1600, 1310, 1180, 980, 830 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.60 (m, 2 H), 7.69 (d, 1 H, $J = 16$ Hz), 7.60–7.36 (m, 7 H), 7.29 (d, 1 H, $J = 16$ Hz), 7.07 (d, 1 H, $J = 16$ Hz), 4.28 (q, 2 H, $J = 7$ Hz), 1.35 (t, 3 H, $J = 7$ Hz).

1c: mp 98–99 °C; IR(KBr) 1700, 1600, 1180, 980, 825 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.60 (m, 2 H), 7.69 (d, 1 H, $J = 16$ Hz), 7.60–7.36 (m, 7 H), 7.29 (d, 1 H, $J = 16$ Hz), 7.07 (d, 1 H, $J = 16$ Hz), 4.18 (t, 2 H, $J = 7$ Hz), 1.74 (m, 1 H), 1.01 (t, 3 H, $J = 7$ Hz).

Poly-1a: IR(KBr) 1730, 1170, 820 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.28 (d, 2 H, $J = 5$ Hz), 7.14–7.00 (m, 4 H), 6.80 (d, 2 H, $J = 5$ Hz), 4.60–3.70 (m, 4 H), 3.16 (m, 3 H).

Dimer 2. 2b was obtained by the irradiation of crystals **1b** with $\lambda \geq 365$ nm, and by successive purification by preparative TLC (silica gel, ethyl acetate). **2b** could be purified to 100% ee by recrystallization from ethanol. **2c** and **2c′** were obtained from crystals **1c** in a similar manner as described above.

2b: mp 108–110 °C; IR(KBr) 1710, 1180, 820 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.56–8.54 (m, 4 H), 7.53 (d, 1 H, $J = 16$ Hz), 7.35 (d, 2 H, $J = 8$ Hz), 7.32 (m, 2 H), 7.28 (d, 2 H, $J = 8$ Hz), 7.24 (m, 2 H), 7.18 (d, 1 H, $J = 16$ Hz), 7.10 (d, 2 H, $J = 8$ Hz), 6.96 (d, 2 H, $J = 8$ Hz), 6.92 (d, 1 H, $J = 16$ Hz), 6.30 (d, 1 H, $J = 16$ Hz), 4.73 (t, 1 H, $J = 10$ Hz), 4.46 (t, 1 H, $J = 10$ Hz), 4.40 (dd, 1 H, $J_1 = 10$ Hz, $J_2 = 4$ Hz), 4.21 (q, 2 H, $J = 7$ Hz), 3.98–3.84 (m, 3 H), 1.29 (t, 3 H, $J = 7$ Hz), 0.95 (t, 3 H, $J = 7$ Hz); MS *m/e* 513 (M − C_2H_5O), 381 (asymmetric cleavage of cyclobutane ring), 279 (M/2), 250 (M/2 − C_2H_5), 234 (M/2 − C_2H_5O), 206 (M/2 − $COOC_2H_5$), 177 (asymmetric cleavage of cyclobutane ring).

Table II. Crystal Data and Parameters Used in Structure Determination

compounds	**1a**	**1b**	**1c**
space group	$P2_1/a$	$P2_12_12_1$	*Pbca*
crystal system	monoclinic (β, 114.62 (1)°)	orthorhombic	orthorhombic
a, Å	7.107 (1)	19.442 (5)	20.4067
b, Å	35.869 (4)	15.112 (4)	40.8276
c, Å	5.948 (1)	10.192 (3)	7.6801
V, Å^3	1378.4	2994.6	6398.7
Z	4	8	16
crystal size, mm^3	0.8 × 0.7 × 0.1	0.6 × 0.4 × 0.2	
d(calcd), g/cm^3	1.28	1.24	1.22
μ(Cu Kα), mm^{-1}	0.64	0.61	0.59
obsd reflcns		2925	6171
unique reflcns	1213	1981	3385
R	0.069	0.068	0.078
R_w	0.067	0.076	0.098
ref	5	7	present study

2c: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.56–8.54 (m, 4 H), 7.53 (d, 1 H, $J = 16$ Hz), 7.35 (d, 2 H, $J = 8$ Hz), 7.32 (m, 2 H), 7.28 (d, 2 H, $J = 8$ Hz), 7.24 (m, 2 H), 7.19 (d, 1 H, $J = 16$ Hz), 7.10 (d, 2 H, $J = 8$ Hz), 6.96 (d, 2 H, $J = 8$ Hz), 6.92 (d, 1 H, $J = 16$ Hz), 6.31 (d, 1 H, $J = 16$ Hz), 4.72 (t, 1 H, $J = 10$ Hz), 4.49 (t, 1 H, $J = 10$ Hz), 4.41 (dd, 1 H, $J_1 = 10$ Hz, $J_2 = 4$ Hz), 4.11 (t, 2 H, $J = 7$ Hz), 3.92 (dd, 1 H, $J_1 = 10$ Hz, $J_2 = 4$ Hz), 3.80 (m, 2 H), 1.68 (m, 2 H), 1.36 (m, 2 H), 0.95 (t, 3 H, $J = 7$ Hz), 0.76 (t, 3 H, $J = 7$ Hz); MS *m/e* 527 (M − C_3H_7O), 395 (asymmetric cleavage of the cyclobutane ring), 293 (M/2), 206 (M/2 − $COOC_3H_7$).

2c′. Judging from the crystal structure of **1c**, two types of dimer are expected to be formed from stack B: One is the δ-type, and the other is the ϵ-type. However, the formation of the ϵ-type dimer is advantageous for a smaller twisted angle (74°) between the double bonds of **1c** molecules, as discussed in the text. This is actually supported by mass spectrometry for **2c′**; the *m/e* 386 and 200 (asymmetric cleavage of the cyclobutane ring) peaks, which are expected in the case of δ-type dimer, were not detected: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.58 (m, 4 H), 7.51 (d, 4 H, $J = 8$ Hz), 7.37 (m, 4 H), 7.35 (d, 4 H, $J = 8$ Hz), 7.29 (d, 2 H, $J = 16$ Hz), 7.01 (d, 2 H, $J = 16$ Hz), 4.49 (dd, 2 H, $J_1 = 10$ Hz, $J_2 = 7$ Hz), 4.00 (dd, 2 H, $J_1 = 10$ Hz, $J_2 = 7$ Hz), 3.71 (m, 4 H), 1.31 (m, 4 H), 0.70 (t, 6 H, $J = 7$ Hz); MS *m/e* 293 (M/2), 234 (M/2 − C_3H_7O), 206 (M/2 − $COOC_3H_7$).

Photoirradiation. The photoirradiation methods used were fundamentally as follows: Finely powdered monomer crystals were dispersed in distilled water containing a few drops of surfactant (NIKKOL TL-10FF) and irradiated, with vigorous stirring, by either a 500-W super-high-pressure mercury lamp set outside of the flask or a 100-W high-pressure mercury lamp set inside of the flask. In the case of irradiation below 0 °C, 30% aqueous CaCl$_2$ was used as a dispersant.[16]

Crystallographic Analysis. The intensity data were measured over the range $2\theta < 128°$, by ω–2θ scanning on a Rigaku four-circle diffractometer with graphite monochromated Cu Kα radiation. Crystallographic data for **1a**, **1b**, and **1c** are summarized in Table II. The observed reflections ($|F_0| > 3\sigma(|F_0|)$) were used in both the solutions and refinements; no absorption correction was made. The structures were solved by direct methods with MULTAN 78 or SHELXS 86, and refined by full-matrix least-squares methods with SHELXS 76. The final molecular coordinates, thermal parameters, bond lengths, and bond angles are given in the supplementary material.

Seeding Procedure and Determination of Enantiomeric Excess. Light yellow prisms were obtained from an ethanolic solution of **1b** by slow evaporation. A single crystal of **1b** (10–17 mg) was cut into two pieces; one piece was then finely powdered and photoirradiated by a 500-W super-high-pressure mercury lamp for 5 h with a cut-off filter (≥365 nm) at room temperature. After photoirradiation, the resulting **2b** was purified by TLC and the sign of optical rotation confirmed. The single crystal that gave (+)-**2b** or (−)-**2b** was called (+)-**1b** or (−)-**1b**, respectively. Crystals of (+)-**1b** or (−)-**1b** (ca. 200–400 mg) were obtained from an ethanolic solution of **1b**, respectively, by seeding with finely powdered crystals of another piece of (+)-**1b** or (−)-**1b** (3–6 mg). Finely powdered crystals of **1b**, obtained by seeding, were photoirradiated by a mercury

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(16) Dispersant has been used so that the surface of the crystals might be uniformly exposed to irradiating light. Photoirradiation without dispersant was also carried out in order to check whether the usage of dispersant is permissible; no appreciable change in photoproduct was detected in comparison with the result of irradiation with dispersant.

lamp located outside of the flask through the same filter at −40 °C. The enantiomeric excess of the resulting **2b**, after purification by TLC, was determined by HPLC on an optically active solid phase, the Chiralcel OC of Daicel Chemical Industries, Ltd., Himeji, Japan.

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Registry No. 1a, 100515-60-4; **1a** (homopolymer), 100515-61-5; **1b**, 135074-89-4; **1c**, 135074-90-7; (+)-**2b**, 135212-22-5; **2c**, 135074-87-2; **2c′**, 135074-88-3; **3**, 74401-03-9; **4**, 101273-76-1; malonic acid, 141-82-2; (−)-**2b**, 135212-23-6.

Supplementary Material Available: Molecular structures and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **1a**, **1b**, and **1c** (11 pages). Ordering information is given on any current masthead page.

Topochemical Induction to an Alternating Zigzag–Linear and "Syndiotactic" Chain Structure in the Course of a [2+2] Photoreaction of Alkyl α-Cyano-4-[2-(2-pyridyl)ethenyl]cinnamate Crystals

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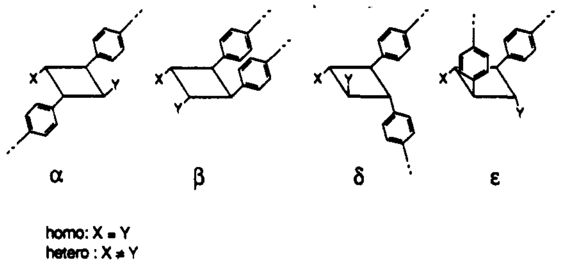
Abstract: Methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1a** and **1b**) crystals are highly photoreactive and are converted by a [2+2] photocycloaddition reaction into dimers (**2a** and **2b**) in high yields or upon further photoirradiation into a tricyclic dimer (**3a**) or oligomers. The photochemical conversion of **1** into **2** was reasonably intepreted by a crystallographic analysis of **1**, based on topochemical considerations. The formation of **3a** by an intramolecular cycloaddition of monocyclic dimer **2a** at an extremely low temperature was attributed to an insufficient thermal energy for **2a** to be rearranged into its stable form. On the other hand, the [2+2] photodimerization of **1b** did not occur at random at the reactive site in the crystal, but was topochemically controlled, resulting in an alternating arrangement of both enantiomers in the solid state. Upon irradiation, crystal **2a** afforded a polymer via an intermediate tetramer (**4a**), whereas from crystal **2b** a tetramer (**4b**) and an octamer were obtained. The tetramers (**4a** and **4b**) were isolated and shown to contain three cyclobutane rings of β-hetero, α-homo, and β-hetero-type structures in this order. The two β-type cyclobutanes in a molecule of these tetramers are opposite in configuration to each other. The structures of **4**, predictable from the crystal structures of **2**, were not predictable from the crystal structures of the corresponding monomers. The high molecular weight polymer ($\overline{Mn}$ = 12 000), obtained from crystal **2a**, has an unusual repeating octamer unit, in which three types of cyclobutane structures are incorporated in a sequence of $[\alpha\beta\epsilon\beta\alpha\beta^{-1}\epsilon^{-1}]$ ("double syndiotactic") where β and β^{-1} are opposite in configuration to each other. In contrast, the octamer derived from crystal **2b** has a repeating unit in which two types of cyclobutane structures are arranged in a sequence of $[\alpha\beta\alpha\beta^{-1}]$ ("syndiotactic").

Introduction

Topochemical photoreactions of organic crystals exhibit a high regio- and stereoselectivity because they proceed under strict control of the crystal lattice. Owing to its high selectivity, the reaction has become of interest in recent years as one means of organic synthesis. The [2+2] cycloaddition reaction has been one of the most extensively studied in the field of organic solid-state photochemistry.[1] The concept of topochemistry was established by Schmidt and co-workers, based on their crystallographic and photochemical studies on the [2+2] dimerization of several olefin derivatives.[2]

By systematic studies of the correlation between the structure and photoproduct of crystals of 1,4-divinylarene derivatives, it has been demonstrated that linear polymers are obtained from α-type packing crystals, whereas dimers, or occasionally cyclophanes, are obtained from β-type packing crystals.[3,4] Furthermore, hetero- and homo-type cyclobutane structures must be taken into consideration when the photoreaction of unsymmetrically substituted diolefin crystals is studied.[4,5] The cyclobutane structures, which have been derived by topochemical [2+2] photoreaction, are mostly α- and β-types, and exceptionally δ- and ϵ-types. These four types of cyclobutane structures are shown below.[6]



The first photochemical [2+2] asymmetric synthesis was accomplished by Lahav et al. through a process of crystallization of achiral unsymmetric, 1,4-divinylarene derivatives into chiral

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[1] For reviews, see: (a) Hasegawa, M. *Chem. Rev.* **1983**, *83*, 507. (b) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

[2] Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647. He suggested a geometrical criteria for [2+2] cycloaddition in an organic crystal; the reacdting double bonds must be within about 4.2 Å, and they must be aligned parallel.

[3] The molecular arrangement in unsymmetric diolefin crystals is roughly classified into α- or β-type packing; in α-type packing, crystal molecules are superimposed with displacement in the direction of long molecular axis by about half a molecule, whereas in β-type packing crystal, molecules are superimposed without the displacement.

[4] Hasegawa, M. In *Photopolymerization and Photoimaging Science and Technology*; Allen, N. S., Ed.; Elsevier Science: London and New York, 1989; pp 187–207.

[5] (a) Hasegawa, M. *Pure Appl. Chem.* **1986**, *58*, 1179. (b) Hasegawa, M.; Saigo, K.; Kato, S.; Harashina, H. *ACS Symp. Ser.* **1987**, *337*, 44.

[6] The classification of configuration of cyclobutane rings is based on that of truxinates and truxillic acids.

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