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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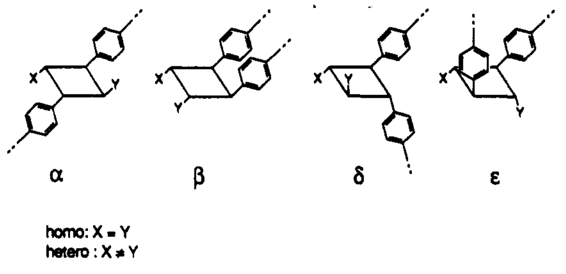
Abstract: Methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1a** and **1b**) crystals are highly photoreactive and are converted by a [2+2] photocycloaddition reaction into dimers (**2a** and **2b**) in high yields or upon further photoirradiation into a tricyclic dimer (**3a**) or oligomers. 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 ($\overline{\mathrm{Mn}}$ = 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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crystals, followed by a topochemical reaction.[7] We also reported a similar asymmetric synthesis through the [2+2] photoreaction of a chiral crystal in a previous communication.[8] However, the crystallization process (or crystal structure) of organic compounds is very sensitive to small changes in the recrystallization conditions, or of the chemical structure of the compounds, and remains largely unpredictable.

The photoreactions of organic crystals are considered to be deeply correlated with molecular dynamics as well as to the starting crystal structure. Some photoreactions proceed with very little molecular motion, as exemplified by the reactions of 2-benzyl-5-benzylidenecyclopentanone (BBCP)[9] or 2,5-distyrylpyrazine (DSP),[10] whereas there are some cases in which the reaction modes are not predictable from the crystal structures of the starting substances, as exemplified by the photodimerization of crystals of 7-methoxycoumarin.[11] In addition, even though ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates have quite an analogous molecular packing in their crystals, the former crystal gives a linear polymer through a typical even-numbered polymerization mechanism,[5a,12] whereas the latter gives a photostable dimer crystal quantitatively[13] owing to a different molecular motion in the two reaction processes.

The molecular motion during the course of a topochemical reaction has been shown to be greatly influenced by the photoirradiation temperature.[14] In the photopolymerization of diolefin crystals, a higher reduced viscosity is observed for a product polymerized at the lower temperature.[1a] In contrast, it was reported that BBCP did not react at liquid nitrogen temperature upon irradiation with ≥340 nm, even though a dimer was obtained at room temperature.[15] Recently, we have also found some diolefinic crystals, such as methyl and ethyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamates, which are photostable at low temperature (~−40 °C), even though they show high photoreactivity at room temperature.[16] Lack of photoreactivity at low temperature suggests that the topochemical photoreaction requires an appropriate thermal motion of the reacting molecules.[17]

In the present work, the photoreactions of methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1a** and **1b**) and their dimer (**2a** and **2b**) crystals were investigated, focusing on product control by changing the irradiation temperature and on a topochemical induction, resulting in the formation of unusual chain structures. Parts of the results were reported in previous communications.[18]

Experimental Section

Measurements. ^{1}H NMR spectra were obtained on a JEOL JMR GX 400 spectrometer with tetramethylsilane used as an internal standard with a resolution of 0.5 Hz. The IR spectra were recorded with a JASCO IR-810 spectrophotometer. Differential scanning calorimetry (DSC) curves were recorded on a Shimadzu DSC-50 calorimeter under a nitrogen stream at a heating rate of 5 °C/min for about 5 mg of the sample. Gel permeation chromatography (GPC) was performed at 40 °C by using Shodex GPC (AD 800/P + AD 805/S + AD 803/S + AD 802/S) columns (DMF solution). X-ray powder diffraction (XRD) was measured on a RIGAKU Rotaflex RU-200 X-ray diffractometer. The melting points were recorded with a Laboratory Devices MEL-TEMP, and are uncorrected. The inherent viscosities were measured at 30 °C at a concentration of 0.30 g/dL in *m*-cresol.

Photoirradiation. Finely powdered monomer crystals were dispersed in distilled water containing a few drops of surfactant (NIKKOL TL-10FF), and were irradiated, with vigorous stirring, by either a 500-W super-high-pressure mercury lamp (Ushio USH-500D) or an Ar ion laser photolysis apparatus (LEONIX 95-4 HEAD) set outside of the flask through a Pyrex glass under a nitrogen atmosphere. For photoirradiation below 0 °C, 30% aqueous $CaCl_2$ was used in the place of water. After irradiation, the products were collected by reduced filtration and washed with a large amount of water. They were then dried at room temperature overnight in vacuo.

Monomers. Monomers **1** were synthesized from 2-[2-(4-formylphenyl)ethenyl]pyridine (**5**) by a reaction with alkyl cyanoacetate. Precursor **5** was prepared by a reaction of terephthalaldehyde with 2-picoline according to a previously reported method.[19]

To a solution of **5** (16.5 g) and methyl cyanoacetate (11.7 g, 1.5 equiv to **5**) in methanol (1650 mL) was added a few drops of piperidine. This mixture was stirred at 64 °C for 1 h. After cooling, the precipitate was collected by reduced filtration and dried to give crude methyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1a**). Recrystallization from methanol gave pure crystals of **1a** (74% yield).

The ethyl ester **1b** was prepared in a similar manner by using ethyl cyanoacetate and ethanol as a reactant and a solvent, respectively (82% yield).

1a: mp 179–181 °C (methanol); IR (KBr) 2220 (m), 1720 (s), 1590 (s), 1270 (s), 970 (s), 820 (s), 530 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.64 (m, 1 H), 8.24 (s, 1 H), 8.02 (d, 2 H, *J* = 9 Hz), 7.72 (m, 1 H), 7.70 (d, 1 H, *J* = 9 Hz), 7.69 (d, 1 H, *J* = 16 Hz), 7.67 (d, 1 H, *J* = 8 Hz), 7.43 (d, 1 H, *J* = 8 Hz), 7.30 (d, 1 H, *J* = 16 Hz), 7.24–7.19 (m, 1 H), 3.94 (s, 3 H); UV λ_{max} (ϵ in CH_2Cl_2) 370 nm (43 000). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.34; H, 4.57; N, 9.64.

1b: mp 134–135 °C (ethanol); IR (KBr) 2220 (m), 1715 (s), 1585 (s), 1260 (s), 1180 (s), 975 (m), 820 (s), 530 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.65 (m, 1 H), 8.25 (s, 1 H), 8.02 (d, 2 H, *J* = 9 Hz), 7.72 (m, 1 H), 7.70 (d, 1 H, *J* = 9 Hz), 7.69 (d, 1 H, *J* = 16 Hz), 7.67 (d, 1 H, *J* = 8 Hz), 7.42 (d, 1 H, *J* = 8 Hz), 7.30 (d, 1 H, *J* = 16 Hz), 7.24–7.19 (m, 1 H), 4.40 (q, 2 H, *J* = 7 Hz), 1.41 (t, 3 H, *J* = 7 Hz); UV λ_{max} (ϵ in CH_2Cl_2) 370 nm (33 000). Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.91; H, 5.08; N, 9.28.

Dimers. Dimers **2** were prepared by the irradiation of **2** with λ ≥ 410 nm, followed by successive purification by preparative TLC (silica gel, ethyl acetate/hexane = 80/20 v/v).

2a: mp 196–198 °C (methanol/1,2-dichloroethane = 85/15 v/v); IR (KBr) 2225 (m), 1730 (s), 1600 (s), 1270 (s), 970 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.64 (m, 1 H), 8.58 (m, 1 H), 8.12 (s, 1 H), 7.82–7.72 (m, 3 H), 7.64 (t, 1 H, *J* = 8 Hz), 7.53 (d, 1 H, *J* = 16 Hz), 7.47–7.38 (m, 3 H), 7.35 (d, 1 H, *J* = 8 Hz), 7.32–7.25 (m, 1 H), 7.20 (d, 2 H, *J* = 8 Hz), 7.16–7.10 (m, 2 H), 7.07 (d, 2 H, *J* = 8 Hz), 5.23 (dd, 1 H, J_1 = 11 Hz, J_2 = 10 Hz), 4.98 (d, 1 H, *J* = 11 Hz), 4.76 (d, 1 H, *J* = 10 Hz), 3.88 (s, 3 H), 3.54 (s, 3 H); UV λ_{max} (ϵ in CH_2Cl_2) 314 nm (46 000); MS *m/e* 580 (M^+), 392 (asymmetric cleavage of the cyclobutane ring), 290 ($M^+/2$, symmetric cleavage), 188 (asymmetric cleavage).

2b: mp 211–213 °C (ethanol); IR (KBr) 2220 (m), 1740 (s), 1720 (s), 1600 (s), 1260 (s), 1210 (s), 1190 (s), 960 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.64 (m, 1 H), 8.58 (m, 1 H), 8.10 (s, 1 H), 7.79 (d, 2 H, *J* = 9 Hz), 7.76–7.62 (m, 2 H), 7.52 (d, 1 H, *J* = 16 Hz), 7.44 (d, 2 H, *J* = 8 Hz), 7.44 (d, 1 H, *J* = 8 Hz), 7.35 (d, 1 H, *J* = 8 Hz), 7.31–7.27 (m, 1 H), 7.20 (d, 2 H, *J* = 9 Hz), 7.15–7.12 (m, 1 H), 7.10 (d, 1 H, *J* = 16 Hz), 7.05 (d, 2 H, *J* = 8 Hz), 5.26 (dd, 1 H, J_1 = 11 Hz, J_2 = 10 Hz), 4.98 (d, 1 H, *J* = 11 Hz), 4.76 (d, 1 H, *J* = 10 Hz), 4.34 (q, 2 H, *J* = 7 Hz), 4.09–3.92 (m, 2 H), 1.35 (t, 3 H, *J* = 7 Hz), 0.96 (t, 3 H, *J* = 7 Hz); UV λ_{max} (ϵ in CH_2Cl_2) 317 nm (35 000); MS *m/e* 608 (M^+), 406 (asymmetric cleavage of the cyclobutane ring), 304 ($M^+/2$, symmetric cleavage), 202 (asymmetric cleavage).

[2.2]Paracyclophane. [2.2]Paracyclophane **3a** was obtained by the photoirradiation of **1a** crystals with λ ≥ 300 nm at −40 °C, followed by successive washing with ethyl acetate. The structure of **3a** was confirmed

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[8] Hasegawa, M.; Chung, C.-M.; Muro, N.; Maekawa, Y. *J. Am. Chem. Soc.* **1990**, *112*, 5676.

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

[12] The photoproducts consisted of molecular species only of even-numbered degree of polymerization during the whole course of the photoreaction.

[13] (a) Hasegawa, M.; Kato, S.; Saigo, K.; Wilson, S. R.; Stern, C. L.; Paul, I. C. *J. Photochem. Photobiol., A: Chem.* **1988**, *41*, 385. (b) Maekawa, Y.; Kato, S.; Saigo, K.; Hasegawa, M.; Ohashi, Y. *Macromolecules* **1991**, *24*, 2314.

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[15] Swiatkiewicz, J.; Eisenhardt, G.; Prasad, P. N.; Thomas, J. M.; Jones, W.; Theocharis, C. R. *J. Phys. Chem.* **1982**, *86*, 1764.

[16] Unpublished result.

[17] Dwarkanath and Prasad demonstrated by the use of phonon spectra that photoreacdtions in some organic crystals were thermally assisted. See: Dwarkanath, K.; Prasad, P. N. *J. Am. Chem. Soc.* **1980**, *102*, 4254.

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[19] Ichimura, K.; Watanabe, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 420, 1420.

by a comparison of the ^{1}H NMR spectrum with that of a tricyclic [2.2]paracyclophane derivative, derived from a mixed crystal of ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates; the structure was confirmed by crystal structure analysis.[20] The proton signals of the benzene rings in **3a** (δ 7.25 (d, 2 H, J = 8 Hz), 7.02 (s, 4 H), and 6.76 (d, 2 H, J = 9 Hz)) were almost the same as those of the reference cyclophane. From the result, the structure of **3a** was concluded to be a highly strained [2.2]paracyclophane derivative. The formation of **3a** was also rationalized from the crystal structure of **1a**: IR (KBr) 2250 (m), 1750 (s), 1435 (s), 1230 (s), 820 (s) cm^{-1}; ^{1}H NMR (trifluoroacetic acid (TFA)) δ 8.97 (d, 2 H, J = 6 Hz), 8.78 (t, 2 H, J = 8 Hz), 8.37 (d, 2 H, J = 8 Hz), 8.19 (t, 2 H, J = 7 Hz), 7.25 (d, 2 H, J = 8 Hz), 7.02 (s, 4 H), 6.76 (d, 2 H, J = 9 Hz), 5.69 (d, 2 H, J = 11 Hz), 5.47 (dd, 2 H, J_1 = 11 Hz, J_2 = 10 Hz), 4.66 (d, 2 H, J = 10 Hz), 3.93 (s, 6 H).

Tetramers. Tetramers **4** were obtained by the photoirradiation of the recrystallized **2** with $\lambda \geq 300$ nm at −40 °C, followed by successive separation on preparative TLC (silica gel, ethyl acetate/dichloromethane = 80/20 v/v). Tetramer **4b** was also obtained directly by the photoirradiation of **1b**.

4a. From a ^{1}H NMR analysis of **4a**, the number of the cyclobutane protons was determined to be eight (4.88–5.79 ppm), suggesting that **4a** was formed by the cycloaddition of the ester side olefins in **2a**. This structure coincided with that predicted from the X-ray crystallography of **2a**: IR (KBr) 1750 (s), 1590 (m), 1440 (m), 1240 (s), 1210 (s), 1100 (s) cm^{-1}; ^{1}H NMR (TFA) δ 8.99 (m, 2 H), 8.76 (t, 2 H, J = 7 Hz), 8.64 (d, 2 H, J = 6 Hz), 8.56 (t, 2 H, J = 7 Hz), 8.26–8.34 (m, 4 H), 8.19 (t, 2 H, J = 7 Hz), 7.89 (t, 2 H, J = 7 Hz), 7.81 (d, 2 H, J = 16 Hz), 7.64 (d, 4 H, J = 7 Hz), 7.32–7.43 (m, 10 H), 7.20 (d, 4 H, J = 7 Hz), 5.79 (d, 2 H, J = 11 Hz), 5.52 (dd, 2 H, J_1 = 11 Hz, J_2 = 11 Hz), 5.20 (s, 2 H), 4.88 (d, 2 H, J = 11 Hz), 3.88 (s, 6 H), 3.54 (s, 6 H).

4b. Since the number of cyclobutane protons of **4b** was determined to be ten (4.57–5.15 ppm), it was concluded that **4b** was formed, contrary to **4a**, by the cycloaddition of the pyridyl side olefins in **2b**. The structure of **4b** was also correctly predicted from the crystal structure of **2b**. The tetramer obtained directly from **1b** showed a ^{1}H NMR spectrum identical with that of **4b**: mp 237.5–239 °C (ethanol); IR (KBr) 1740 (s), 1720 (s), 1600 (s), 1570 (s), 1270 (s), 1210 (s) cm^{-1}; ^{1}H NMR (TFA) δ 8.98 (d, 2 H, J = 6 Hz), 8.76 (t, 2 H, J = 8 Hz), 8.55–8.45 (m, 6 H), 8.27 (d, 2 H, J = 8 Hz), 8.20 (dd, 2 H, J_1 = 8 Hz, J_2 = 7 Hz), 7.98 (d, 2 H, J = 8 Hz), 7.89 (d, 4 H, J = 8 Hz), 7.84 (t, 2 H, J = 6 Hz), 7.30–7.15 (m, 12 H), 5.66 (d, 2 H, J = 12 Hz), 5.46 (dd, 2 H, J_1 = 12 Hz, J_2 = 11 Hz), 5.20–5.05 (m, 4 H), 4.78 (d, 2 H, J = 10 Hz), 4.53 (q, 4 H, J = 7 Hz), 4.40–4.15 (m, 4 H), 1.45 (t, 6 H, J = 7 Hz), 1.23 (t, 6 H, J = 7 Hz).

Polymer from 2a. In the ^{1}H NMR spectrum of the polymer, five types of signals of cyclobutane protons appeared. The proton signals at δ 5.64 (d, 2 H), 5.44 (dd, 2 H), 5.10 (s, 2 H), and 4.83 (d, 2 H) were assigned to the protons of the cyclobutane rings of a **4a** unit by a comparison with the ^{1}H NMR spectrum of **4a**; in both spectra, the peaks of the cyclobutane protons were almost identical in shape, although the chemical shifts of the cyclobutane protons of the polymer shifted upfield by 0.05–0.15 ppm. A new cyclobutane signal at δ 4.11–4.58 (m, 2 H) was assigned to arise from the cyclobutane formed by the cycloaddition of the pyridyl side olefins, which is the sole reactive olefin in **4a** crystal. The signal pattern for this cyclobutane was observed to have a symmetry that is quite different from that of the α-type cyclobutane of **4b**. The cyclobutane structure was concluded to be the ϵ-type on the basis of this result and the crystal structure of **2a**: $\overline{Mn}$ = 12 000 (estimated by GPC), η_{inh} = 0.80 dL/g (0.30 g/dL in *m*-cresol at 30 °C); IR (KBr) 1750 (s), 1735 (s), 1585 (m), 1430 (m), 1235 (m) cm^{-1}; ^{1}H NMR (TFA) δ 8.95 (d, 2 H, J = 5 Hz), 8.90–8.70 (m, 4 H), 8.63 (t, 2 H, J = 8 Hz), 8.28 (d, 2 H, J = 8 Hz), 8.20–8.10 (m, 4 H), 8.03 (t, 2 H, J = 6 Hz), 7.40–7.00 (m, 16 H), 5.64 (d, 2 H, J = 12 Hz), 5.44 (dd, 2 H, J_1 = 12 Hz, J_2 = 10 Hz), 5.10 (s, 2 H), 4.83 (d, 2 H, J = 10 Hz), 4.58–4.11 (m, 4 H), 3.84 (s, 6 H), 3.62 (s, 6 H).

Crystallographic Analysis. The recrystallization solvents for single crystals were the same as those described above in the Experimental Section. The intensity data were measured over the range $2\theta < 128°$ by a ω–2θ scan on a Rigaku four-circle diffractometer with graphite monochromated Cu Kα radiation. There were 2469, 2637, 5135, and 5442 unique reflections observed for **1a**, **1b**, **2a**, and **2b**, respectively, of which 1947, 1934, 4083, and 3275 reflections with $|F_o| > 2\sigma(|F_o|)$ were used in the solutions and refinements; no absorption correction was made. The structures were solved by a direct method with the MULTAN 78 or 84, and refined by a full-matrix least-squares method with SHELX 76. The final molecular coordinates, thermal parameters, bond lengths, and bond angles of **1a**, **1b**, **2a**, and **2b** are given in the supplementary material.

Table I. Photoirradiation Conditions and Products in the Reaction of **1a**, **1b**, **2a**, and **2b**

		photoirradiation			
run	reactant	time, h	temp, °C	filter[a]	product (wt %)[b]
1	crystal **1a**	2	−40	A	**2a** (~100)
2		2	2	A	**2a** (~100)
3		4	40	A	**2a** (88)
4		6	−40	B	**2a** (45), **3a** (42)
5		6	2	B	**2a** (39), **3a** (2)
6	as-prepared **2a**[c]	4	−40	B	**2a** (73), **3a** (11)
7		4	−40	B	**2a** (57), **3a** (1)
8		12	−40	B	**2a** (29), **3a** (5)
9	crystal **2a**	28	−40	B	polymer (~100)
10[d]	crystal **1b**	3	−40 to +90	A	**2b** (~100)
11		6	−78	B	**2b** (94)
12	as-prepared **2c**[e]	3	2	B	**2b** (73), **4b** (5)
13		4	−40	B	**2b** (41), **4b** (44)
14	crystal **2b**	28	rt	B	**4b** (81), octamer[f]
15		4	−40	B	**4b** (~100)

[a] The filter A cuts off <410 nm, and B, <300 nm. [b] Indefinable oligomeric material was excluded. [c] The as-prepared **2a** for runs 6 and 8 was the photoproduct in run 1, and for run 7, run 2. In run 8, the as-prepared **2a** by run 1 was stored at room temperature for 3 days before photoirradiation. [d] Ar ion laser (457.9 nm) was used for photoirradiation. [e] The as-prepared **2b** for run 12 was the photoproduct obtained at −40 °C in run 10, and for run 13, at 70 °C. [f] Confirmed by GPC.

Results and Discussion

Photochemical Behavior of Crystals of 1a and 2a. Monomer **1a** was highly photoreactive in the crystalline state and was converted into dimer **2a** in high yield or into a mixture of oligomers and cyclophane **3a**, depending on the wavelength of the irradiating light and the irradiation temperature. The photoirradiation conditions and photoproducts are shown in Table I. When **1a** was irradiated at −40 and +2 °C (runs 1 and 2) with a cut-off filter (≥410 nm), which was used in order to excite the monomer while leaving the dimer in the ground state, the final product was amorphous **2a** in nearly quantitative yield. In contrast, when the photoreaction was carried out at 40 °C (run 3), the photoproduct mainly consisted of **2a** with an appreciable amount of oligomers, in spite of using the filter.

It was confirmed from both NMR and MS analyses that all of the reactions of **1a** carried out in the persent study gave only one type of monocyclic dimer **2a**, which had a hetero-adduct-type cyclobutane structure (Scheme I). From this result, it is obvious that the reaction proceeds under crystal lattice control, although the starting crystals are gradually transformed into an amorphous product as the photoreaction progresses. However, the result of run 3 indicates that the degree of topochemical control is reduced to some extent, owing to an enhanced thermal movement of the molecules at 40 °C. The dimer structure was also reasonably predictable from the crystal structure of **1a**, based on topochemical considerations. Finally, the chemical structure of **2a** was definitely determined by a crystal structure analysis; **2a** consists of a β-hetero-type cyclobutane.

Upon further photoirradiation with $\lambda \geq 300$ nm (run 7), as-prepared **2a** (which was obtained at −40 °C through run 1) afforded tricyclic dimer **3a** (Scheme I). However, in run 8 only a trace amount of **3a** was generated upon irradiation of as-prepared **2a** (which was obtained through run 2) even under the same irradiation conditions as for run 7. Furthermore, when the photoproduct of run 1 was further photoirradiated (run 9) after storage for 3 days at room temperature, the final yield of **3a** decreased to 5% (11% in run 7). In contrast, the photoirradiation of **1a** crystal with $\lambda \geq 300$ nm at −78 °C (run 4) resulted in the highest yield of **3a** (65%) among all of the experiments carried out. Upon irradiation at 2 °C, however, only a small amount of **3a** was obtained (run 6). These results indicate that there exists

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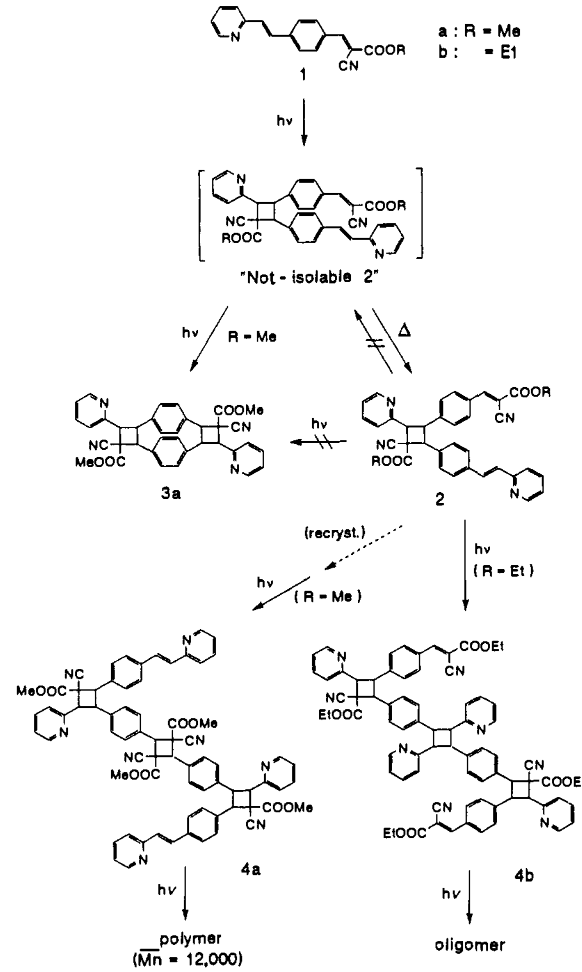
[20] In the structure of the mixed crystal, two molecules make a molecular pair, which is related to the neighboring pairs by glide plane; this type of molecular packing is very unusual in a β-packing crystal. See: (a) Hasegawa, M.; Maekawa, Y.; Kato, S.; Saigo, K. *Chem. Lett.* **1987**, 907. (b) Maekawa, Y.; Kato, S.; Hasegawa, M. *J. Am. Chem. Soc.* **1991**, *113*, 3867.

Scheme I



a certain highly strained "not-isolable dimer" at low temperature, which has two double bonds within the reactive distance and can be converted into **3a** upon further photoirradiation (Scheme I). The two possible paths for the not-isolable dimer to **2a** or to **3a** depend on the irradiation temperature; the former transformation occurs more favorably with increasing temperature. By a NMR study, **3a** was confirmed to be a tricyclic [2.2]paracyclophane derivative, as described in the Experimental Section.

Dimer **2a** has two crystal modifications: One is highly photoreactive and is obtained upon recrystallization from a mixed solvent (methanol/1,2-dichloroethane = 85/15 v/v); the other is from a methanol solution and is much less reactive. Upon photoirradiation with a filter (≥300 nm), the former crystals gave a highly crystalline polymer (run 10). In this reaction, the XRD pattern of **2a** was gradually shifted to that of the photoproduct along with a retention of high crystallinity. The high polymer ($\overline{Mn}$ = 12 000) afforded a transparent flexible film upon casting from a hexafluoro-2-propanol solution.

Intermediate tetramer **4a** was isolated in order to characterize the repeating structure of the polymer. The NMR analysis of **4a** and the X-ray crystallography of starting **2a** suggest that **4a** is an α-homo-type adduct formed by the cycloaddition of ester side olefins of **2a** (Scheme I). Finally, the polymer was determined to have **4a** as a repeating unit by a NMR analysis of the polymer; this structure coincided with that predicted from the crystal structure of **2a**. However, taking into account the configurations of β-type cyclobutanes in repeating units, one repeating unit comprises eight molecules of **1a** since the configuration of a β-type cyclobutane ring is opposite for every two neighboring ones (as discussed later).

Photochemical Behavior of Crystals of 1b and 2b. Upon photoirradiation with a filter (≥410 nm), **1b** converted into β-hetero-type dimer **2b** nearly quantitatively over a wide range of temperatures (run 11, Scheme I). However, cyclophane was not detected in all of the reactions of **1b**, carried out in the present study, even at a very low temperature (run 12). No formation of cyclophane from **1b** is attributable to a greater molecular motion of "not-isolable **2b**", which is converted into **2b** more readily compared to the case of "not-isolable **2a**". The chemical structure of **2b** was determined by means of a crystal structure analysis of **2b**.

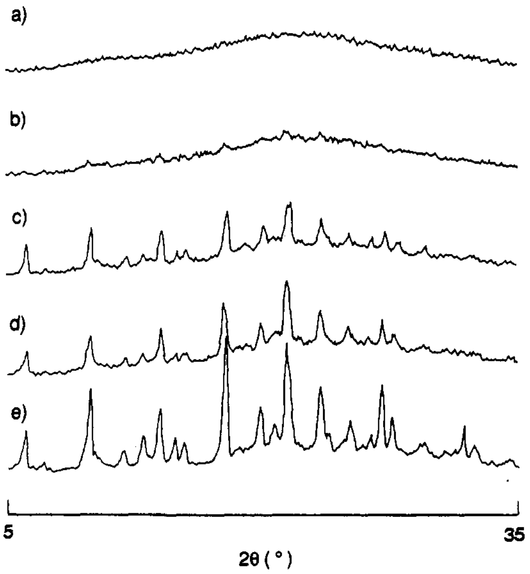


Figure 1. X-ray diffraction patterns of the photoproducts from crystal **1b**, photoirradiated (a) at 2 °C, (b) at 30 °C, and (c) at 70 °C, (d) of the sample (a) annealed at 135 °C for 10 min, and (e) of **2b** recrystallized from ethanol solution.

The crystallinity of as-prepared **2b** increased with increasing the photoirradiation temperature, as shown in Figure 1; as-prepared **2b** obtained at 70 °C showed a high crystallinity, although **1b** gave amorphous **2b** at about 2 °C or below. In addition, the crystallization of as-prepared amorphous **2b** occurred when it was annealed at 135 °C, which is far below its crystal melting point (211–213 °C), for 10 min. Both as-prepared crystalline **2b** and annealed **2b** showed XRD patterns identical with that of **2b** recrystallized from an ethanol solution (Figure 1). The DSC curve of as-prepared dimer **2b** showed an exothermic peak at 90–170° and an endothermic peak of the crystal melting point near 212 °C. The exothermic peak can be attributed to the heat of crystallization. It should be noticed that, in comprison with the crystallization of as-prepared **2b** at 90–170 °C by annealing, during the photoreaction the same crystallization can occur, even below 70 °C.

Amorphous as-prepared **2b**, which was obtained at −40 °C through run 11, gave a small amount of **4b** upon further photoirradiation at 2 °C (run 13, Scheme I). As would be expected, as-prepared **2b** with a higher crystallinity afforded **4b** in a relatively higher yield (run 14, 44%). Furthermore, the photoreaction of recrystallized **2b** at room temperature gave photoproducts containing mainly tetramer **4b** (81%) with a small amount of octamer (run 15), whereas at −40 °C **2b** gave **4b** nearly quantitatively. This temperature dependence of the photoreaction of crystal **2b** may be attributed to a greater molecular motion at higher temperature. Tetramer **4b** is an α-homo-type adduct formed by the cycloaddition of pyridyl side olefins, as opposed to **4a** (Scheme I).

Crystallographic Intepretation of Photochemical Behaviors. Crystallographic data of **1a**, **1b**, **2a**, and **2b** are shown in Table II. The crystal structures of the monomers in Figure 2 and of the dimers in Figure 3 reasonably elucidate the photoreaction of **1** and **2**, respectively. In the crystals of **1a** and **1b**, of which the crystal systems are similar to each other, two molecules form a molecular pair and are arranged in a β-type packing. Considering the intermolecular distances between the double bonds, each molecule can react only with its partner of the molecular pair, whereas it cannot react with any molecule of other molecular pairs. The distances between two facing double bonds in the pair are

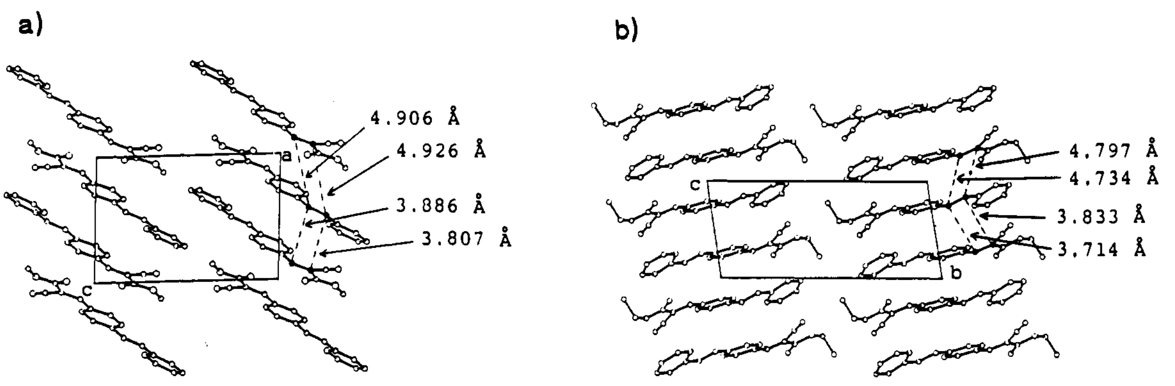


Figure 2. Crystal structures of (a) **1a** viewed along the *b* axis and (b) **1b** viewed along the *a* axis.

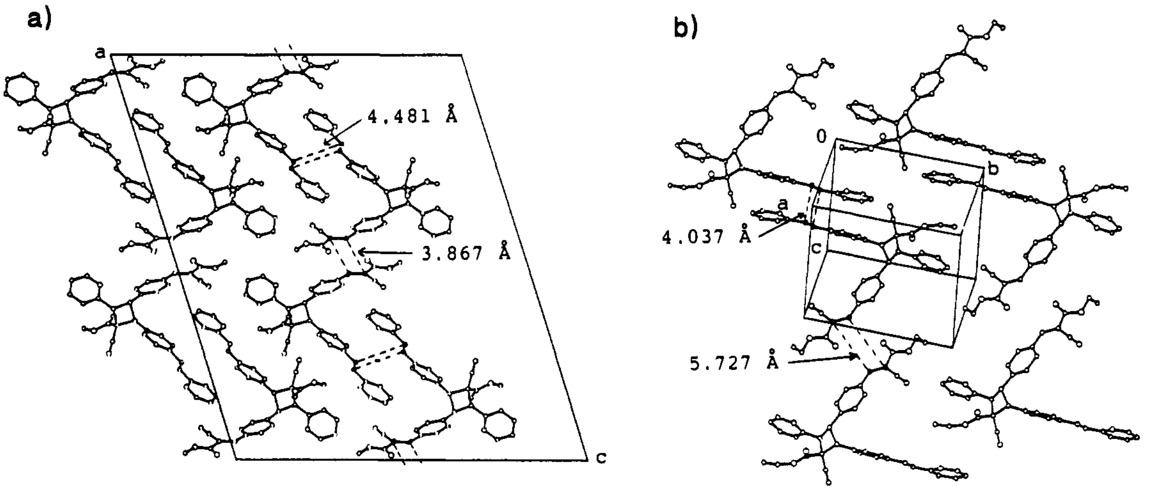


Figure 3. Crystal structures of (a) **2a** viewed along the *b* axis and (b) **2b**.

Table II. Crystallographic Data of **1a**, **1b**, **2a**, and **2b**

	1a	**1b**	**2a**	**2b**
space group	$P\bar{1}$	$P\bar{1}$	$A2/a$	$P\bar{1}$
crystal system	triclinic	triclinic	monoclinic	triclinic
a, Å	12.269 (2)	7.628 (2)	33.52 (4)	15.261 (1)
b, Å	7.489 (1)	16.807 (2)	6.542 (5)	8.831 (1)
c, Å	8.486 (2)	7.474 (2)	29.372 (14)	13.669 (1)
α, deg	97.74 (1)	88.04 (2)		106.34 (1)
β, deg	92.41 (1)	113.90 (2)	107.34 (6)	109.11 (1)
γ, deg	74.41 (1)	113.58 (2)		73.88 (1)
V, Å^3	743.8	793.0	6147.9	1635.1
Z	2	2	8	2
D_x	1.30	1.27	1.25	1.24
μ, mm^{-1}	0.70	0.64	0.64	0.62
R	0.080	0.066	0.079	0.085
ref	18a	18b	18b	18b

3.886 and 3.807 Å for **1a**, and 3.714 and 3.833 Å for **1b**. These distances are considered to be allowed for a [2+2] photoreaction according to the topochemical principle proposed by Schmidt,[2] although the reacting double bonds are not exactly in parallel. Furthermore, since paired molecules are related by a centrosymmetry, two pairs of facing double bonds should be equal to photoreactivity, affording two enantiomeric cyclobutanes.

The formation of **3a** can be explained as follows: When one pair of facing double bonds in a reactive molecular pair of **1a** reacts to form cyclobutane, the other olefinic pair moves too far apart to react in order to release the strained bond angle if the thermal energy is sufficient. At an extremely low temperature, however, the motion of the two chains having the unreacted double bonds in not-isolable **2a** would be "frozen" (to some extent) along with the reaction of a favorable distance for the intramolecular cycloaddition. It is thought that this type of unstable strained form is retained efficiently by a "steric compression" of the nearest-neighboring molecules, of which the motion is strictly restricted owing to insufficient thermal energy.

Recently, such a product-control technique by steric compression in the solid state was successfully extended to the photoreaction of propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamate crystal at an extremely low temperature, resulting in the formation of the same type of tricyclic [2.2]paracyclophane.[21] In contrast to the present result, in the photoreaction of a mixed crystal of ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates, a [2.2]paracyclophane derivative crystal was formed quantitatively, even at room temperature, by virtue of a lattice-controlled steric compression of the neighboring molecules.[20]

Judging from the XRD study, the molecular arrangement in the crystalline region of as-prepared **2b** should be the same as that of crystal **2b**. Indeed, crystalline as-prepared **2b** gave tetramer **4b** upon photoirradiation (Table I, run 14). Even in the amorphous region of as-prepared **2b**, it is expected that the molecular arrangement should be very close to that of crystal **2b** for the following reasons. Firstly, the **2b** molecules were rearranged during annealing at 135 °C, which is far below its crystal melting point (212 °C). Secondly, upon photoirradiation of amorphous as-prepared **2b**, tetramer **4b** was obtained (Table I, run 13). Thirdly, in addition to the same space group of crystal **1b** and **1b** ($P\bar{1}$), a similarity in the molecular arrangement between the crystal structures of **1b** and **2b** was visualized, as can be seen from Figures 2b and 3b. Such a similar packing arrangement between crystals **1b** and **2b** strongly suggests that the dimerization of **1b** into crystalline **2b** proceeds with a relatively small movement of **2b** molecules by anisotropic thermal movement. When the irradiation temperature is sufficiently low, the movement of **2b** molecules after dimerization is restricted because of insufficient thermal energy; this maintains a relatively high molecular orientation, although the crystals become amorphous, determined by XRD measurements. This highly oriented region could

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[21] Chung, C.-M.; Nakamura, F.; Hashimoto, Y.; Hasegawa, M. *Chem. Lett.* **1991**, 779.

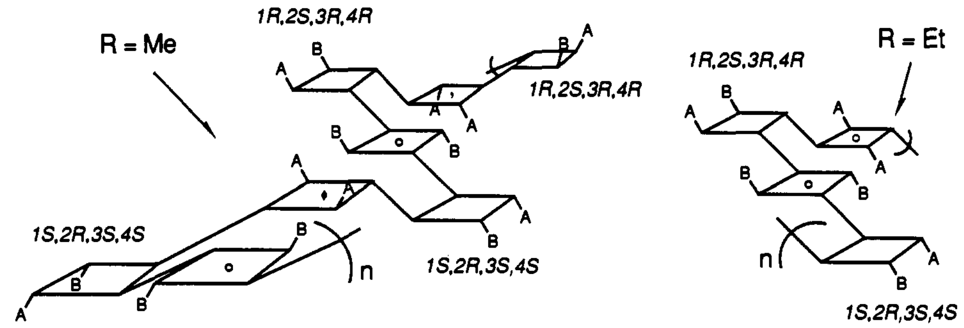
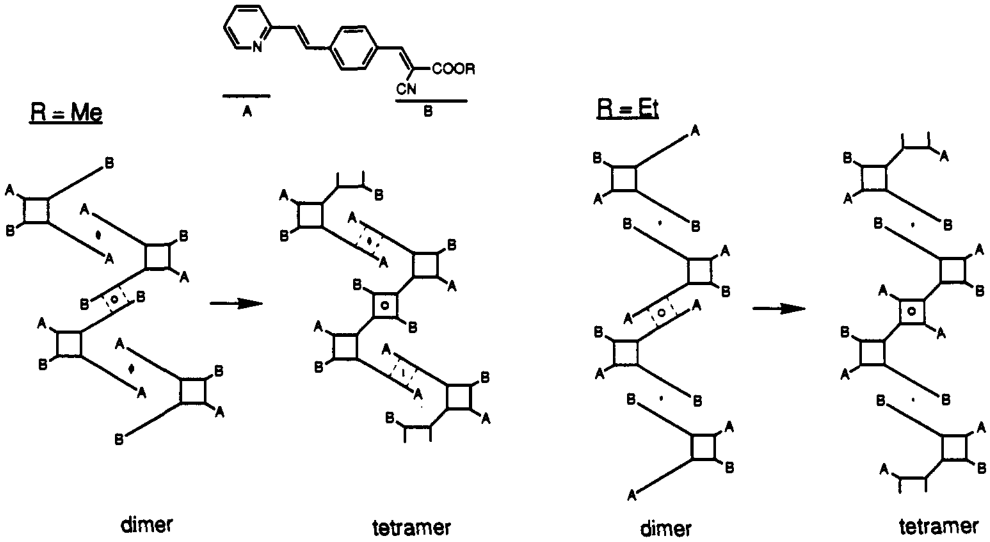


Figure 4. Possible structures of the polymer derived from crystal **2a** and the octamer from crystal **2b**. Benzene rings are omitted as a matter of convenience. Substituents A and B are identical with those designated in Scheme II.

Scheme II



crystallize very easily during the annealing process, since the molecular arrangement in this region must be very close to that in crystal **2b**.

These results lead to the conclusion that both enantiomers of **2b** are formed alternatively during the photoreaction of **1b** into **2b**, although the two pairs of facing double bonds of every molecular pair in crystal **1b** should be equal in reactivity (as discussed above). As can be seen from the crystal structure of **2b** (Figure 3b), both enantiomers of **2b** are arranged alternatively along the $[1\bar{2}1]$ direction. Such an alternating arrangement of both enantiomers implies that, after one enantiomer is formed from one molecular pair, the other enantiomer should be formed from the neighboring molecular pair (Scheme II). This unusual structure formation is explainable by a steric repulsion between the dimer being formed and the neighboring molecular pair. That is to say, the steric repulsion enhances the relative reactivity of the opposite-side olefin pair in the enantiomers was spontaneously generated by "topochemical induction" in an achiral crystal of prochiral molecules. Although a similar behavior to such an alternating arrangement is very common in the crystallized process of racemates,[22] this is the first demonstration for an organic reaction of prochiral molecules in an achiral environment. In addition, the direct formation of **4b** from crystals **1b** implies that the whole course of the photoreaction, starting from **1b** to **4b** (and further oligomers), proceeds topochemically.

On the other hand, in the photoreaction of **1a**, tetramer **4a** was not formed directly from crystals **1a**, and as-prepared **2a** did not crystallize under any of the annealing conditions attempted. This is presumably because the crystal structure of **2a** is quite different from that of **1a** with a different space group, in contrast to the correlation between the crystal structures of **1b** and **2b**. As is obvious in Figure 3 and Scheme II, **2a** molecules in the crystal cross in a different manner compared to that of **2b**.

The structures of **4a** and **4b** were readily predicted from the crystal structures of the corresponding dimers (**2a** and **2b**), respectively. In both crystals **2a** and **2b**, the two reacting molecules are centrosymmetrically related to each other (Figure 3 and Scheme II). The two facing olefinic bonds are parallel and separated by 3.867 Å for the methyl ester side of **2a** and 4.037 Å for the 2-pyridyl side of **2b**; these distances are within that of normal reactive bonds. The intermolecular distances between the two double bonds of the 2-pyridyl side of **2a**, which are related to each other by a 2-fold rotation axis, and between the centrosymmetrically related ester side double bonds of **2b**, seem to be too far to react (4.481 and 5.727 Å, respectively). The structures of **4a** and **4b** definitely coincided with those determined by means of a ^{1}H NMR spectral analysis.

It should be noted that the tetramers contain three cyclobutane rings of the β-hetero-type, the α-homo-type, and the β-hetero-type structures, and that the configurations of the two β-hetero-type cyclobutanes are opposite to each other.

How did crystal **2a** give a polymer, despite the fact that only one of the two double bonds of **2a** was within the reactive distance? As can be seen from the crystal structure of **2a** (Figure 3a, Scheme II), when the double bonds of the methyl ester side reacted to form cyclobutane, the pyridyl side double bonds presumably approached each other, resulting in an orientation favorable for further photodimerization. A similar behavior has been observed concerning the topochemical polymerization of ethyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate.[13] On the basis of the geometry of two pyridyl side olefins of **2a**, the olefinic pair is expected to yield an ε-type cyclobutane; this is actually supported by NMR analysis.[23] Thus, the polymer structure should have a very unique

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[22] Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; John Wiley and Sons: New York, 1981.

[23] At the pyridyl side of **2a**, a possibility to give a δ-type cyclobutane cannot be excluded. Thus, another structure of the repeating unit of the resulting polymer may be $[\alpha\beta\delta\beta\alpha\beta^{-1}\delta\beta^{-1}]$.

repeating unit in which three types of cyclobutane structures are incorporated in a sequence of $[\alpha\beta\epsilon\beta\alpha\beta^{-1}\epsilon\beta^{-1}]$, where β and β^{-1} are opposite in configuration to each other (see Figure 4). Considering the stereochemistry of cyclobutane, every two neighboring β-type cyclobutanes are opposite in configuration ("double syndiotactic"). From the viewpoint of synthetic polymer chemistry, although the formation of stereospecific polymers (isotactic and syndiotactic) is very popular, especially by using a Ziegler-type catalyst, the present polymer is the first example of the polymer having a double syndiotactic structure. In contrast, since the main product is only tetramer **4b** in the photoreaction of crystal **2b**, the ethyl ester side olefins doubtlessly still stay beyond the reactive distance, even after the pyridyl side olefins in **2b** have reacted. However, since the octamer was obtained without any other appreciable byproducts at room temperature, the structure of the octamer is expected to have a repeating unit in which two types of cyclobutane structures are arranged in a sequence of $[\beta\alpha\beta^{-1}\alpha]$ ("syndiotactic"), as shown in Figure 4.

Conclusions

The topochemical behavior of alkyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamates (**1a** and **1b**) and their dimers (**2a** and **2b**) was investigated on the basis of crystallographic, mechanistic, and product analyses.

In the reaction of crystal **1a**, the product of the topochemical photoreaction was controlled not only by the wavelength of the irradiating light, but also by the irradiation temperature. The monocyclic dimer **2a** was a main product when **1a** was irradiated under various conventional irradiation conditions. On the other hand, at an extremely low temperature (−40 °C), the thermal motion of the monocyclic dimer **2a** was restricted; upon further irradiation, a highly strained tricyclic [2.2]paracyclophane (**3a**) was obtained as a major product. In the photoreaction of **1b**, the monocyclic dimer **2b** was obtained in very high yield over a wide range of irradiation temperatures (−40 to ∼+90 °C). A phase change of amorphous **2b** into the crystalline state occurred upon annealing at 135 °C, or even during the photoreaction when sufficient thermal energy was supplied, and the tetramer **4b** was obtained by prolonged photoirradiation.

Although the photoreactions of **1** into **2**, and of **2** into **4** or polymer were reasonably interpreted by crystallographic analyses of **1** and **2**, the structure of the tetramer and the polymer were unpredictable from the crystal structures of the corresponding monomers. On the basis of the similarity between the crystal structures of **1b** and **2b**, it was concluded that the photoreaction of **1b** into **2b** and tetramer **4b** is topochemically controlled and is accompanied by a topochemical induction that causes the formation of an alternating arrangement of both enantiomers and a zigzag-linear structure. The formation of an alternating sequence of both enantiomers is the first demonstration of such a process through an organic reaction of prochiral molecules in an achiral environment.

Finally, very unique structures of the polymer and the oligomer, in which the cyclobutane structures are arranged in a sequence of $[\alpha\beta\epsilon\beta\alpha\beta^{-1}\epsilon\beta^{-1}]$ and $[\beta\alpha\beta^{-1}\alpha]$, respectively, were formed in the photoreaction of the dimer crystals **2a** and **2b** under crystal lattice control.

Acknowledgment. We thank Dr. S. Sato (Sankyo Co., Tokyo, Japan) for making available to us the crystallographic data of **1a**, **1b**, **2a**, and **2b**.

Registry No. 1a, 106366-65-8; **1b**, 124067-51-2; **2a**, 135413-74-0; **2a** (polymer), 135310-68-8; **2b**, 135413-75-1; **3a**, 135310-66-6; **4a**, 135413-76-2; **4b**, 135413-77-3; **5**, 135310-65-5; methyl cyanoacetate, 105-34-0; ethyl cyanoacetate, 105-56-6.

Supplementary Material Available: Molecular structures and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **1a**, **1b**, **2a**, and **2b** (13 pages). Ordering information is given on any current masthead page.

Phytochrome Models. 11.[†] Photophysics and Photochemistry of Phycocyanobilin Dimethyl Ester[‡]

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Abstract: Phycocyanobilin dimethyl ester (3) undergoes a self-sensitized oxidation by a singlet oxygen $[O_2(^1\Delta_g)]$ mechanism with a quantum yield of 10^{-5}–10^{-6}, depending on the solvent, excitation wavelength, and concentration. The main photooxidation products are a tripyrrolic aldehyde (7) and three stereoisomeric peroxides (8–10) formed from two units of 3. Near-IR emission of $O_2(^1\Delta_g)$—formed upon sensitization by 3 under both steady-state irradiation and pulsed excitation—constitutes the first direct evidence for the intersystem crossing of a bilatriene. The low photooxidation yield results from a low intersystem crossing yield from 3, $\Phi_{isc} < 10^{-4}$, estimated by the energy-transfer method in flash photolysis. A total rate constant of $k_q = (3.4 \pm 0.3) \times 10^8$ M^{-1} s^{-1} was determined for the quenching of $O_2(^1\Delta_g)$ by 3. Possible relations between these findings and the photophobic movement of *Anabaena variabilis* are discussed. In analogy to biliverdin dimethyl ester, two types of conformations (a helical form and a family of stretched forms) for 3 [and for its 3,3′-dihydro-3′-thioethoxy derivatives (3′*S**)-5] were detected in methanol at room temperature by stationary fluorescence and excitation spectra. The wavelength dependence of the self-sensitized photooxidation of 3 is due to the selective reaction of the helical conformer, while a selective photoisomerization of the stretched forms of 3 and 5 was observed by time-resolved laser-induced optoacoustic spectroscopy. For 3 the latter process takes place with a quantum yield > 0.5, and the resulting isomer (probably a C-10 stereoisomer of the parent compound) reverts to the ground state with a lifetime of around 200 ns.

Introduction

Phytochromobilin (1) and phycocyanobilin (2), the bilatriene chromophores of the plant photoreceptor phytochrome and the algal pigment phycocyanin, respectively, have very similar structures (Scheme I). They differ only in the substitution of ring D: 1 possesses a vinyl group and 2 an ethyl group instead.[1] Since 2 is much more readily accessible from algae than 1 is from plants, this study was directed toward the photophysical and

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[†] For Phytochrome Models. Part 10, see ref 6.

[‡] This work is taken in parts from the Ph.D. Theses of D.S., Ruhr-Universität Bochum/MPI für Strahlenchemie, 1988, and of S.N., Institut Químic de Sarrià/MPI für Strahlenchemie, 1988. It has been presented at the XIIth IUPAC Symposium on Photochemistry, Bologna, 1988.

(1) Scheer, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 241–261.

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