

Quantitative Formation of a Highly Strained Tricyclic [2.2]Paracyclophane Derivative from a Mixed Crystal of Ethyl and Propyl α -Cyano-4-[2-(4-pyridyl)ethenyl]cinnamates through a Topochemical Reaction

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Abstract: A mixed crystal of ethyl and propyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamates (**1a**·**1b**) has a molecular arrangement quite different from each of the pure crystals, **1a** and **1b**, although the crystal structures of **1a** and **1b** are extremely similar to each other. The photoreaction of mixed crystals having a molar ratio of **1a** and **1b** between 70:30 and 5:95 afforded a highly strained tricyclic [2.2]paracyclophane derivative (**3**) in quantitative yield. During the entire course of the photoreaction of **1a**·**1b**, high crystallinity was maintained. An intermediate monocyclic dimer (**2**) was also obtained in quantitative yield when the mixed crystal was irradiated at wavelengths longer than 410 nm. Two phenylene rings in cyclophane **3** come into contact with each other at a shorter distance than the van der Waals distance and bend similarly to [2.2]paracyclophane, as previously reported. The reaction from **1a**·**1b** to **3** could be sufficiently interpreted by means of a topochemical transformation based on crystal structure analyses of **1a**·**1b** and **3**. Upon irradiation at a wavelength of 254 nm, the cyclobutane rings in **3** were readily cleaved to afford **2**, not only in solution but also in the crystalline state.

Introduction

It has generally been observed that the product structure is determined by the crystal structure of the starting compound in a topochemical reaction¹ and that highly crystalline polymers having an extremely stereoregular structure are produced in nearly quantitative yields through crystalline state polymerization. [2 + 2] Photopolymerization of the 2,5-distyrylpyrazine (DSP) crystal was the first example of this type of polymerization.² In this polymerization, a direct correlation was substantiated for the first time between the crystal structures of the starting compound and the product. That is, the space group is retained in the entire course of reaction from DSP crystal to poly-DSP crystal. Thereafter, a great number of linear high polymer crystals have been prepared by topochemical [2 + 2] photopolymerization of diolefin crystals.³ Recently, we have succeeded in preparing several types of dimers and polymers from unsymmetrically substituted diolefin crystals.⁴ On the basis of the topochemical study on diolefin compounds so far, the processes can be represented, as shown in Scheme I, in which well-defined photoproducts have been obtained except for zigzag-type high polymers and cyclophane derivatives from a β -type packing crystal.

In several series of photoreactive diolefin crystals we have observed that a few α -type photoreactive crystals having a similar chemical structure have very similar molecular arrangements in these crystals.^{1,3b,c,5} The results suggested to us that the photoreactive mixed crystal would be obtained from two similar diolefin compounds and, subsequently, the mixed crystal would give a copolymer through topochemical copolymerization.^{3d}

The crystal structures of ethyl and propyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamate crystals (**1a** and **1b**) are very similar to each other, as described in previous papers.⁵ However, contrary to our expectation of obtaining an α -homo-type linear copolymer,

the mixed crystal of **1a** and **1b** (**1a**·**1b**) did not afford a linear copolymer but, rather, afforded a highly strained tricyclic [2.2]paracyclophane derivative crystal quantitatively by "double" photocycloaddition between two molecules. In the present paper we wish to report on the topochemical behavior of mixed crystal **1a**·**1b** and the structure and properties of the resulting cyclophane **3**.⁶

Results and Discussion

We have already reported the crystal structures and topochemical behavior of pure crystals **1a** and **1b**.⁵ In both crystals, one molecule is related to its neighboring molecules by two different inversion centers to make a plane-to-plane stack, although irradiation of **1a** and **1b** crystals afforded an α -homo-type polymer (see Scheme I) and the same type of photostable dimer, respectively.⁵ On the basis of similarity in molecular arrangements between **1a** and **1b** crystals, it was expected that **1a** and **1b** would form a mixed crystal which would give a copolymer.

Preparation of the Mixed Crystals of 1a and 1b. Mixed crystals of **1a** and **1b** (**1a**·**1b**) in various molar ratios were obtained by the cocrystallization of **1a** and **1b** from an ethanolic solution. X-ray powder diffraction analysis of the mixed crystals and characterization of the photoproducts indicated the presence of three crystal phases (denoted A, B, and C). Phase A, which has the same crystal structure as the **1a** crystal, was observed in the proportion of **1b**, ranging from 0 to 20 mol % in the mixed crystal. Phase B is a new crystal phase which is different from both pure **1a** or **1b** crystals; it was achieved in the proportion of **1b** ranging approximately from 30 to 95 mol %. Phase C, which has the same structure as crystal **1b**, was observed in the proportion of **1b**, ranging from 90 to 100 mol %.

However, accurate boundaries between phases A and B as well as between phases B and C could not be clearly defined. This was because reproducibility of experimental runs regarding the boundaries was not satisfactory: in the proportion of **1b** ranging from 20 to 30 mol %, the photoproduct was comprised of cyclophane, an α -homo-type polymer, or a mixture of them; in the proportion of **1b** ranging from 90 to 100 mol %, the photoproduct was comprised of cyclophane, an α -homo-type dimer, or a mixture of them.

In contrast to the successful formation of mixed crystals from **1a** and **1b**, methyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamate, of which the crystal structure is quite different from **1a** and **1b**,

(1) (a) Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2014. (b) Schmidt, G. M. *J. Pure Appl. Chem.* **1971**, 27, 647.

(2) (a) Hasegawa, M.; Suzuki, Y.; Suzuki, F.; Nakanishi, H. *J. Polym. Sci.* **1969**, A1, 7, 2319. (b) Nakanishi, H.; Hasegawa, M.; Sasada, Y. *J. Polym. Sci.* **1972**, A2, 10, 1537.

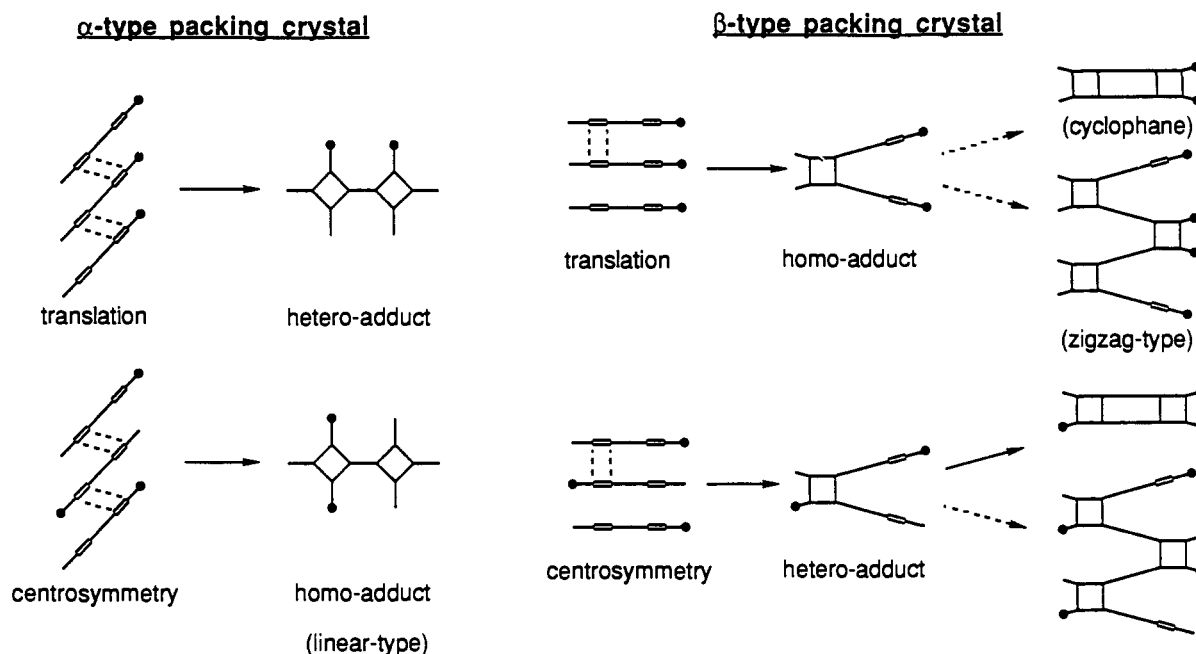
(3) Hasegawa, M. *Chem. Rev.* **1983**, 83, 507.

(4) (a) Hasegawa, M. *Pure Appl. Chem.* **1986**, 58, 1179. (b) Hasegawa, M.; Katsumata, T.; Ito, Y.; Saigo, K. *Macromolecules* **1988**, 21, 3134. (c) Hasegawa, M.; Aoyama, M.; Maekawa, Y.; Ohashi, Y. *Macromolecules* **1989**, 22, 1568. (d) Hasegawa, M.; Endo, Y.; Aoyama, M.; Saigo, K. *Bull. Chem. Soc. Jpn.* **1989**, 62, 1556. (e) Hasegawa, M. *Comprehensive Polymer Science, Vol. 5, Step Polymerization*; Allen, G., Ed.; Pergamon Press: Oxford, 1989; pp 217-232.

(5) (a) Hasegawa, M.; Kato, S.; Saigo, K.; Wilson, S. R.; Stern, C. L.; Paul, I. C. *J. Photochem. Photobiol.* **1988**, 41, 385. (b) Maekawa, Y.; Kato, S.; Saigo, K.; Hasegawa, M.; Ohashi, Y. *Macromolecules*, in press.

(6) A preliminary results: Hasegawa, M.; Maekawa, Y.; Kato, S.; Saigo, K. *Chem. Lett.* **1987**, 907.

Scheme 1



did not cocrystallize into a mixed crystal with either **1a** or **1b** from an ethanol solution under several conditions.

Topochemical Photoreaction of 1a·1b. Mixed crystal **1a·1b** (1:1) (phase B) showed an extremely high photoreactivity and, upon irradiation for 2 h at room temperature with a 500-W super-high-pressure mercury lamp, gave a highly crystalline product

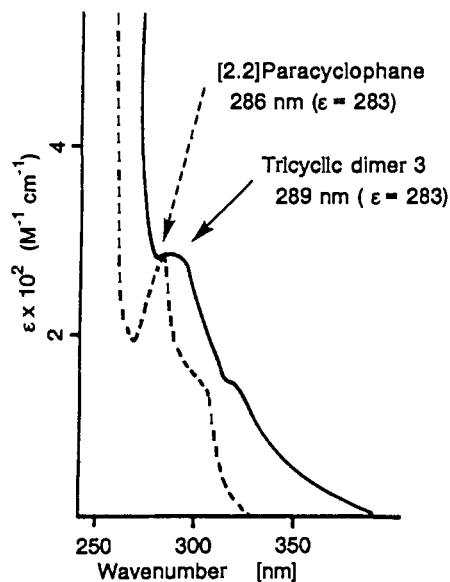


Figure 1. UV spectrum of tricyclic dimer **3** (solid line) and [2.2]paracyclophane (dashed line).

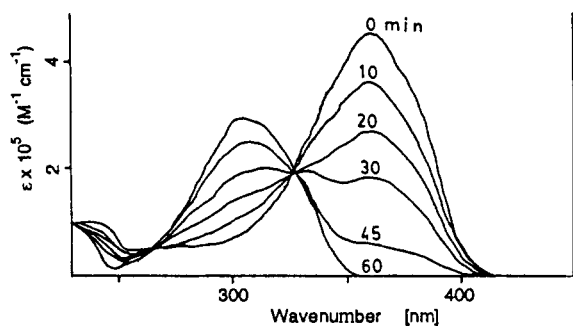
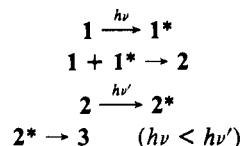


Figure 2. UV spectral change of mixed crystal **1a·1b** during the irradiation at the wavelengths longer than 410 nm.

quantitatively. In the ^1H NMR spectrum of the product, no olefinic proton signal was observed, and there existed three signals assigned to the protons of a cyclobutane ring at δ 4.64, 5.36, and 5.51 ppm: doublet (2 H, $J = 9$ Hz), double doublet (2 H, $J_1 = 11$ Hz, $J_2 = 9$ Hz) and doublet (2 H, $J = 11$ Hz), respectively. The ABC pattern and the proton ratio indicates that there are two cyclobutane rings having the same configuration of a hetero-type structure in one molecule (see Scheme 1). The UV spectrum of the product (Figure 1) shows a shoulder peak at 289 nm ($\epsilon = 283$) which is not observed in the absorption of the usual 1,4-disubstituted benzene. Such a shoulder peak is also observed in tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene ([2.2]-paracyclophane) at 286 nm ($\epsilon = 283$) and has been well-established as being characteristic of the close contact of two aromatic rings in a molecule at a distance shorter than the van der Waals contact.⁷ On the basis of spectroscopic results, it is concluded that the product is a tricyclic dimer (**3**), having a [2.2]paracyclophane skeleton.

When mixed crystal **1a·1b** (1:1) was irradiated at wavelengths longer than 410 nm by using a cutoff filter in order to excite only the starting monomers, the UV spectral change during the irradiation, which was measured in CH_2Cl_2 , shows clear isosbestic points. After irradiation for 60 min the reaction leveled off while retaining a highly crystalline phase; in the product the absorption ($\lambda_{\text{max}} = 369$ nm) due to **1a** and **1b** completely disappeared (Figure 2). Since these UV spectra showed that the starting monomers are completely converted into a sole product, spectroscopic measurements were carried out for the photoproduct without purification. In the ^1H NMR spectrum of the product, the olefinic proton signals still remained one-half in the integration, and proton signals, which corresponded to one cyclobutane ring, newly appeared. Upon further irradiation without a filter, the product was quantitatively converted into **3** in the crystalline state. From all these results the photoproduct is concluded to be a monocyclic dimer (**2**) having a hetero-type cyclobutane ring.

The isolation of monocyclic dimer **2** reveals that the photochemical process from mixed crystal **1a·1b** (1:1) to **3** occurs through step-growth photocycloaddition via **2**, as shown below



(7) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691.

Scheme II

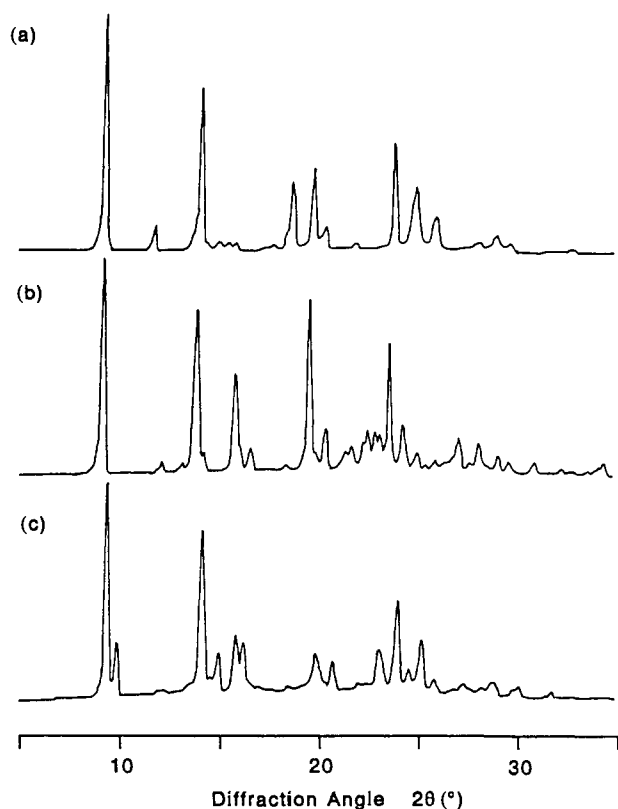
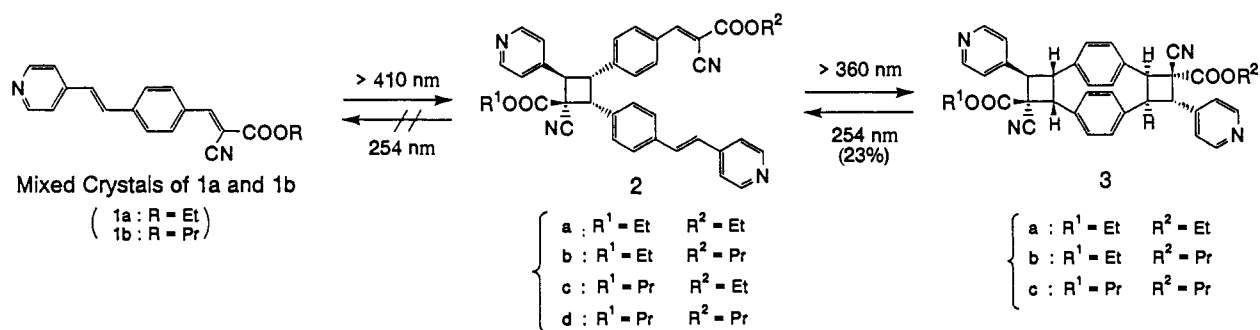


Figure 3. X-ray powder diffraction patterns of (a) mixed crystal **1a·1b** (1:1), (b) monocyclic dimer **2**, and (c) tricyclic dimer **3**.

where **1** denotes **1a** or **1b** in the mixed crystals, and **1*** and **2*** denote the photoexcited species of **1** and **2**, respectively.

X-ray powder diffraction patterns of **1a·1b**, **2**, and **3** are shown in Figure 3a–c, respectively. The continuous changes in the X-ray powder diffraction pattern from **1a·1b** to **2** and from **2** to **3** indicate that extremely high crystallinity is maintained during the entire course of the photoreaction; namely, these reactions proceed through a crystal-to-crystal transformation.

In order to determine the molecular arrangement of **1a** and **1b** in mixed crystal **1a·1b** (1:1), high-performance liquid chromatography (HPLC) of **2** was undertaken. Since four peaks with equal peak areas were observed in the chromatogram (Figure 4), these peaks doubtlessly correspond to **2a–d** in Scheme II; it is concluded that the molecular arrangement is a disordered sequence (a solid solution crystal). Though HPLC of **3** could not be measured because of the insolubility in common solvents, the HPLC result of **2** indicates that the final photoproduct comprises three kinds of tricyclic dimers **3a–c** with a ratio of 1:2:1 (Scheme II).

The same type of tricyclic dimer **3** was obtained quantitatively from a mixed crystal not only in a 1:1 ratio of **1a:1b** but also in the range from 70:30 to 5:95 (phase B).

The mixed crystals in phase A (where the proportion of **1a** was above 80 mol %) gave a homo-type linear copolymer (ca. $\overline{M}_n =$



Figure 4. High-performance liquid chromatogram of **2**.

2600) having the same skeleton as that in a polymer prepared from a pure crystal of **1a**.^{5b}

It is surprising that when **1b** contains only 5 mol % of **1a**, the crystal structure dramatically changes, resulting in the formation of **3**, and that only mixed crystals within such a very limited molar ratio give linear copolymers.

Molecular Structure of 3. A crystal structure analysis of tricyclic dimer **3** of **1a** and **1b** in a molar ratio of 5:95, was carried out. When **3** was recrystallized from a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and ethanol, a single crystal of the complex of **3** with HFIP in a 1:2 molar ratio was obtained. Figure 5a shows the molecular structure of tricyclic dimer **3** with the atom numbering; both of the ester alkyl moieties are depicted by a propyl group. Since there is a pseudocenter of symmetry between the phenylene rings facing toward each other, four carbon atoms in one cyclobutane ring have opposite chirality to the corresponding carbon atoms in the other.

Figure 5b shows the molecular structure viewed along the phenylene planes. The intramolecular nonbonded distance (*c*) between the para carbon atoms, C(5) and C(8'), is 2.85 Å. The distance (*d*) between the least-square planes formed by four carbon atoms in each of the facing benzene rings, C(6)–C(7)–C(9)–C(10) and C(6')–C(7')–C(9')–C(10'), is 3.13 Å. These distances are considerably shorter than the van der Waals contact (3.4 Å). The para carbon atoms, C(5) and C(8), bend 12.8° and 13.5°, respectively, out of the other four atoms of the aromatic ring.

The short nonbonded distances and deformation of the benzene rings are similar to those of [2.2]paracyclophane, as previously reported.⁸ The bond lengths and angles as well as the intramolecular nonbonded distances between the facing benzene rings of both **3** and [2.2]paracyclophane are listed in Table I.

(8) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr.* **1972**, *B28*, 1733.

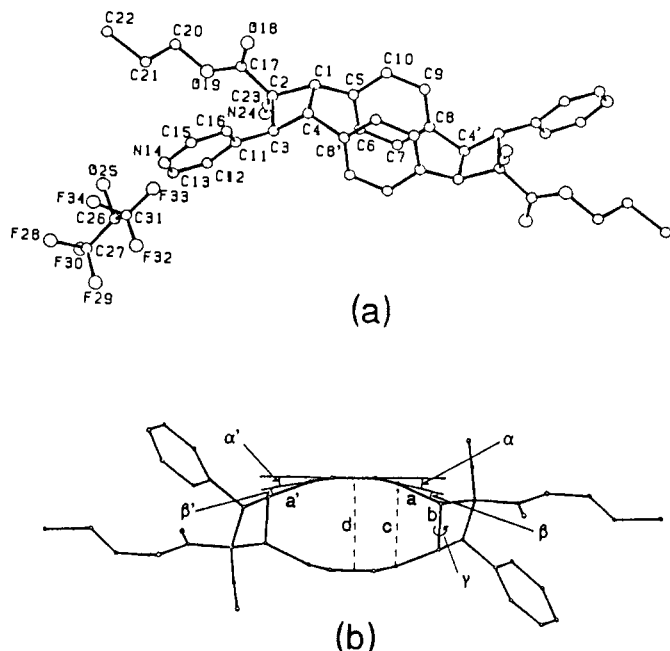


Figure 5. Molecular structures of **3**; (a) with the numbering of atoms and (b) viewed along the phenylene planes.

Table I. Bond Lengths, Angles, and Intramolecular Nonbonded Distances of **3** and [2.2]Paracyclophane

compounds	3	[2.2]paracyclophane
<i>a</i> , (Å)	1.52	1.51
<i>a'</i> , (Å)	1.50	
<i>b</i> , (Å)	1.61	1.59
<i>c</i> , (Å)	2.85	2.78
<i>d</i> , (Å)	3.13	3.09
α (deg)	12.8	12.6
α' (deg)	13.5	
β (deg)	10.6	11.2
β' (deg)	12.9	
τ (deg)	13.9	6
ref	this work	8

The bond length (*b*) of the methylene moiety (C(1) and C(4)) in **3** is slightly longer than that in [2.2]paracyclophane (*b* = 1.61 Å for **3**; *b* = 1.59 Å for [2.2]paracyclophane). Moreover, the torsion angle about the bridged methylene carbons, C(5)–C(1)–C(4)–C(8'), is larger than that of [2.2]paracyclophane (γ = 13.9° for **3**; γ = 6° for [2.2]paracyclophane). These differences may stem from the nature of the cyclobutane rings condensed to the [2.2]paracyclophane moiety, because the σ bond length of cyclobutane is longer than that of cyclohexane (0.02 Å); the ring in a cyclobutane compound puckers in order to minimize the steric repulsions between the substituents on the cyclobutane ring. Thus, the [2.2]paracyclophane skeleton has a twist shape about an axis perpendicular to and passing through the benzene rings, resulting in slightly larger values of α , β , and *d* than those in [2.2]paracyclophane.⁹ Compared to [2.2]paracyclophane, the longer length of *b* and the greater average angles of α and β in **3** indicate that tricyclic dimer **3** has a strain energy caused by two cyclobutane rings and a torsion about two methylene carbons (C(1)–C(4)) which bond the phenylene rings, in addition to that caused by the deformation of the benzene rings.

Of great interest is that the topochemical driving force is sufficient to give such a highly strained molecule **3** quantitatively, even though a great amount of internal energy should be exhausted in twisting two phenylene rings during the reaction from **2** to **3**.

Photochemical Properties of 3. The strained structure of **3** is remarkably reflected in the photochemical behavior in solution and in the crystalline state.

Table II. Summary of Crystal Data, Intensity Collection Parameters, and Refinement Details

compounds	1a·1b	3
formula	C ₁₉ H ₁₆ N ₂ O ₂ ·C ₂₀ H ₁₈ N ₂ O ₂	C ₄₀ H ₃₆ N ₄ O ₄ ·2[C ₃ H ₂ OF ₆]
crystal system	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /a
<i>a</i> , Å	18.604 (6)	9.162 (3)
<i>b</i> , Å	11.969 (6)	35.296 (15)
<i>c</i> , Å	7.521 (4)	7.662 (2)
β , deg	99.63 (5)	109.80 (2)
<i>V</i> , Å ³	1651 (1)	2331 (1)
<i>Z</i>	4	2
crystallzn solvent	ethanol	ethanol/HFIP
crystal size, mm ³	0.6 × 0.4 × 0.2	0.8 × 0.3 × 0.1
<i>D</i> _{calc} , g/cm ³	1.25	1.38
μ , cm ⁻¹	5.79	9.87
radiation, Å	Cu K α (1.541 82)	Cu K α (1.541 82)
scan mode	2 θ - ω	2 θ - ω
2 θ _{max} , deg	130	100
unique reflcns	2741	2240
obsd reflcns	2132	1520
	(<i>F</i> _o > 3 σ (<i>F</i> _o))	(<i>F</i> _o > 2.5 σ (<i>F</i> _o))
<i>R</i> factor	0.088	0.076
<i>R</i> _w factor	0.103	0.082
largest shift/esd	0.67	0.17
largest peak, e/Å ³	0.38	0.26

In poly(2,5-distyrylpyrazine) and its derivative polymers, which have cyclobutane rings in the main chain, no appreciable photocleavage was observed when these topochemically produced as-prepared crystals were irradiated.¹⁰

On the other hand, when an as-prepared crystal of **3** was irradiated with a low-pressure mercury lamp (254 nm) for 2 h, monocyclic dimer **2** was produced as a major product (23% conversion). However, further irradiation did not give detectable amounts of the monomer (**1a** and **1b**) but resulted in the formation of indefinable materials, being soluble neither in HFIP nor in trifluoroacetic acid. The enhanced tendency for a cycloreversion of **3** in the crystalline state, in comparison with poly-DSP and some other crystals, would be explained by the higher strain of **3**.

When tricyclic dimer **3** in a HFIP solution was irradiated at wavelengths of 254 ± 10 nm for 10 h, the photocleavage of one cyclobutane ring in **3** occurred, while giving **2** (69%) and the starting monomers, **1a** and **1b** (16%). The difference between the photocleavage behavior in solution and in the crystalline state indicates that the crystal lattice suppresses any cycloreversion of the cyclobutane ring to a certain extent. This type of matrix effect is very commonly observed in the thermal and photochemical behavior of the products obtained through a topochemical [2 + 2] photoreaction.¹¹

Crystallographic Interpretation of the Photoreaction of the Mixed Crystal. Figure 6a shows the crystal structure of **1a·1b** viewed along the *c*-axis with the numbering of atoms; the ester alkyl moiety is depicted by an ethyl group. The molecular arrangement of **1a·1b** (P2₁/c) is entirely different from those of pure **1a** and **1b** (P1̄).^{5,12}

The reactive molecules, which are related by a pseudocenter of symmetry, make a pair and are superimposed along the [011] direction without any displacement of the molecular long axis. The double bond at the pyridyl side in one molecule (B) is separated from the double bond at the ester side in the other molecule (C) by 3.736 (C(7)–C(16')) and 3.749 Å (C(8)–C(15')), which

(10) Unpublished result.

(11) Suzuki, Y.; Tamaki, T.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 210.

(12) There are some reports, in which the mixed crystal (a solid solution) has the different space group and molecular arrangement from the pure crystals though each pure crystal has the same space group: Kitaigorodsky, A. I. *Mixed Crystals*; Springer-Verlag: Berlin, 1984; Addadi, L.; van Mil, J.; Lahav, M. *J. Am. Chem. Soc.* **1982**, *104*, 3422.

(9) Lonsdale, L.; Milledge, H. J.; Rao, K. V. K. *Proc. Roy. Soc., Ser. A* **1960**, *555*, 82.

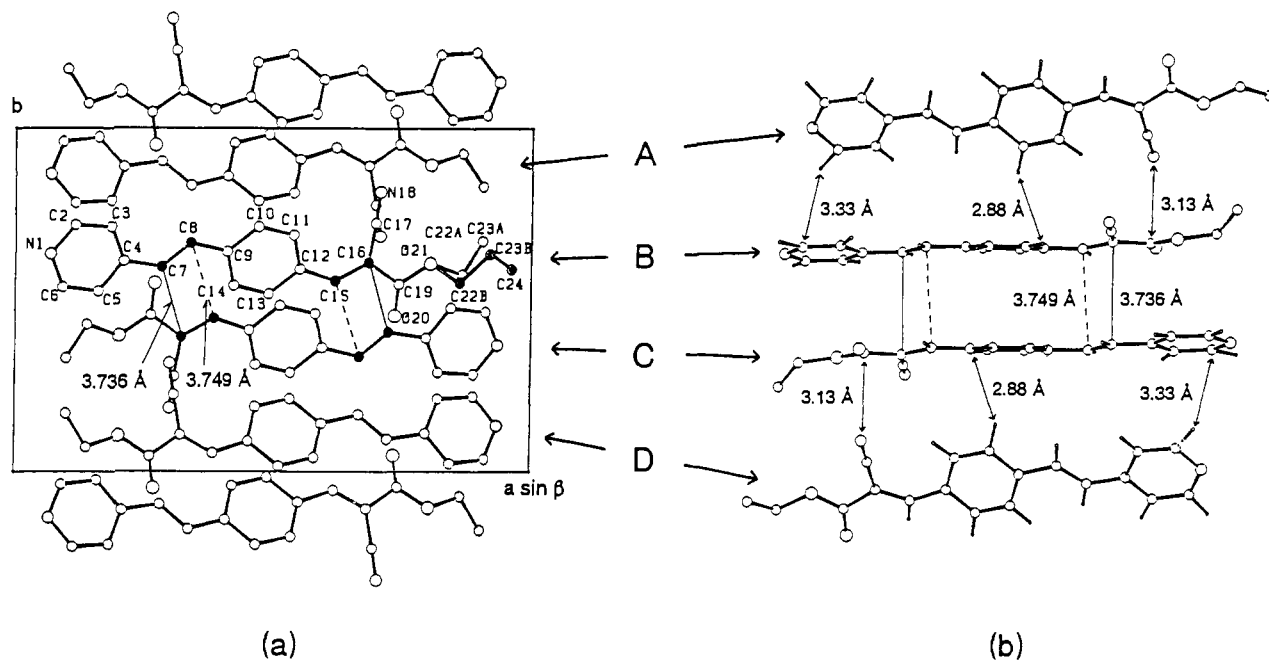


Figure 6. (a) A crystal structure of mixed crystal **1a·1b** (1:1) viewed along *c*-axis. The shaded atoms in molecule **B** correspond to propyl group; the ester moiety of the other molecules are depicted by an ethyl group. (b) Two molecules making a pair (**B** and **C**) and two neighboring molecules in the other pairs (**A** and **D**) viewed along the phenylene groups in molecules **B** and **C**.

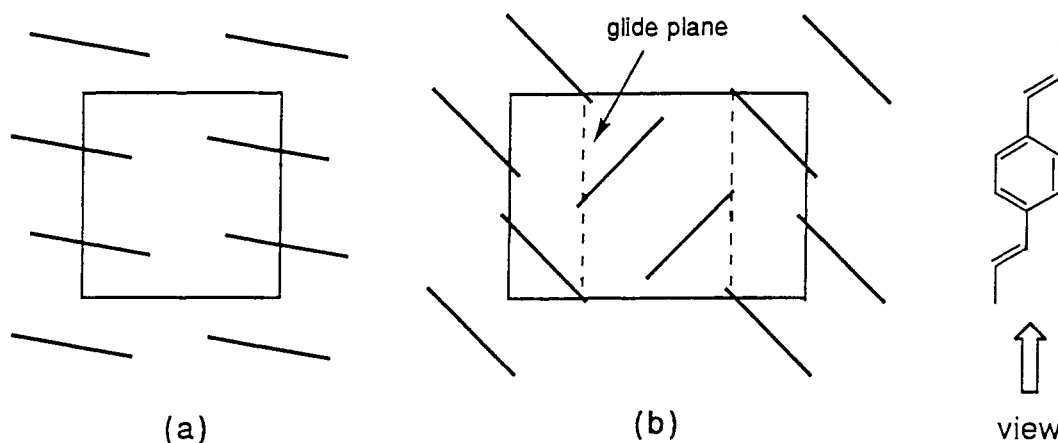


Figure 7. Schematic molecular arrangements of (a) a photoreactive β -type crystal and (b) **1a·1b** viewed along the molecular long axis.

are within the distance topochemically allowed for [2 + 2] photocycloaddition.¹⁸ Figure 6b shows the molecular arrangement of the reacting paired molecules (**B** and **C**) as well as the molecules in neighboring pairs (**A** and **D**). As is obvious in Figure 6a,b, the irradiation of **1a·1b** should give a β -type dimer having a hetero-type cyclobutane ring.

Figure 7a,b shows two typical molecular arrangements in a β -type packing crystal viewed along the direction of the molecular long axis. Each line in Figure 7 depicts the average plane of a diolefin compound. In the cases of photoreactive diolefin compounds in the β -type packing reported so far, the aromatic planes of the neighboring molecules in both sides are parallel and are superimposed to make a plane-to-plane stack (Figure 7a). The direction of the molecular plane should not be changed so greatly by the first cycloaddition under the topochemical process. Thus, the residual double bonds in the resulting dimer could still be parallel to the double bonds in the neighboring monomer; as a result, those olefins could react with each other. In contrast, in the case of **1a·1b**, which corresponds to the crystal type in Figure 7b, a pair of reacting molecules is isolated from the neighboring pairs by a glide plane. Thus, the residual double bonds in the resulting monocyclic dimer **2** could not be parallel to the double bonds in any neighboring pair. Consequently, a second cycloaddition should occur only between intramolecular olefins to give **3**, not between intermolecular olefins.

In Figure 6b molecules **A** and **B** (also **C** and **D**) come into contact with each other at the van der Waals distances (C19...N18', 3.13 Å; C12...H10', 2.88 Å, and C2...H2', 3.33 Å). Thus, after the first cycloaddition between two molecules in one pair, the residual olefins in monocyclic dimer **2** would be forced to stay within the reactive distance by virtue of a repulsion with the neighboring molecules.

The quantitative formation of highly strained compound **3** is reasonably interpreted in terms of the crystal structure of **1a·1b**, which was formed by an unexpected shuffle of the molecular arrangement from **1a** or **1b** to **1a·1b**.¹³

There is no evidence whether the crystal lattice and symmetry of **1a·1b** are the same as those of **2**, since we have not yet succeeded in a crystal structure analysis of an as-prepared crystal of **2**. However, the molecular structure of **3** coincides with that expected from the molecular arrangement of **1a·1b**; namely, the two reactive molecules in the starting crystal **1a·1b** and the tricyclic dimer molecule **3** are related by a pseudocenter of symmetry, as shown in Figures 5a and 6a. This coincidence of the crystal symmetry strongly suggests that photoreaction proceeded with a retention of the crystal lattice and symmetry of **1a·1b**.

Conclusion

A photoreactive mixed crystal (**1a·1b**) was obtained over a wide range of molar ratios of ethyl and propyl α -cyano-4-[2-(4-

pyridyl)ethenyl]cinnamates (**1a** and **1b**). The resulting crystal had a molecular arrangement quite different from pure crystals **1a** and **1b** in molar ratios from 70:30 to 5:95. Photoreaction of the mixed crystal gave a highly strained [2.2]paracyclophane derivative **3** in quantitative yield through a crystal-to-crystal transformation. The mixed crystal afforded the monocyclic dimer **2** in quantitative yield upon irradiation at wavelengths longer than 410 nm, indicating that the photoreaction of mixed crystal **1a·1b** into tricyclic dimer **3** proceeded through a step-growth mechanism.

The intramolecular aromatic rings in tricyclic dimer **3** are placed within the van der Waals distance and bend in a way similar to those of [2.2]paracyclophane. An enhanced photocycloreversion of the cyclobutane ring in the crystalline state was interpreted by such a highly strained structure of **3**.

Experimental Section

Measurements. Infrared spectra were measured on a Jasco IR-810 spectrophotometer, and ^1H NMR spectra were measured on a Jeol GX-400 instrument. Ultraviolet absorption spectra were measured on a Shimadzu UV-260 spectrophotometer at a concentration of 10.0 mg/L in CH_2Cl_2 or HFIP. HPLC was performed on a steel column (4 mm \times 250 mm) packed with LiChrosorb Si 60 (5 μm , Merck and Co.) at a flow rate of 0.5 mL/min with ethyl acetate as an eluent, and the absorbance at 330 nm was monitored on a Shimadzu SPD-2A spectrophotometric detector. Differential scanning calorimetry (DSC) was measured on a Shimadzu DSC-50 instrument or a Rigaku Thermoflex TG-DSC under a 50 mL/min nitrogen stream at a heating rate of 5 $^\circ\text{C}/\text{min}$ for about 5 mg of the sample. X-ray powder diffraction analyses were carried out with a Rigaku Rotaflex RU-200 spectrometer ($\lambda = 1.54184 \text{ \AA}$).

Preparation of the Mixed Crystals of 1a and 1b in Various Ratios. Monomers **1a** and **1b** were prepared as previously described.¹⁴ Mixed crystals of **1a** and **1b** in various ratios were obtained by the cocrystallization of a mixture of **1a** and **1b** in the corresponding ratio from ethanol. The ratios of **1a** and **1b** in the mixed crystals were determined by 400-MHz ^1H NMR. Melting points of **1a·1b** were measured by DSC (**1a:1b**): phase A, 90:10 = 163–173 $^\circ\text{C}$, 82:18 = 158.5–168.5 $^\circ\text{C}$; phase B: 70:30 = 153.5–165 $^\circ\text{C}$, 60:40 = 144.5–151 $^\circ\text{C}$, 50:50 = 145.5–151.5 $^\circ\text{C}$, 31:69 = 143.5–148.5 $^\circ\text{C}$, 19:81 = 142–150 $^\circ\text{C}$, 5:95 = 146.5–151 $^\circ\text{C}$.

Photocycloaddition. Fine powder of mixed crystals **1a·1b** were dispersed in 90 mL of a mixture of water/methanol (90/10 v/v) containing a few drops of a surfactant (NIKKOL TL-10FF) and were irradiated with a 500-W super-high-pressure mercury lamp (EIKOUSA EHB WF-500) set outside of the flask with vigorous stirring under a nitrogen atmosphere at room temperature.

(1RS,2RS,3RS,4RS)-1-Cyano-3-[4-[(2-alkoxycarbonyl)-2-cyanoethyl]phenyl]-2-(4-pyridyl)-4-[4-[2-(4-pyridyl)ethenyl]phenyl]cyclobutanecarboxylic acid ester 2: a mixture of ethyl ethyl, ethyl propyl, propyl ethyl, and propyl propyl for alkyl groups of alkoxy carbonyl and ester. Mixed crystal **1a·1b** was quantitatively converted into dimer **2** upon irradiation through a cutoff filter (Kenko L42). **2:** IR (KBr) 2230, 1720, 1600, 980, 840 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.98 (t, 1.5 H, $J = 8$ Hz), 1.08 (t, 1.5 H, $J = 8$ Hz), 1.28 (t, 1.5 H, $J = 7$ Hz), 1.48 (t, 1.5 H, $J = 7$ Hz), 1.69 (q, 1 H, $J = 7$ Hz), 1.88 (q, 1 H, $J = 7$ Hz), 4.0–4.4 (m, 2 H), 4.43 (t, 2 H, $J = 6$ Hz), 4.53 (q, 1 H, $J = 7$ Hz), 4.90 (d, 1 H, $J = 10$ Hz), 5.45 (t, 1 H, $J = 11$ Hz), 5.63 (d, 1 H, $J = 11$ Hz), 7.2–7.3 (m, 3 H), 7.40 (d, 2 H, $J = 8$ Hz), 7.63 (d, 2 H, $J = 8$ Hz), 7.74

(d, 1 H, $J = 16$ Hz), 7.96 (d, 2 H, $J = 8$ Hz), 8.09 (d, 2 H, $J = 6$ Hz), 8.23 (d, 2 H, $J = 6$ Hz), 8.47 (s, 1 H), 8.63 (d, 2 H, $J = 6$ Hz), 8.98 (d, 2 H, $J = 6$ Hz); UV λ_{max} (ϵ in CH_2Cl_2) 304.8 nm (59700). The melting range (101–145 $^\circ\text{C}$) and decomposition (191 $^\circ\text{C}$) were detected by TG-DSC.

(2RS,3RS,4RS,5RS,10SR,11SR,12SR,13SR)-3,11-Dicyano-4,12-di(4-pyridyl)pentacyclo[12.2.2.2^{6,9}.0^{2,5}.0^{10,13}]jicosa-6,8,14,16,17,19-hexaene-3,11-dicarboxylic acid diester 3: a mixture of ethyl ethyl, ethyl propyl, propyl ethyl, and propyl propyl diesters. Mixed crystal **1a·1b** was quantitatively converted into dimer **3** upon irradiation without any cutoff filter. **3:** IR (KBr) 2220, 1740, 1420, 1220, 830 cm^{-1} ; ^1H NMR (TFA-d) δ 1.02 (t, 3 H, $J = 7$ Hz), 1.34 (t, 3 H, $J = 7$ Hz), 1.75 (q, 2 H, $J = 7$ Hz), 4.2–4.5 (m, 4 H), 4.44 (d, 2 H, $J = 9$ Hz), 5.36 (dd, 2 H, $J_1 = 11$ Hz, $J_2 = 9$ Hz), 5.51 (d, 2 H, $J = 11$ Hz), 6.77 (d, 2 H, $J = 8$ Hz), 7.01 (s, 4 H), 7.26 (d, 2 H, $J = 9$ Hz), 8.25 (d, 4 H, $J = 6$ Hz), 8.95 (d, 4 H, $J = 6$ Hz); UV (ϵ in HFIP) 247.4 nm (696), 285.6 nm (283).

Photochemical Reactions of 3. (1) Photoreaction in solution: A solution of **3** (30 mg) in HFIP (4 mL) was irradiated at wavelengths of 254 ± 10 nm, generated from a spectroirradiator equipped with a 2000-W xenon lamp and a grating monochromator (Jasco CRM-FM). (2) Photoreaction in the crystalline state: As-prepared crystal **3**, consisting of **1a** and **1b** (1:1), was dispersed in 300 mL of water containing a few drops of a surfactant (Nikkol TL-10FF) and was irradiated with a 20-W low-pressure mercury lamp (Eikousha EL J-20) set inside the flask with vigorous stirring under a nitrogen atmosphere.

X-ray Structure Determinations. 1a·1b. Intensity data were measured on a Mac-Science four-circle diffractometer (MXC-18) with graphite monochromated $\text{Cu K}\alpha$ radiation. Accurate cell dimensions were obtained by a least-squares refinement of 20 reflections in the range $40^\circ < 2\theta < 60^\circ$. Data were collected with three check reflections. The observed reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the solutions and refinements; no absorption correction was made. The structures were solved by a direct method with the MULTAN 78 program and refined by a full-matrix least-squares method with the SHELXS 76 program. The positions of hydrogen atoms were obtained from a difference map. Final refinements were performed with the anisotropic thermal parameters for the non-hydrogen atoms and with isotropic ones for the hydrogen atoms. The hydrogen atoms of the ester alkyl groups could not be located in the difference map and were not included in the least-squares calculation. The occupancy factors of the ethyl and propyl groups in the disordered ester moiety were fixed with 0.5; the bond lengths in the alkyl groups were fixed with 1.50 \AA for the C–C bond and 1.46 \AA for the O–C bond.

3: Intensity data were measured on a Rigaku four-circle diffractometer (AFC-5) with graphite monochromated $\text{Cu K}\alpha$ radiation. Accurate cell dimensions were obtained by a least-squares refinement of 20 reflections in the range $40^\circ < 2\theta < 60^\circ$. Data were collected with three check reflections. The observed reflections with $|F_o| > 2.5\sigma(|F_o|)$ were used in the solutions and refinements; no absorption correction was made. The structures were solved by a direct method with the MULTAN 82 program and refined by a full-matrix least-squares method with the SHELXS 76 program. The positions of hydrogen atoms were obtained from a difference map. Final refinements were performed with the anisotropic thermal parameters for the non-hydrogen atoms and with isotropic ones for the hydrogen atoms. Isotropic thermal parameters of hydrogen atoms attached to sp^3 carbons are constructed to 1.2 times the B_{eq} of parent carbons.

The intensity data collection, refinement details, and crystal data are summarized in Table II.

Supplementary Material Available: Tables of final molecular coordinates, thermal parameters, bond lengths, and bond angles for **1a·1b** and **3** (5 pages). Ordering information is given on any current masthead page.

(13) An alternative arrangement of paired molecules related by glide and 2-fold axis symmetries similar to **1a·1b** was reported for the pyrene crystal: Kitaigorodsky, A. I. *Organic Crystals and Molecules*; Academic Press: New York, 1973.

(14) Ichimura, K.; Watanabe, S. *J. Polym. Chem. Ed.* **1982**, *20*, 1420.