Crystallographic Interpretation of the Topochemical Behavior of Alkyl α-Cyano-4-[2-(4-pyridyl)ethenyl]cinnamates in the Crystalline State. Enhancement of Photopolymerizability by Complex Formation[1]

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ABSTRACT: The photochemical behavior of methyl, ethyl, and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]-cinnamates (**1a**–**1c**) was investigated in the crystalline state. The behavior was highly diversified and was found to be strongly dependent on even a slight modification of the ester alkyl group in these monomers and on the solvent used for recrystallization. Irradiation of crystal **1a** gave a β-homo-type dimer and oligomers. On the other hand, irradiation of monomers **1b** and **1c** gave either an α-homo-type dimer or a linear polymer; **1b** led to a polymer ($\overline{M}_n$ = 3100) through an "even-numbered polymerization mechanism", whereas **1c** led to a photostable dimer crystal in quantitative yield. Two dimers (**2b** and **2c**) crystallized as complexes with solvents when the dimers were recrystallized from solutions of conventional solvents, such as alcohols, butyl acetate, and *p*-xylene. Those dimer complexes consisting of a dimer with ethanol or propanol showed a higher photoreactivity compared with the corresponding dimer alone. Regarding photoirradiation, these complexes gave linear high polymers having the same type repeating structure as that obtained directly from **1b**. The topochemical behavior of the monomers (**1a**–**1c**) and of the dimer complexes (**2b**·EtOH and **2c**·PrOH) was completely interpreted from their crystal structures. Furthermore, the crystal structure required for the formation of a high polymer is discussed in terms of the length of the monomer repeating unit in the stack in those crystals.

Introduction

As a result of intensive studies concerning topochemical [2 + 2] photopolymerization during the last decade, the correlation between the molecular structure and the topochemical reactivity has been revealed for a large number of photochemical reactions of diolefinic crystals. In our previous reports,[2] it was established that 1,4-diethenylaromatic derivatives, substituted by phenyl, 2- or 4-pyridyl, pyrazyl, or alkoxycarbonyl, with or without the cyano group, were potent in forming photoreactive α- or β-packing crystals. Recently, such an empirical rule concerning potent substituents was successfully applied to unsymmetrically substituted diolefin crystals as being photoreactive. As a result, a variety of topochemical products were prepared by [2 + 2] photoreactions of these crystals.[3]

The molecular arrangements in photoreactive, unsymmetrically substituted diethenylaromatic crystals are roughly classified into α- and β-type packings, similar to those of monoolefin compounds. In α-type packing, molecules are superimposed in the direction of the long molecular axis displaced by about half a molecule. In β-type packing, molecules are superimposed without displacement in the direction of the long molecular axis. Each packing of the α- and β-types is further classified into translation- and centrosymmetry-type packings. Thus, we define here the four kinds of molecular arrangements for unsymmetric diethenylaromatic crystals, as shown in Scheme I.

Corresponding to the molecular arrangements, the photoproducts are also classified into four types: α- and β-type, and homo- and hetero-type adducts. The α-type photoadduct is derived from an α-type packing monomer and is characterized by a cyclobutane ring trans-1,3-substituted with arylene groups. The β-type photoadduct is derived from a β-type packing monomer and is characterized by a cyclobutane ring cis-1,2-substituted with the arylene groups. Each adduct of the α- and β-types is further classified into homo- and hetero-type adducts. A homo-type adduct, which is derived from either the α-centrosymmetry- or the β-translation-type packing, is formed from the same olefin groups. On the other hand, the hetero-type adduct, which is derived from either the α-translation- or the β-centrosymmetry-type packing, is formed from different olefin groups.

As a result, four types of polymers having a linear or zigzag main-chain structure can be assumed to be formed, depending on the molecular arrangements of the starting diethenylaromatic crystals.

In the β-type crystals of the unsymmetric diolefin molecules, each two molecules often make a pair and react preferentially to each other for the first photocyclodimerization.[4] In a few examples cyclophane-type dimers were obtained from such β-hetero-type packing crystals.[5] However, neither the zigzag type of high polymer nor the homo-type cyclophane has been obtained yet.

In the present paper we demonstrate the various photochemical behaviors of methyl, ethyl, and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate crystals (**1a**–**1c**) and the enhancement of polymerizability of the dimers by means of complex formation with a small molecule. Furthermore, the photochemical behavior of these unsymmetric diolefin crystals is interpreted in correlation to the crystal structures of the monomers, dimers, and the dimer complexes.

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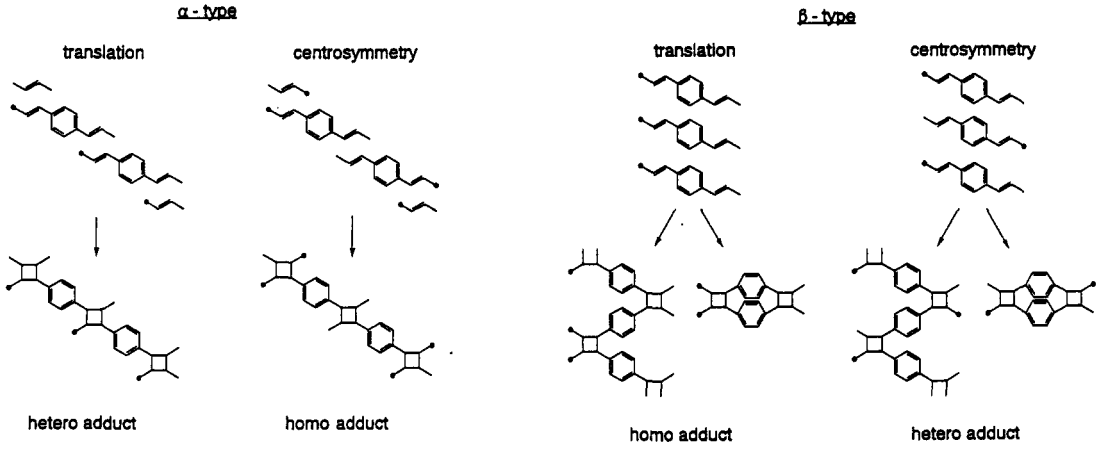
Scheme I



Results and Discussion

Diversified Photochemical Behavior on Varying the Ester Alkyl Group in the Monomers. (a) Photochemical Behavior of Methyl, Ethyl, and Propyl α-Cyano-4-[2-(4-pyridyl)ethenyl]cinnamates (1a–1c). Irradiation of **1a** for 26 h at room temperature gave amorphous oligomers (η_{inh} = 0.13 dL/g) containing a considerable amount of a dimer. The dimer (**2a**) was separated from the monomer and oligomers by preparative TLC. The cyclobutane in **2a** was confirmed by ^{1}H NMR and MS spectroscopy to be of the β-homo-type structure, to which two pyridyl groups are attached; no other types of dimer were detected. Even though the dimerization proceeded with a morphological transformation from the crystalline to the amorphous phase, the β-homo-type dimer was exclusively obtained. The ^{1}H NMR of the resulting oligomers showed indefinable broad signals in the region of a cyclobutane proton. The spectral evidence implies that the dimerization proceeded under the lattice control of the monomer crystal, whereas a succeeding reaction occurred nontopochemically to give the amorphous oligomers.[3e]

Upon irradiation of **1b** for 7 h at room temperature, a homo-type linear polymer ($\overline{M}_n$ = 3100) was produced with the accumulation of one type of the dimer at the intermediate stage.[6] Exclusive photoexcitation of the monomer with wavelengths longer than 410 nm resulted in a quantitative formation of the dimer **2b**. The structure of **2b** was confirmed by ^{1}H NMR and MS spectroscopy to have an α-homo-type cyclobutane, on which two ester and two cyano groups are substituted. This cyclobutane structure was later substantiated by crystal structure analysis.

The GPC profile (Figure 1a) showed that the products consisted of molecular species of only an even-numbered degree of polymerization during the early stage of the photoreaction (2 h). On further irradiation (7 h), the polymerization of **1b** proceeded along with a morphological transformation from the crystalline to the amorphous phase; the GPC profile (Figure 1b) became bimodal with polymerization. Its NMR spectrum showed two types of signals of cyclobutane protons: two proton signals appearing at δ 4.57 and 4.66 ppm (broad singlet) were assigned to be a cyclobutane ring substituted by two pyridyl groups, and proton signal appearing at δ 5.04 ppm (singlet) was assigned to be a cyclobutane ring substituted by two cyano and two ethoxycarbonyl groups. The GPC and ^{1}H NMR analyses indicated that the final products comprised mainly an α-homo-type polymer produced by a topochemically controlled process accompanied by a small amount of a nontopochemically produced polymer, which corresponded to a region of higher molecular weight in the GPC profile.[3e]

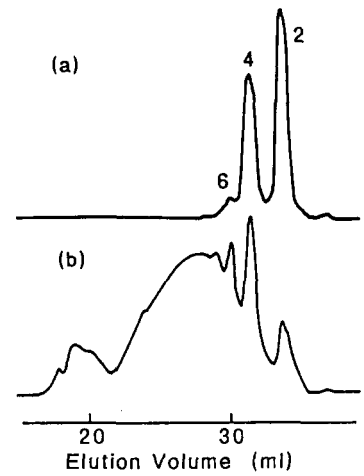


Figure 1. GPC profiles of the reaction products of **1b**: (a) irradiated for 2 h and (b) irradiated for 7 h.

As previously reported,[3c] the irradiation of **1c** led quantitatively to a photostable dimer, which had the same structure as **2b**.

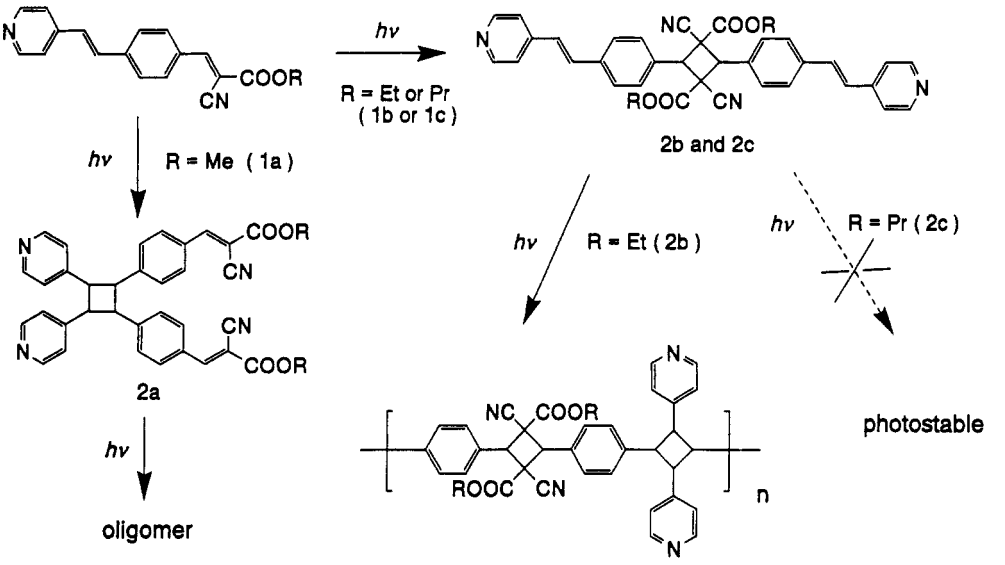
As shown in Scheme II, the photochemical behavior of the monomers in the crystalline state was quite different from each other in spite of the only slight modification in the chemical structure of the ester alkyl group in these monomers. The results doubtlessly reflect typical topochemical reaction behavior.

(b) Crystal Structure Analyses of 1a–1c. The crystal structures of **1a–1c**, determined by X-ray crystallography, were compared with each other in order to explain the observed topochemical behavior.

The molecular arrangements in the stacks of **1a–1c**, related to the photoreaction, are shown in Figure 2.

In the crystal of **1a** (Figure 2a), the monomer molecules are superimposed along the *b* axis to form a parallel plane-to-plane stack; the nearest molecules in the stack are related by a β-translation. Namely, the molecules in the crystal of **1a** are not displaced by half a molecule in the direction of the molecular long axis, in contrast to photopolymerizable α-type packing crystals.[7] The translationally related double bonds having the same substituents are the nearest (4.049 Å) and are within the photoreactive range accepted for the topochemical reaction in the crystalline state. This molecular arrangement results in the formation of a β-homo-type cyclobutane ring. Of further interest is the fact that the first reaction occurs

Scheme II



exclusively at the pyridyl side, although the distance between the double bonds substituted by the pyridyl group is absolutely equal to that between the double bonds substituted by the ester group. Such a reaction cannot be explained in terms of the topochemical rule, since this rule involves only the positional relationship between the reactive olefin pairs. However, this regioselective reaction of double bonds in the identical topochemical environment could be reasonably explained by both steric factors (cavity and potential energy) and electronic factors (perturbation energy from orbital interaction).[8] Figure 2b shows that the crystal of **1b** has an α-centrosymmetry-type packing structure, in which the molecule is related to its neighboring molecules by two different inversion centers to make a plane-to-plane stack. The double bonds related by one inversion center are separated by a distance of 3.758 Å (C(15)=C(16)), whereas the double bonds on the other side of the molecule by the other inversion center are separated by a distance of 4.868 Å (C(7)=C(8)). Accordingly, the former double bonds react predominantly according to the topochemical principle.

As shown in Figure 2c,[3c] the crystal structure of **1c** is nearly isomorphous to that of **1b**. The distance between the double bonds on the ester side (3.729 Å) is within the photoreactive range, whereas the distance between the double bonds on the pyridyl side (5.088 Å) is too far to react.

On the basis of crystal structure analyses, the experimental results concerning the exclusive formation of β-type adducts from **1a** and α-type adducts from **1b** and **1c** could be clearly explained.

Although the molecular arrangements in stacks of **1b** and **1c** are quite similar to each other, **1c** photodimerized quantitatively into a photostable α-type dimer (**2c**), whereas **1b** photodimerized into a photoreactive dimer (**2b**); further irradiation gave a polymer. The different topochemical behavior would be explained by the difference in the distances between the residual double bonds on the pyridyl side in as-prepared dimers, **2b** and **2c**. In the case of photostable dimer **2c**, the distance between the residual double bonds is longer than that accepted for a photoreaction in the crystalline state (5.066 Å). In contrast, although it has not yet yielded crystallographic information concerning as-prepared dimer **2b**, the dimerization of **1b** makes the distance between the residual double bonds in the dimer close to being reactive.

Even-Numbered Polymerization Mechanism of 1b. In order to explain the even-numbered polymerization mechanism of **1b**, various elementary processes were considered regarding photoreaction. If photoadducts greater than a trimer are simply represented by P, all the elementary processes can be expressed in eqs 1–7, where M, D, P_o, and P_e represent the monomer, dimer, and polymers (greater than trimer) with odd- and even-numbered degrees of polymerization; M*, D*, P_o*, and P_e* represent the corresponding excited species, respectively.

$$M \xrightarrow{h\nu} M^* \qquad D \xrightarrow{h\nu} D^* \qquad P_e \xrightarrow{h\nu} P_e^*$$

$$M^* + M \xrightarrow{k_1} D \tag{1}$$

$$M^* + D \xrightarrow{k_2} P_o \tag{2}$$

$$M + D^* \xrightarrow{k_3} P_o \tag{3}$$

$$D^* + D \xrightarrow{k_4} P_e \tag{4}$$

$$D^* + P_e \xrightarrow{k_5} P_e \tag{5}$$

$$D + P_e^* \xrightarrow{k_6} P_e \tag{6}$$

$$P_e^* + P_e \xrightarrow{k_7} P_e \tag{7}$$

Upon irradiation with the wavelengths longer than 280 nm, the monomer **1b** almost disappeared during the early stage of polymerization; the dimer and the tetramer were predominantly produced with a small amount of hexamer, as shown in Figure 1a. The accumulation of the dimer and tetramer without the trimer indicates that not only is the excited monomer unable to react with the dimer, but also the excited dimer with the monomer: namely, eqs 2 and 3 do not occur. This means that the monomer in either ground or excited state cannot react with any species produced during photopolymerization. This selective reaction of the monomer is strongly supported by the fact that dimer **2b** was obtained in quantitative yield

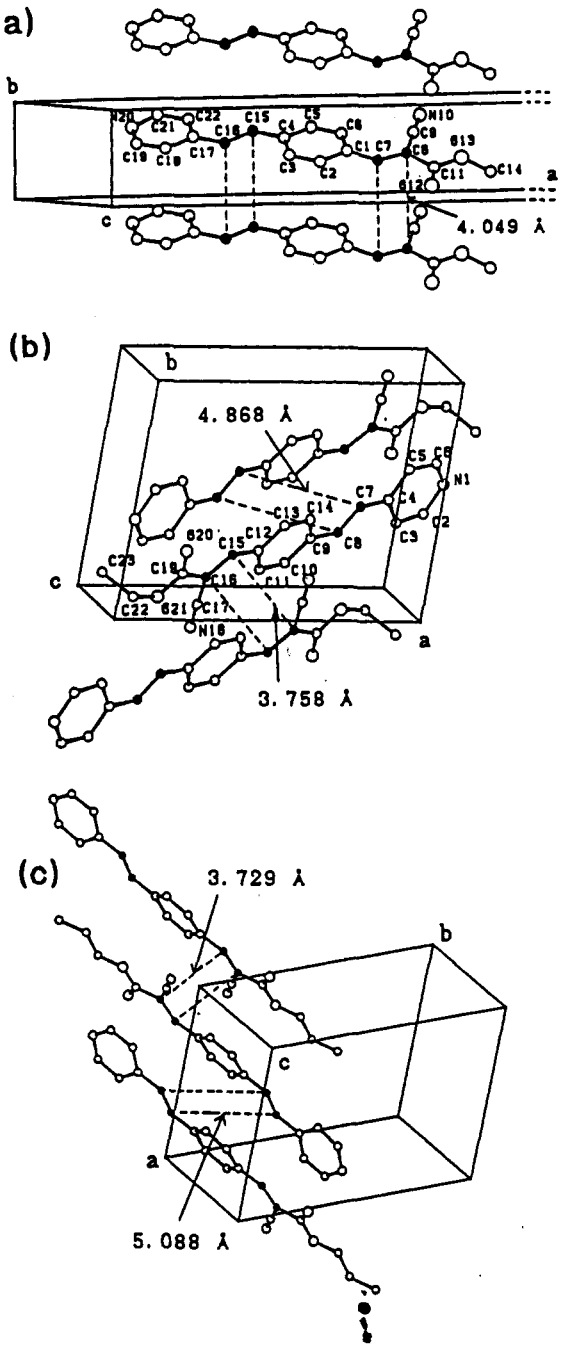


Figure 2. Crystal structures of **1a** (a), **1b** (b), and **1c** (c). The darkened atoms correspond to ethylenic carbons.

when monomer **1b** was exclusively photoexcited with light of a wavelength longer than 410 nm. There is therefore no chance to yield photoproducts with an odd-numbered degree of polymerization (P_o). As a result, the polymerization of **1b** should proceed by eqs 1 and 4–7, resulting in even-numbered polymerization. Moreover, since only the ester side double bonds react in the dimerization, all of the growing species should have pyridylethenyl groups at both sides of the terminals during the entire course of polymerization.

It is obvious that the even-numbered polymerization mechanism can be interpreted in terms of the influence of the topochemical environment of the double bonds during the photopolymerization, as shown in Figure 3.

Since the molecule in a symmetric diolefin crystal has a center of symmetry, the molecule is related to its two neighboring molecules by an equivalent inversion center (Figure 3a), resulting in the same topochemical environment around both double bonds. Thus, symmetric diolefin crystals do not have a definitive even-numbered polymerization mechanism with an accumulation of the dimer, which has been confirmed by gel permeation chromatography (GPC) analyses of the oligomers obtained on the photoirradiation of diolefins with wavelengths longer than 280 nm.[9]

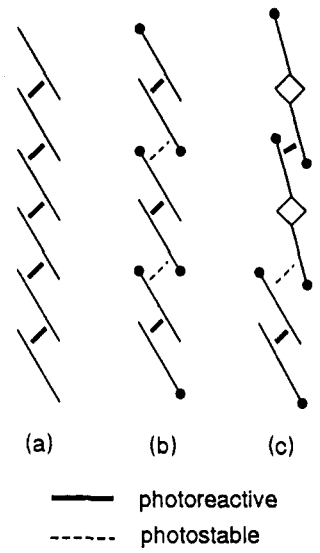


Figure 3. Schematic molecular arrangements (a) in the monomer crystal of a symmetric diolefin, (b) in the monomer crystal of an unsymmetric diolefin, and (c) in the partially dimerized crystal of an unsymmetric diolefin.

In contrast, as shown in Figure 3b, the molecule of unsymmetric diolefins in an α-centrosymmetry-type packing is related to its neighboring molecules by two different inversion centers, since the unsymmetric diolefin molecule has two double bonds substituted by different groups. This means that the topochemical environment around the double bonds is different (in the crystal of **1b**, the ester side and pyridyl side double bonds are separated by 3.758 and 4.868 Å, respectively). Therefore, a single type of dimer can be accumulated spontaneously during the intermediate stage of polymerization without any control of the wavelength of irradiating light. Furthermore, the distance between the residual double bond of the resulting dimer and the pyridyl side double bond of the neighboring monomers would be out of the photoreactive range, whereas the distance between the residual double bonds of two neighboring dimers would be suitable to react with each other (Figure 3c). Consequently, polymerization completely proceeds through the even-numbered polymerization mechanism.

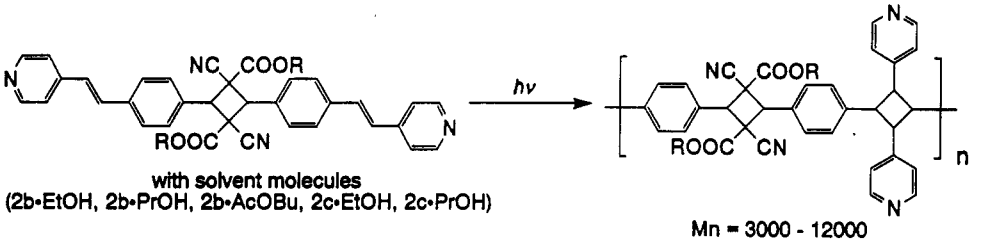
Ethyl methyl 1,4-phenylenediacrylate (**1d**) is arranged according to the same α-centrosymmetry-type packing (the methyl ester side and ethyl ester side double bonds are separated by 3.891 and 4.917 Å, respectively).[3a] The polymerization of **1d** mainly gave products having an even-numbered degree of polymerization with the accumulation of dimer. However, a small amount of the trimer was detected during the early stage of polymerization, indicating the occurrence of a reaction of the monomer with the dimer.[3a,10] Moreover, though monomer **1c** is also arranged in the α-centrosymmetry-type packing, irradiation of **1c** with wavelengths longer than 280 nm gave a photostable dimer. The difference in the reaction behavior of **1b**, **1c**, and **1d** in the same α-centrosymmetry-type packing depends on the distances between the monomer and the dimer and between the dimers, which are mainly governed by the topochemical environment of the initial monomer crystals.

Table I
Polymerization of the Dimer Complexes[b]

compound	light source,[a] W	dispersant	reactn time, h	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	morphology of photoproducts
1b	100	water	7	99	3100	1.81	amorphous
2b·EtOH	500	water	5	94	5000	1.77	amorphous
2b·PrOH	500	no	5	99	5200	1.72	amorphous
2b·AcOBu	500	no	5	96	3600	1.91	amorphous
2b·xylene	500	no	5	0			
1c	500	water	2	100	(dimer)		crystal
2c·EtOH	100	water	4	99	12000	1.42	crystal
2c·PrOH	100	water	4	99	3000	1.78	crystal

[a] 100-W lamp set inside of the flask; 500-W lamp set outside of the flask. [b] The reaction of the monomers and dimers was carried out at room temperature and −20 °C, respectively.

Scheme III



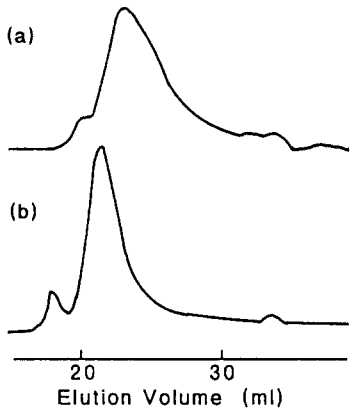


Figure 4. GPC profiles of the reaction products of **2b**·EtOH (a) and **2c**·EtOH (b).

Strategies for Obtaining High Molecular Weight Polymer. (a) Photochemical Behavior of Complexes of the Dimers with Small Molecules. When **2b** was recrystallized from ethanol, 1-propanol, butyl acetate, or *p*-xylene, 1:1 complexes of **2b** with a solvent molecule were obtained (**2b**·EtOH, **2b**·PrOH, **2b**·AcOBu, and **2b**·xylene). As shown in Figure 4a, irradiation of **2b**·EtOH for 5 h gave an amorphous polymer with a molecular weight ($\bar{M}_n$) of 5000, higher than that of the polymer obtained directly from **1b** ($\bar{M}_n$ = 3100). Its GPC profile was nearly a unimodal molecular weight distribution, and its ^{1}H NMR spectrum showed a predominant formation of two kinds of cyclobutane rings; two proton signals appearing at δ 4.57 and 4.66 ppm (broad singlet) were assigned to be a cyclobutane ring substituted by two pyridyl groups, and the proton signal appearing at δ 5.04 ppm (singlet) was assigned to be a cyclobutane ring substituted by two cyano and two ethoxycarbonyl groups. These analyses indicate that polymerization proceeds strictly under the control of the crystal lattice of **2b**·EtOH to give an α-homo-type polymer having the same structure as that obtained from **1b**.

Complexes **2b**·PrOH and **2b**·AcOBu showed the same type X-ray powder diffraction pattern as **2b**·EtOH and also photopolymerized into amorphous polymers having an α-homo-type structure with molecular weights ($\bar{M}_n$) of 5200 and 3600, respectively, as well as that from **2b**·EtOH. However, **2b**·xylene, which showed a different X-ray powder diffraction pattern, was photostable.

The photopolymerization of the complex of a dimer with an alcohol molecule, was also attempted with dimer **2c**, which was photostable in an as-prepared crystal. A complex of **2c** with an equimolar amount of 1-propanol (**2c**·PrOH), which was obtained by recrystallization of **2c** from 1-propanol, was converted into a crystalline polymer ($\bar{M}_n$ = 3000) upon irradiation for 1 h. The cyclobutane rings in the resulting polymer were the same type structure as those from **2b**.

Complex **2c**·EtOH, which was also formed by recrystallization from ethanol, showed an X-ray powder diffraction pattern different from **2c**·PrOH. Irradiation of **2c**·EtOH gave a crystalline polymer with a molecular weight ($\bar{M}_n$) of 12 000, which was extremely higher than that of **2c**·PrOH, as shown in Figure 4b. Polymerization proceeded by control of the crystal lattice, which was confirmed by its GPC profile and ^{1}H NMR spectrum. The resulting polymer had cyclobutane rings of the same structures as those from **2b**, **2b**·EtOH, and **2c**·PrOH.

The α-homo-type dimers generally crystallized as complexes with an appropriate small solvent molecule; these dimer complexes with an alcohol often enhanced the reactivity and polymerizability of the dimers. The relationship between the complexation and photopolymerizability of these crystals strongly suggests that complexation may be a useful method for a crystal design aimed at enhancing photopolymerizability.

(b) Crystal Structure Analyses of 2b·EtOH and 2c·PrOH. In order to elucidate the role of an alcohol molecule for the enhancement of the photoreactivity of the dimers, crystal structure analyses of as-prepared dimer crystals and the complexes of the dimers with the alcohol were performed. The crystal structure analyses were successful for **2b**·EtOH and **2c**·PrOH. However, the crystal structure analyses of **2b** and **2c**·EtOH could not be solved since recrystallized **2b** showed a different crystal packing from as-prepared **2b** (determined by X-ray powder diffraction analysis) and the standard reflections of **2c**·EtOH changed during data collection.

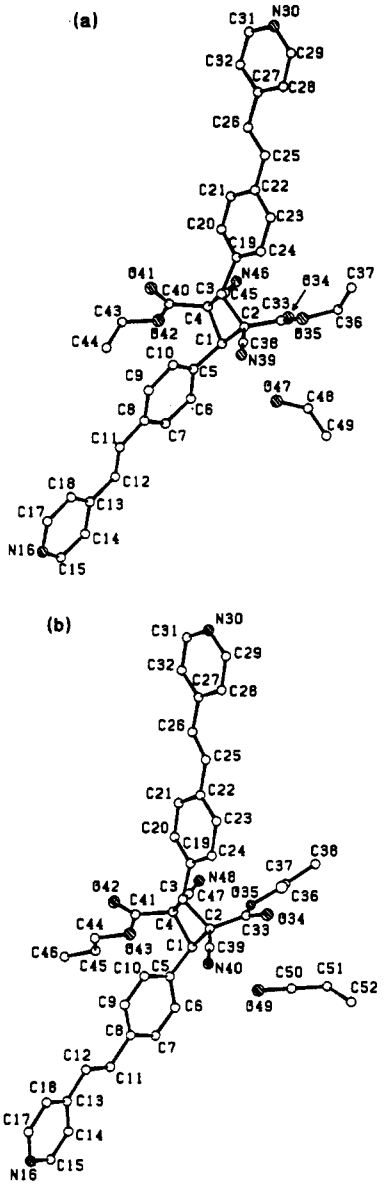


Figure 5. Molecular structures of **2b**·EtOH (a) and **2c**·PrOH (b) with numbering of atoms. The shaded atoms correspond to heteroatoms.

The molecular structures with the numbering of atoms of **2b**·EtOH and **2c**·PrOH are shown in Figure 5a and b, respectively. Though the molecular structures of the dimers in complexes **2b**·EtOH and **2c**·PrOH are almost identical with each other, they are different from that in the **2c** crystal. Since the dimer molecule in the crystal of **2c** occupies a crystallographic center of symmetry, as reported in our previous paper,[3c] the cyclobutane ring is required to be planar, and the phenylene groups are also required to be parallel to each other according to symmetry. On the other hand, since the dimer molecules in complexes **2b**·EtOH and **2c**·PrOH have no inversion center in the molecule, the cyclobutane rings are puckered and the two phenylene rings, attached to cyclobutane rings, are nearly perpendicular to each other, as is shown in Figure 5a.[11]

The crystal structures of complexes **2b**·EtOH and **2c**·PrOH are shown in Figure 6a and b, respectively. The dimer component in complex **2c**·PrOH is related to its neighboring molecules by two different inversion centers. Two pairs of residual double bonds are separated by distances of 3.835 (C(11)=C(12)) and 4.208 Å (C(25)=C(26)). Therefore, the photoreaction would proceed through the formation of α-type cyclobutane rings.

A suitable length of the monomer repeating unit in a stack (L) is considered to be ~7.5 Å for the formation of a cyclobutane ring (confirmed by using CPK molecular models). Moreover, this length seems to be reasonable on the basis of the fact that L is 7.0–7.7 Å for the monomers, which gave a linear high polymer upon irradiation in the crystalline state (eight compounds satisfied this range among the nine compounds for which the structures have been solved so far).[2,3] In addition, since the polymers, which were obtained both from the monomer and from the dimer, have the same main-chain structure, L would be a common parameter for the polymerizability of both monomer and dimer crystals. We thus examined the relationship between L and photoreactivity in order to explain the enhanced reactivities of **2b**·EtOH and **2c**·PrOH in comparison with as-prepared crystals **2b** and **2c**. The dependence of the topochemical reactivity on L is summarized in Table II.

The elongation of L from 5.800 Å in as-prepared crystal **2c** to 6.736 Å in **2c**·PrOH enhances the photopolymerizability of **2c**, although the elongation is still not sufficient for high-polymer formation. As shown in Figure 6b, the 1-propanol molecule (x, y, z) in **2c**·PrOH is hydrogen-bonded with the pyridyl nitrogen atom of the dimer ($1-x, -y, 1-z$) (O(49)···N(16) 2.780 Å) and also makes contact with the carbonyl carbon of the dimer (x, y, z) within the van der Waals distance (O(49)···C(33) 3.027 Å). Subsequently, the 1-propanol molecule causes two reactant dimer molecules to separate from each other to a distance ($2L$) from 11.600 to 13.472 Å (Figure 7).

The crystal structure of complex **2b**·EtOH is similar to that of complex **2c**·PrOH. Two pairs of residual double bonds in **2b**·EtOH are arranged within the photoreactive distances (3.707 and 4.010 Å). The ethanol molecule doubtlessly plays the same role as does the 1-propanol molecule in complex **2c**·PrOH. Length L (6.987 Å) in complex **2b**·EtOH is also longer than that of monomer **1b** (5.792 Å).

Although no crystal structure analysis of **2c**·EtOH was successful, accurate cell dimensions were obtained by data collections during the early stage: monoclinic, a = 9.835 (11), b = 21.210 (8), c = 10.545 (14) Å; β = 106.97 (9)°; V = 2108 (4) Å^3. The crystal system of **2c**·EtOH (monoclinic) is different from those of **2b**·EtOH and **2c**·PrOH (triclinic), and therefore, the molecular arrangement of **2c**·EtOH would also be different from **2b**·EtOH and **2c**·PrOH.

Though the **2c**/EtOH ratio has not been accurately determined, the ratio can be estimated from the volume per dimer molecule (V/Z). In the case of **2c**·EtOH, assuming that Z = 2, V/Z is 1054 Å^3. On the other hand, the V/Z values of **2c** and **2c**·PrOH are 835 and 949 Å^3, respectively. On the basis of these values it can be concluded that complex **2c**·EtOH comprises a dimer and ethanol in the ratio of 1:2. The second ethanol molecule would be hydrogen-bonded with the pyridyl group and replaced between two dimers. Subsequently, L is elongated to make the molecular arrangement more favorable for polymerization.

These results demonstrate that complexation of the dimer with a solvent, such as alcohol, causes an elongation of the value of L, to make the crystal structure of diolefinic compounds suitable for the [2 + 2] photopolymerization.

Conclusion

Topochemical reactions of methyl, ethyl, and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates (**1a–1c**) in the crystalline state afford homo-type dimers, oligomers, and

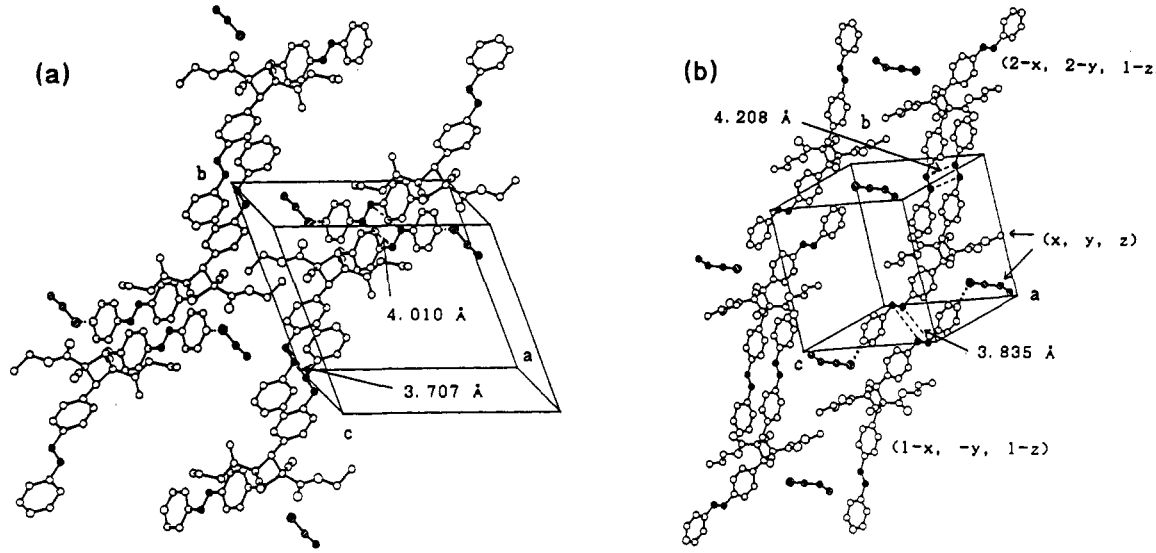


Figure 6. Crystal structures of **2b**·EtOH (a) and **2c**·PrOH (b). The darkened and shaded atoms correspond to ethylenic carbons and the atoms of ethanol or 1-propanol, respectively.

Table II
Correlation between the Length of the Monomer Repeating Unit (L) and the Photochemical Behavior

compound	recryst solvent	L, Å	reactn time, h	$\bar{M}_n$	morphology of photoproducts	ref
1b		5.792	7	3100	amorphous	*a*
2b·EtOH	EtOH	6.987	5	5000	amorphous	*a*
1c		5.753	2	(dimer)	crystal	3c
2c	AcOEt	5.800	2	(photostable)		3c
2c·PrOH	*n*-PrOH	6.736	4	3000	crystal	*a*

[a] This work.

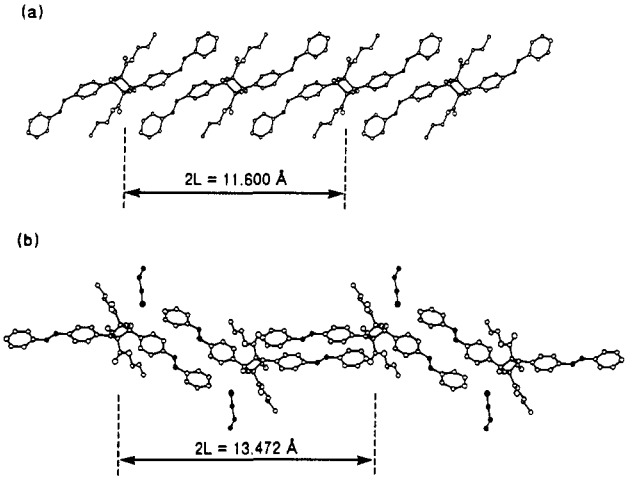


Figure 7. Molecular arrangements of **2c** (a) and **2c**·PrOH (b) viewed perpendicular to the direction of the polymer chain with the length of the repeating units of the dimer ($2L$).

polymers having either α-type (from **1b** and **1c**) or β-type (from **1a**) cyclobutane rings. The diversified photoproducts, which are caused by differences in the ester alkyl moiety, have been elucidated on the basis of their crystal structure analyses.

The photoreaction of **1b** proceeds through an "even-numbered polymerization mechanism" during the entire course of photopolymerization.

Since an alcohol molecule is hydrogen-bonded with the pyridyl group of the dimer, it can be placed between two dimers, making L suitable for polymerization. Therefore, the complex formation of dimers with a solvent (especially alcohols) enhances the polymerizability. Complex formation is one of the promising crystal engineering techniques that can be used for the diolefin compounds in order to obtain polymers with high molecular weight.

Experimental Section

Measurements. Infrared spectra were recorded on a Jasco IR-810 spectrophotometer, and ^{1}H NMR spectra were measured by a JEOL PMX-60SI or JEOL GX-400 instrument. Ultraviolet absorption spectra were measured on a Shimadzu UV-260 spectrophotometer at a concentration of 0.01 g/L in CH_2Cl_2 or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The melting points were measured by a Laboratory Devices Mel-Temp and are uncorrected. 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 + AD 802/S) columns (DMF solution). TG–DSC curves were recorded on a Rigaku Thermoflex TG-DSC instrument under a nitrogen stream with a heating rate of 5 °C/min for ~5 mg of the sample. X-ray powder diffraction analyses were carried out with a Rigaku Rotaflex RU-200 spectrometer (λ = 1.541 84 Å).

Preparation of the Monomers. 4-[2-(4-Pyridyl)ethenyl]benzaldehyde was prepared by the reaction of terephthalaldehyde and γ-picoline according to a method described in a literature.[12] A mixture of 4-[2-(4-pyridyl)ethenyl]benzaldehyde (0.012 mol) and methyl α-cyanoacetate (0.018 mol) in methanol (60 mL) was stirred at room temperature for 7 h. The precipitated crystals were collected and dried. A pure crystal of **1a** was obtained by recrystallization from methanol.

A crystal of **1b** was prepared in a similar manner by a reaction with ethyl cyanoacetate in ethanol, followed by recrystallization from ethanol.

1a: 84%; mp 195–196.5 °C; IR (KBr) 2230, 1720, 1600, 980, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (s, 3 H), 7.17 (d, 2 H, J = 17 Hz), 7.32 (d, 2 H, J = 17 Hz), 7.40 (m, 2 H), 7.66 (d, 2 H, J = 8 Hz), 8.03 (d, 2 H, J = 8 Hz), 8.24 (s, 1 H), 8.62 (m, 2 H); UV (ϵ in CH_2Cl_2) 360 nm (45 300). Anal. Calcd for $C_{18}H_{14}O_2N_2$: C, 74.47; H, 4.87; N, 9.65. Found: C, 74.17; H, 4.70; N, 9.53.

1b: 89%; mp 172–173.5 °C; IR (KBr) 2230, 1720, 1600, 980, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (t, 3 H, J = 7 Hz), 4.40 (q, 2

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

	1a	1b	2b·EtOH	2c·PrOH
formula	$C_{18}H_{14}N_2O_2$	$C_{19}H_{16}H_2O_2$	$C_{38}H_{32}N_4O_4·C_2H_6O$	$C_{40}H_{36}N_4O_4·C_3H_8O$
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	30.965 (2)	11.651 (1)	14.114 (3)	13.706 (2)
b, Å	4.049 (0)	9.151 (1)	12.763 (3)	13.508 (2)
c, Å	11.795 (0)	7.814 (1)	11.055 (3)	12.110 (2)
α, deg		85.84 (1)	110.86 (2)	110.75 (1)
β, deg	97.10 (0)	104.44 (1)	81.01 (2)	102.88 (1)
γ, deg		80.05 (1)	110.66 (3)	105.00 (1)
V, Å^3	1467.5 (1)	787.1 (1)	1740 (1)	1898 (1)
Z	4	2	2	2
crystallzn solvent	methanol	ethanol	ethanol	propanol
cryst size, mm^3	0.35 × 0.2 × 0.04	0.5 × 0.4 × 0.05	0.7 × 0.5 × 0.1	0.3 × 0.2 × 0.05
D_{cal}	1.31	1.28	1.26	1.22
μ, cm^{-1}	6.19	5.97	5.90	6.09
radiation, Å	Cu Kα (1.541 82)	Cu Kα (1.541 82)	Cu Kα (1.541 82)	Cu Kα (1.541 82)
scan mode	2θ–ω	2θ–ω	2θ–ω	2θ–ω
$2\theta_{max}$, deg	125	125	125	125
no. of unique reflcns	2480	2510	4941	5850
no. of obsd reflcns, $\|F_o\| > 3\sigma(\|F_o\|)$	2092	2212	4041	3770
R factor	0.067	0.055	0.098	0.088
R_w factor	0.090	0.074	0.115	0.091
largest shift/esd	0.42	0.22	0.49	0.47
largest peak, e/Å^{-3}	0.26	0.24	0.31	0.22

H, J = 4 Hz), 7.16 (d, 2 H, J = 16 Hz), 7.32 (d, 2 H, J = 16 Hz), 7.40 (m, 2 H), 7.66 (d, 2 H, J = 9 Hz), 8.03 (d, 2 H, J = 9 Hz), 8.24 (s, 1 H), 8.62 (m, 2 H); UV (ε in CH_2Cl_2) 360 nm (43 900). Anal. Calcd for $C_{19}H_{16}O_2N_2$: C, 74.98; H, 5.18; N, 9.20. Found: C, 74.94; H, 5.13; N, 9.25.

Preparation of the Dimers. Finely powdered crystals of **1a** (200 mg) were dispersed in 90 mL of a mixture of water and methanol (90:10 v/v) and irradiated by a 500-W high-pressure mercury lamp (Ushio USH-500D), set outside of the flask, through a Kenko L42 filter (cutoff <410 nm) for 45 h at room temperature with vigorous stirring. Monomer **1a** was mainly converted into dimer **2a** at the stage of ca. 50% conversion. Dimer **2a** was separated from the monomer and oligomers by preparative TLC (silica gel, ethyl acetate). **2a**: 48%; IR (KBr) 2230, 1720, 1600, 980, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 6 H), 4.51 (d, 2 H, J = 8 Hz), 4.58 (d, 2 H, J = 8 Hz), 7.01 (m, 2 H), 7.22 (d, 2 H, J = 9 Hz), 7.83 (d, 2 H, J = 9 Hz), 7.83 (d, 2 H, J = 9 Hz), 8.43 (m, 2 H); UV (ε in CH_2Cl_2) 306 nm (53 300); MS m/e 398, 182 (unsymmetric cleavage of the cyclobutane ring).

The photoreaction was carried out for **1b** in the same manner for 6 h. Monomer **1b** was quantitatively converted into dimer **2b**. **2b**: mp 191.5–193 °C dec; IR (KBr) 2250, 1745, 1600, 1000, 990, 975, 850, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 6 H, J = 7 Hz), 4.04 (dq, 2 H, J_1 = 11 Hz, J_2 = 7 Hz), 4.09 (dq, 2 H, J_1 = 11 Hz, J_2 = 7 Hz), 5.17 (s, 2 H), 7.07 (d, 2 H, J = 16 Hz), 7.29 (d, 2 H, J = 16 Hz), 7.39 (m, 4 H), 7.52 (d, 4 H, J = 8 Hz), 7.61 (d, 4 H, J = 8 Hz), 8.56 (m, 4 H); UV (ε in CH_2Cl_2) 315 nm (66 500).

Preparation of the Complexes 2b. Dimer **2b** was recrystallized from ethanol to form complex **2b**·EtOH in a molar ratio of 1:1. The stoichiometry was confirmed by its ^{1}H NMR spectrum. Moreover, TG–DSC analysis showed a broad endothermic peak at 78–164 °C with 8.1% weight loss (in agreement with the theoretical value (7.0%) for the evaporation of ethanol from complex **2b**·EtOH) and an exothermic peak corresponding to the decomposition at 199 °C.

Complexes **2b**·PrOH, **2b**·AcOBu, and **2b**·xylene were formed by recrystallization of **2b** with the corresponding solvent. The stoichiometries were confirmed by their ^{1}H NMR spectra and TG–DSC analyses.

Complexes **2c**·EtOH and **2c**·PrOH were formed by the recrystallization of **2c** with the corresponding solvent. The stoichiometries were confirmed by their ^{1}H NMR spectra and TG–DSC analyses.

Photoirradiation. Photopolymerization was carried out as follows. Method 1: Finely powdered crystals (**1a**, **1b**, **2b**·EtOH, **2c**·EtOH, or **2c**·PrOH) were dispersed in 300 mL of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a 100-W high-pressure mercury lamp (Eikousha EHB WF-100), set inside of the flask, through a Pyrex glass filter with vigorous stirring under a nitrogen atmosphere. Method 2: Finely powdered crystals (**2b**·EtOH, **2b**·PrOH, **2b**·AcOBu, or **2b**·xylene) were mixed with quartz particles and irradiated with a 500-W super-high-pressure mercury lamp (Eikousha EHB WF-500), set outside of the flask, through a UV 30 filter (cutoff < 280 nm) with vigorous stirring under a nitrogen atmosphere. The photopolymerization of the dimers was carried out at −20 °C to suppress a nontopochemical reaction.

Photoproduct of 2b: IR (KBr) 1740, 1600, 1240 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.7–0.9 (m, 6 H), 3.60 (br s, 2 H), 3.82 (br s, 2 H), 4.57 (br s, 2 H), 4.66 (br s, 2 H), 5.04 (s, 2 H), 7.2–7.4 (m, 12 H), 8.2–8.5 (m, 4 H); UV (ε in CH_2Cl_2) 234.4 nm (10 500).

Photoproduct of 2b·EtOH: IR (KBr) 1740, 1600, 1240 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.7–0.9 (m, 6 H), 3.60 (br s, 2 H), 3.82 (br s, 2 H), 4.57 (br s, 2 H), 4.66 (br s, 2 H), 5.04 (s, 2 H), 7.2–7.4 (m, 12 H), 8.2–8.5 (m, 4 H); UV (ε in CH_2Cl_2) 234 nm (9650).

Photoproducts of **2b**·PrOH and **2b**·AcOBu showed the same NMR spectrum as that of **2b**·EtOH.

Photoproduct of 2c·EtOH: IR (KBr) 1740, 1600, 1240 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.5–0.7 (m, 6 H), 1.2–1.4 (m, 4 H), 3.50 (br s, 2 H), 3.80 (br s, 2 H), 4.57 (br s, 2 H), 4.66 (br s, 2 H), 5.04 (s, 2 H), 7.0–7.4 (m, 12 H), 8.31 (br s, 4 H); UV (ε in CH_2Cl_2) 234 nm (9500).

The photoproduct of **2c**·PrOH showed the same NMR spectrum as that of **2c**·EtOH.

X-ray Measurement. Intensity data were measured on a Rigaku four-circle diffractometer with graphite monochromated Cu Kα radiation. Accurate cell dimensions were obtained by least-squares refinement of 15 reflections for **1a** and **1b** and 20 reflections for **2b**·EtOH and **2c**·PrOH accurately centered reflections in the range 40° < 2θ < 60°. Data were collected with three check reflections. The observed reflections ($|F_o| > 3\sigma(|F_o|)$) 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 SHELXS 76. The intensity data collection, refinement details, and crystal data are summarized in Table III. 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 parameters 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 for **2b**·EtOH and **2c**·PrOH. The final molecular coordinates, thermal parameters, bond lengths, and bond angles are given in the supplementary materials.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **1a**, **1b**, **2b**·EtOH, and **2c**·PrOH (14 pages). Ordering information is given on any current masthead page.

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