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Photodimerizations and Crystal Structures of Thymine Derivatives Having a Long Alkyl Chain Connected with a Carbamate Bond

Takanori Sugiki, Norimitu Tohnai,† Yuhua Wang,† Takehiko Wada,† and Yoshiaki Inaki*,†

Central Research Laboratory, Nichiban Co., Ltd., Anjo, Aichi 446

†Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

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Photodimerizations of thymine derivatives having a long alkyl chain on a carbamate bond were investigated by irradiation of UV light at 280 nm in amorphous and crystalline film states. The amorphous films obtained by spin-coating from chloroform solution had higher initial rate constants for photodimerization relative to those of the crystalline films after annealing. X-Ray crystal structure analysis showed that the thymine derivatives had intermolecular hydrogen bonds that led to disadvantageous molecular orientation for the photodimerization. The photodimerization, however, is preferred in the localized layer structures of thymine units and alkyl chain.

Nucleic acids are known to be denatured by irradiation of UV light. Thymine bases in DNA undergo [2+2] cycloaddition reaction by irradiation of UV light, this reaction is the origin of the death of cells and mutation.[1,2] The photodimerization is a reversible reaction where the photodimer dissociates to the original monomers very effectively upon irradiation at a shorter wavelength as shown in Fig. 1.[3] Although thymine derivatives in solution give four isomers of photodimers, only *cis-syn* isomer is obtained by irradiation of UV light on DNA.

Preparations and the photodimerizations of the monomeric and polymeric derivatives of thymine in solution were studied in detail for poly(methacrylate), poly(ethyleneimine), and polylysine.[4—6] The results indicated that the thymine monomers gave a photodimer through triplet state, and thymine polymers gave a photodimer mainly through singlet state. The reversible photodimerization of thymine derivatives can be applied to negative or positive type photo resist materials by controlling the irradiation UV light wavelength.[3,7,8] The solubility of the thymine derivatives in alkaline solution or organic solvents can be varied by photodimerization or photodissociation. These systems, therefore, may satisfy the requirements for a high resolution photo resist.

The reversible photodimerization of thymine derivatives can also be applied to a photo recording system.[9,10] Both the conversions of thymine units to the photodimer and the reverse photoreaction can be followed by monitoring the decrease and increase in absorbance at 270 nm, respectively. Then this system can be a high density photo recording system due to reversible photoreaction and monitoring at the area of deep-UV. For applications of the thymine system to photo resists and photo recording systems, however, the reversible photodimerization reactions of the thymine derivatives should be effective and complete in thin film state.

Thymine derivatives are very resistant to UV irradiation

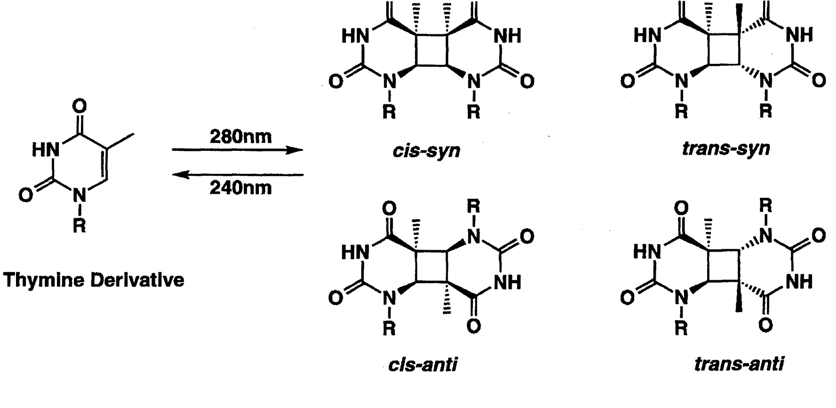
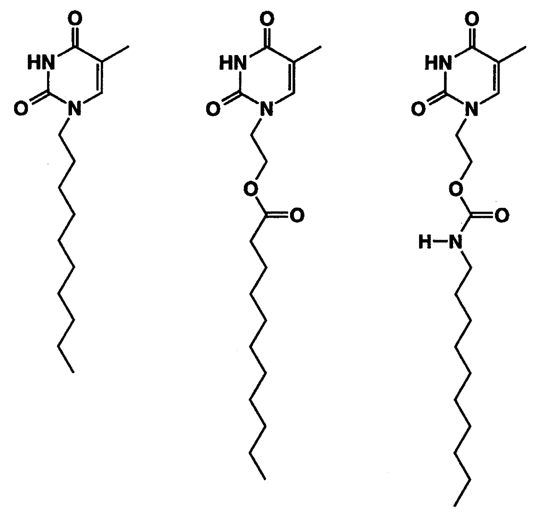


Fig. 1. Reversible photodimerization of thymine derivatives.



(1) **(2)** **(3)**

Fig. 2. Thymine derivatives containing long alkyl chain.

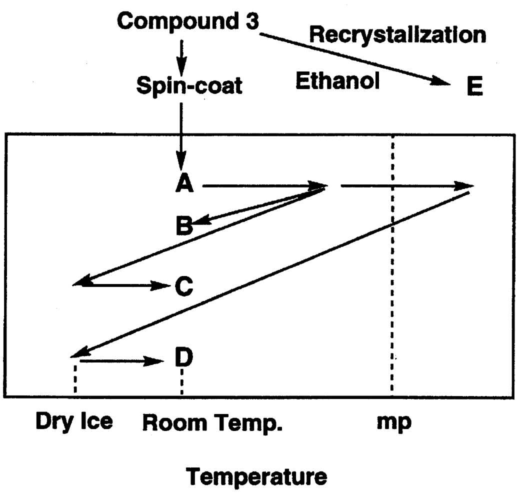


Fig. 3. Preparation of films.

in dilute solution, where the triplet state is the precursor of the photodimer.[11—14] In solid state, however, the photodimerization reaction is fast and proceeds through singlet state.[15—17] Another interesting fact is reported for the crystal of thymine that the quantum yield for photodimerization of thymine crystal from water is higher than that of the crystal from ethanol or that for sublimation.[18,19] The adjacent thymine molecules in the crystal from water stacked in a position that is suitable for photodimerization (3.6—4.1 Å).[12] On the other hand, thymines in the crystal from ethanol are hydrogen-bonded in a position that is not suitable for photodimerization. These facts indicate that the stacked structure of the adjacent thymine molecules is an important factor for efficient photodimerization of thymine.

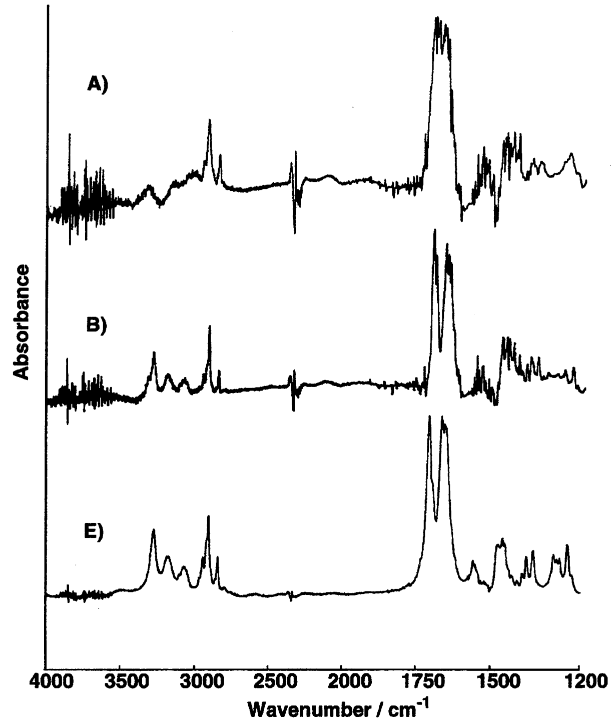


Fig. 4. IR spectra of the decyl derivative (**3f**: C_{10}): (**A**) spin-coated film, (**B**) annealed film, and (**E**) single crystal.

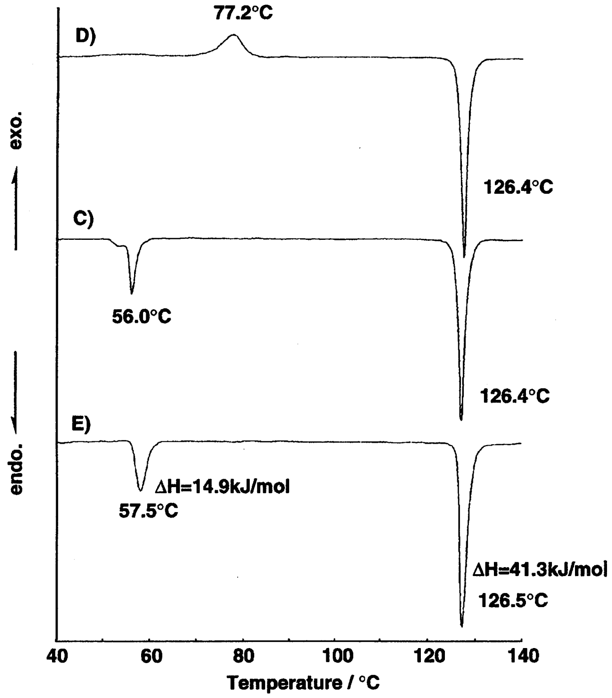
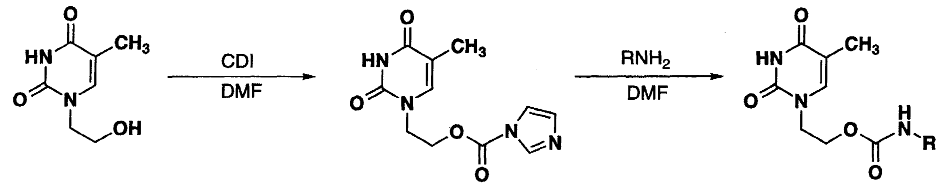


Fig. 5. DSC curves (scanning rate, 5 °C min^{-1}) of the decyl derivative (**3f**: C_{10}): (**D**) quenching after heating below melting point, (**C**) quenching after heating above melting point, and (**E**) single crystal.

A stacked conformation of thymine can be obtained in a polymer having thymine in the side chain. Photodimerization reactions of the thymine in the polymer have been reported elsewhere.[3—8] Another system is the thymine derivative with the group that has high interaction ability. Thymine derivatives with long alkyl chain were prepared such as shown in Fig. 2. In these compounds, *n*-alkyl chains can interact with each other, and have no absorption around the UV region. The photodimerization reaction of the long alkyl chain derivatives (**1**) in solid film was reversible and was very fast



4 5 3, R: $(CH_2)_nCH_3$

3a: n=4 ~ 3j: n=13

Scheme 1. Synthesis of the thymine derivatives having long alkyl chain.

Table 1. Analytical Data of Compounds **3**

3	Carbon number of alkyl chain	Mp	Calcd/%			Found/%		
		°C	H	C	N	H	C	N
3a	5	148—149	7.47	55.11	14.83	7.45	54.95	14.85
3b	6	138—139	7.80	56.55	14.13	7.80	56.30	14.15
3c	7	125—126	8.09	57.86	13.49	8.12	57.86	13.55
3d	8	111—112	8.36	59.06	12.91	8.42	59.03	12.91
3e	9	121—122	8.61	60.16	12.38	8.61	59.87	12.37
3f	10	123—124	8.84	61.66	11.89	8.99	61.26	11.94
3g	11	119—120	9.05	62.10	11.43	9.08	62.10	11.43
3h	12	116—117	9.25	62.96	11.01	9.36	62.73	10.98
3i	13	119—120	9.43	63.77	10.62	9.47	63.75	10.63
3j	14	116—117	9.60	64.52	10.26	9.60	64.54	10.20

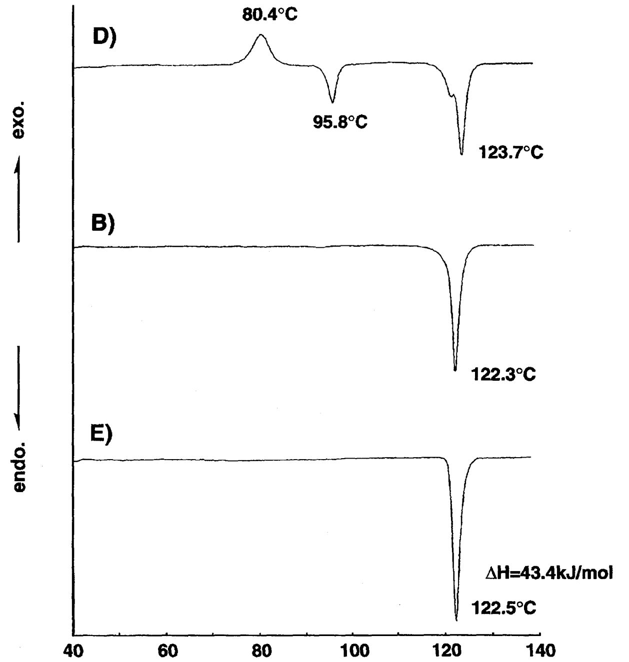


Fig. 6. DSC curves (scanning rate, 5 °C min^{-1}) of the undecyl derivative (**3g**: C_{11}): (**D**) quenching after heating below melting point, (**B**) annealed film, and (**E**) single crystal.

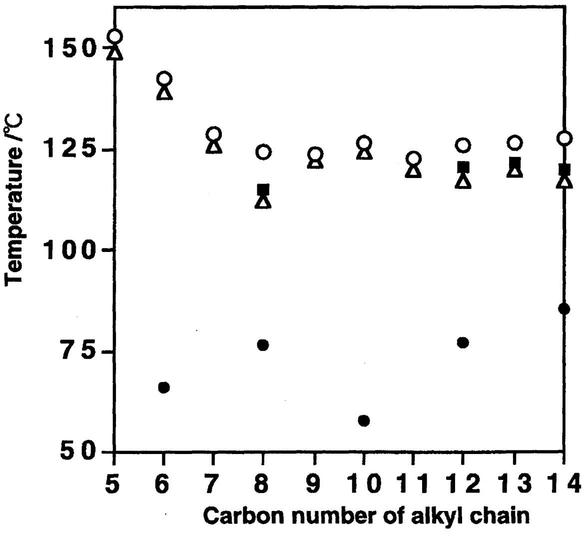


Fig. 7. Endothermic points and melting points for the crystal of **3**. (△); melting point, (○, ■, and ●): endothermic point.

compared with the reaction in solution.[21—23] The thymine derivatives of long alkyl chain with large carbon numbers above C_{12} (**1**), however, gave opaque films because of the high crystallinity of *n*-alkyl chains. Also in the case of the ester derivatives (**2**), a clear film was not obtained for the large carbon number derivatives.[22] Therefore, the photodimerization reactions were carried out in polymer matrices such as poly(acrylonitrile), poly(vinyl acetate), and poly(vinyl alcohol). In the case of the carbamate compounds (**3**), on the other hand, a transparent film was obtained even with long alkyl chain derivatives. Film transparency is an important factor for efficient absorption of UV light by thymine chromophore.

This paper deals with the preparation and photodimerization reactions in film state of the long alkyl chain derivatives of thymine connected by carbamate bond (**3**). Reactivities of the thymine derivatives with long alkyl chain were found to depend on length of alkyl chain. The reactivity decreased by annealing of the thin film, and the crystallinity of the film was found to increase by annealing. The structure of the

Table 2. Crystallographic Data of Compounds **3f** and **3g**

Compound	**3f**	**3g**
Empirical formula	$C_{18}H_{31}N_3O_4$	$C_{19}H_{33}N_3O_4$
Formula weight	353.46	367.49
Crystal color, Habit	Colorless, Plate	Colorless, Prismatic
Crystal dimensions/mm	0.250 × 0.300 × 0.500	0.300 × 0.300 × 0.300
Crystal system	Monoclinic	Triclinic
No. reflections used for unit cell determination (2θ range)	25 (26.8—27.4°)	25 (26.6—27.5°)
Omega scan peak width at half-height	0.32	0.31
Lattice parameters: a/Å	15.356(1)	16.190(3)
b/Å	8.533(2)	23.434(4)
c/Å	17.014(2)	5.7217(8)
α/°		91.79(1)
β/°	111.642(6)	96.53(1)
γ/°		101.72(1)
V/Å^3	2077.1(6)	2108(1)
Space group	$P2_1/a$ (#14)	$P\bar{1}$ (#2)
Z value	4	4
D_{calcd}/g cm^{-3}	1.130	1.158
F_{000}	768	800
μ(Mo $K\alpha$)/cm^{-1}	0.75	0.76

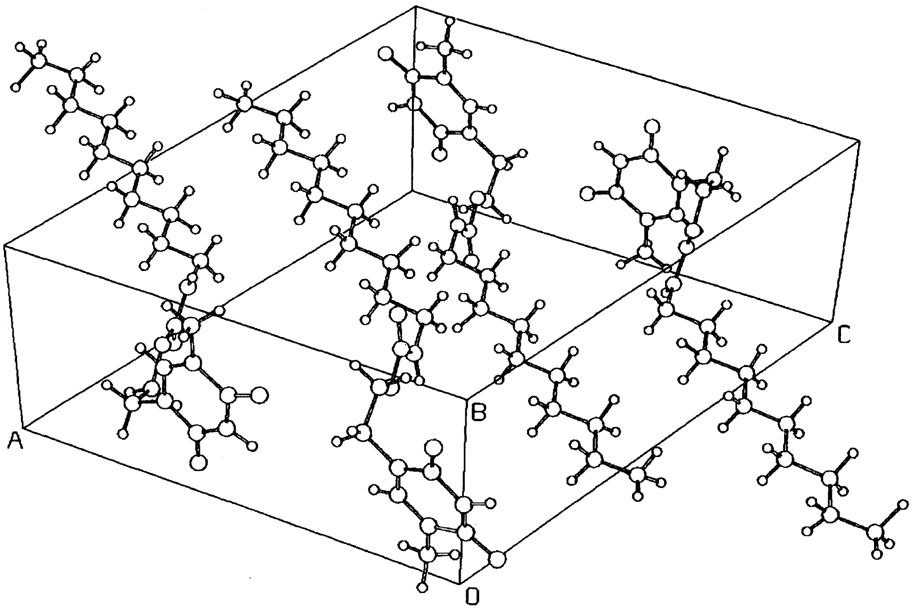


Fig. 8. Crystal structure of decyl derivative (**3f**: C_{10}): unit cell.

crystal, therefore, was determined by X-ray crystal structure analysis in order to clarify the low reactivity of thymine in crystal state.

Results and Discussion

Synthesis of Long Alkyl Chain Derivatives of Thymine. Thymine derivatives with long alkyl chain (**3a**—**3j**) were prepared according to Scheme 1. Reaction of 1-(2-hydroxyethyl)thymine (**4**)[5] with 1, 1′-carbonyl diimidazole afforded 1-imidazolyl carbonyl derivative (**5**). The obtained 1-imidazolyl carbonyl derivative was then reacted with *n*-alkylamines to give the thymine derivatives of long alkyl chains connected with carbamate bond (**3**) in almost quantitative yield. The products obtained were assigned by elemental analysis, IR, and NMR spectra (Table 1).

Preparation of Thin Film. The compound **3** (10 mg) was dissolved in chloroform (0.5 ml), and spin-coated on a quartz plate for UV measurement or on a silicon wafer for IR measurement (presented by Shin-Etsu Chemical Co., Ltd.) to give a clear film (**A**). The spin-coated film (**A**) was heated at 100—135 °C for 5 min, followed by cooling to room temperature to give the annealed film (**B**). The films **C** and **D** were prepared by heating of the spin-coated film **A** below or above melting temperature, followed by quenching with Dry Ice.® The single crystal (**E**) for IR and DSC measurements was obtained by recrystallization from ethanol (Fig. 3).

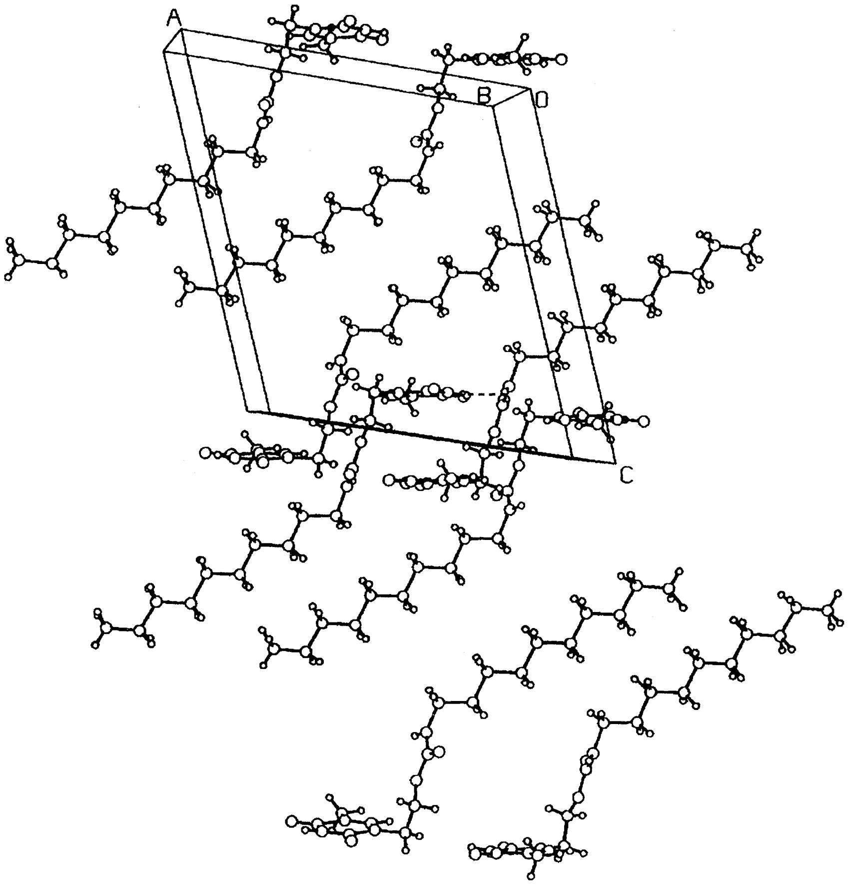


Fig. 9. Crystal structure of decyl derivative (**3f**: C_{10}): short range.

Infrared Spectra of the Film and Crystal. The hydrogen bonding in the thymine derivatives can be observed from IR spectra around 3000—3500 cm^{-1}. FT-IR Spectra of the spin-coated film (**A**) and the annealed film (**B**) of the decyl derivative (**3f**: C_{10}) were compared with that of the single crystal (**E**) obtained by recrystallization from ethanol (Fig. 4). The spectrum **A** was weak and broad, but the spectrum **E** was strong and sharp. IR spectrum of the annealed film (**B**) was similar to that of the single crystal (**E**) over a wide range of wavenumbers. It seemed that the treatment of the spin-coated film by annealing induced mobility of the molecules, and the thymine bases formed hydrogen bonds. The ordered structure in the film **B** is probably close to or the same as the structure produced by recrystallization from ethanol. Similar results by annealing were obtained for the undecyl derivative (**3g**: C_{11}).

Thermal Analysis of the Thymine Derivatives. For characterization of the film state, thermal analysis of decyl derivative (**3f**: C_{10}) was performed as shown in Fig. 5. DSC of the single crystal (**E**) produced by recrystallization from ethanol showed two endothermic peaks; solid-solid transition point at 57.5 °C, and melting point at 126.5 °C. Two similar endothermic peaks were observed for even carbon number alkyl derivatives of thymine (Fig. 7). The sample (**D**) prepared by cooling rapidly with Dry Ice® after melting at 130 °C, showed a broad exothermic peak at 77 °C without transition peak around 57 °C. The amorphous state may be produced by cooling rapidly after melting, and the change of amorphous state to the more stable solid state occurs exothermally at 77 °C. Because the values of ΔH at 126.5 °C are almost equal, the stable solid state in film **D** is probably close to or the same as the crystal state (**E**). The sample (**C**) prepared by cooling rapidly with Dry Ice® after heating below the melting point (100 °C, 5 min) of the spin-coated film was also measured by DSC. Appearance of the endothermic peak at 56 °C and disappearance of the exothermic peak at 77 °C were observed, similarly to the single crystal (**E**). These results indicated the presence of three kinds of structure in the decyl derivative of thymine (**3f**) and also in the even carbon number derivatives: an amorphous state, an unstable structure that melts at 57 °C, and a stable structure that melts at 126 °C.

Long alkyl chain derivatives of odd carbon number show only one peak in DSC curves of crystal (**E**) and annealed film (**B**) as shown in Fig. 6 for undecyl derivative (**3g**: C_{11}), and in Fig. 7. The amorphous sample (**D**) of the undecyl derivative obtained by quenching after melting shows two exothermic peaks at 96 °C with 124 °C, and one endothermic peak at 80 °C. The annealed sample (**B**) under melting point shows only one peak at 122 °C. This fact indicates that crystals of the odd carbon number derivatives have a stable single state without metastable state.

In Fig. 7, the endothermic peaks and melting points of crystals **E** are plotted against carbon number of the *n*-alkyl chain. For even carbon number and C_{13}, two endothermic

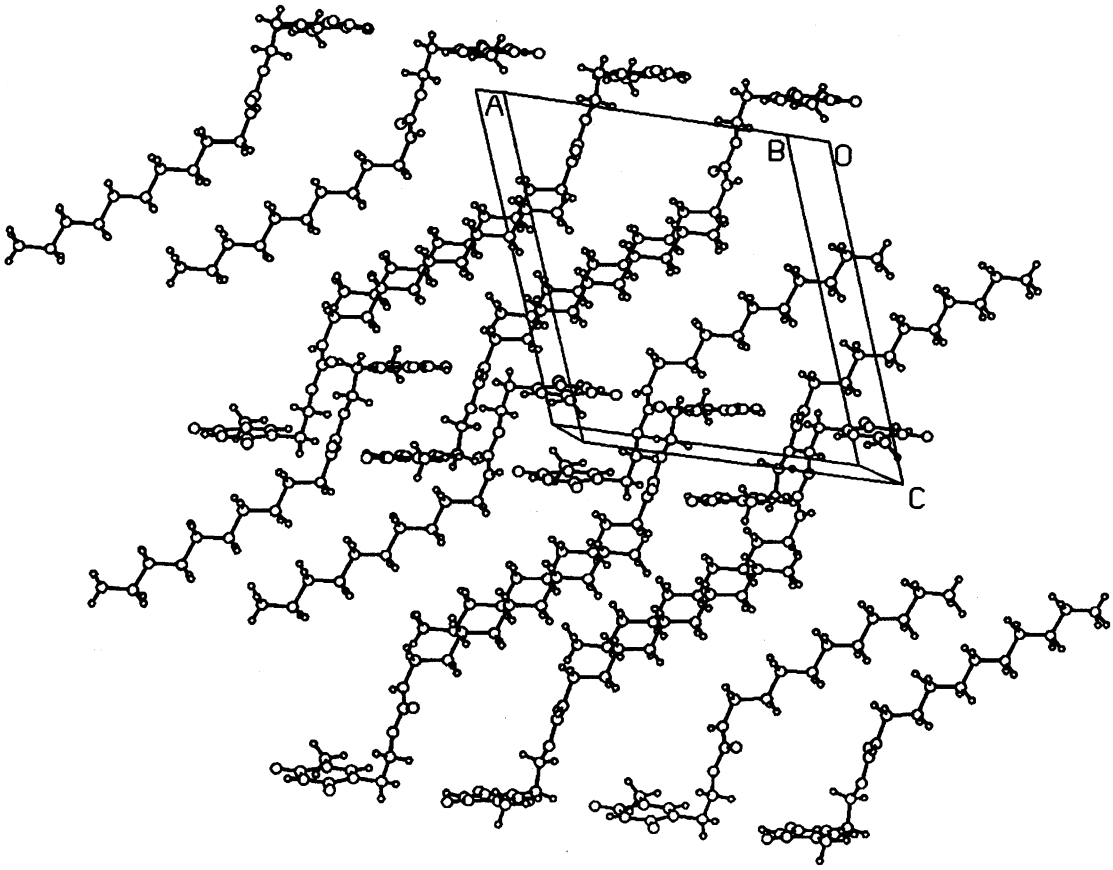


Fig. 10. Crystal structure of decyl derivative (**3f**: C_{10}): long range.

peaks were observed at near melting point. The highest endothermic peak of the compounds decreased from C_5 to C_8, and were nearly constant from C_8 to C_{14}. In the case of the compounds with even carbon number alkyl chain, additional lower endothermic peaks were observed at about 75 °C.

For crystallization of the compound **3**, thymine, carbamate, and alkyl functional groups should be considered as factors. When the alkyl chain is short, the main factor for crystallization is the interaction of thymine units, where thymine bases interact on the same plane by hydrogen bonding, which is known for the thymine crystal obtained from ethanol.[18,19] With increase of carbon number, the interaction between the alkyl chains become the main factor for crystallization in preference to thymine units, and the melting points dropped from C_5 to C_8. The hydrogen bondings between thymine units and/or between thymine and the carbamate bond may stabilize the crystal from C_8 to C_{14}, and show similar melting points. The endothermic peaks after melting may be attributable to melting of these hydrogen bondings.

Crystal Structure of the Thymine Derivatives. The single crystal of the decyl derivative of thymine (**3f**: C_{10}) was obtained from ethanol solution. Crystal data and molecular structure of this compound are shown in Table 2 and Figs. 8, 9, and 10. Only one hydrogen bonding was found between thymine and carbamate (Fig. 9). This fact and the DSC data indicate that the crystal structure of **3f** is unstable. The nearest double bonds (C^5–C^6) of thymines were in opposite position as shown in Fig. 9. Therefore, the formation of the photodimer from this crystal may be difficult. If the photodimerization could occurr in this crystal, the *trans-anti* isomer of the thymine photodimer (Fig. 1) should be obtained.

The single crystal of the undecyl derivative (**3g**: C_{11}) was obtained from ethyl acetate solution. Crystal data of this compound are tabulated in Table 2. Molecular structure in Fig. 11 shows that the thymine base bends toward long alkyl chain, and forms a pair in the crystal with carbamate bond by two hydrogen bonds. One thymine forms two stable hydrogen bondings with the carbamate bond of the other molecule. The other thymine forms two hydrogen bonds with another thymine and another carbamate bond. Therefore, there are four hydrogen bonds in the crystal as shown in Fig. 11, and the crystal structure of **3g** is stable, this conclusion is supported by the DSC data.

As shown in Fig. 12, the distance between thymine to thymine is 3.13 to 3.50 Å, and the distance between double bond (C^5–C^6) and double bond ($C^{5'}$–$C^{6'}$) is 5.72 Å. For the formation of photodimer, the double bonds of two thymines have to approach to 3.6—4.1 Å of the most favorable distance for photodimerization by moving slightly along the plane of thymine base. The *cis-syn* isomer (Fig. 1) of the thymine photodimer should be obtained by photodimerization of this

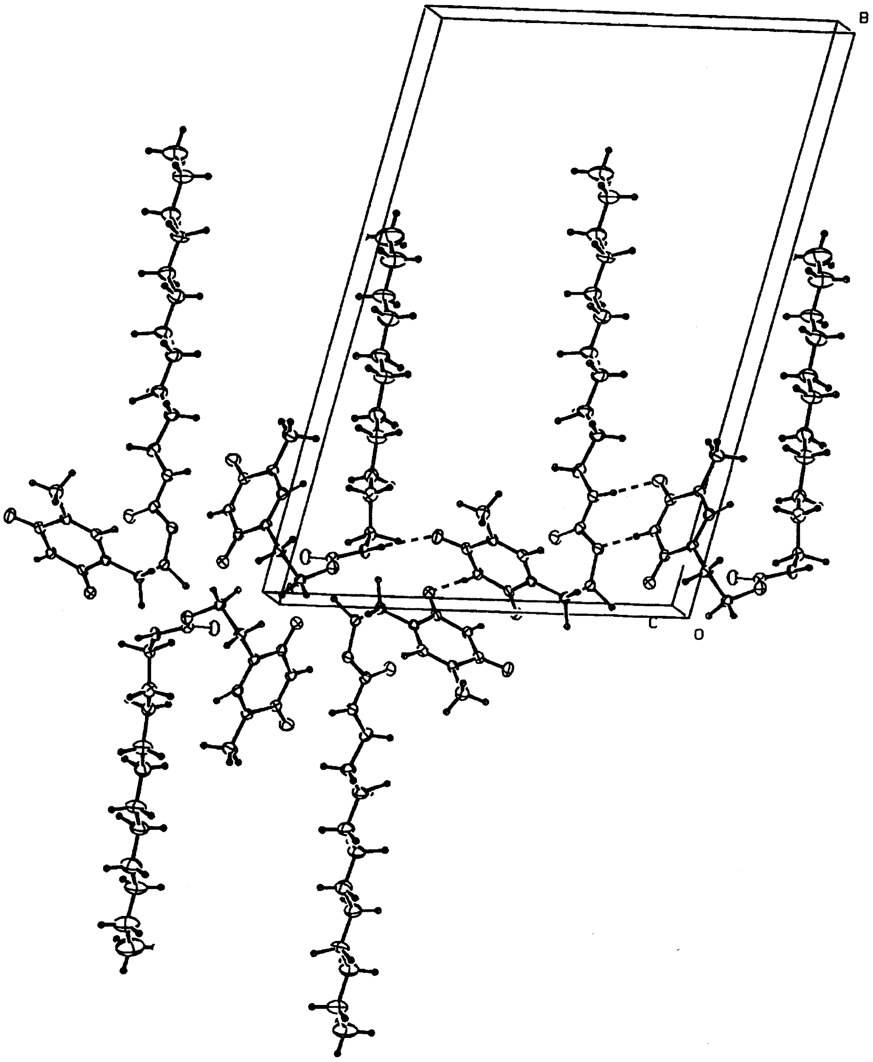


Fig. 11. Crystal structure of undecyl derivative (**3g**: C_{11}): unit cell.

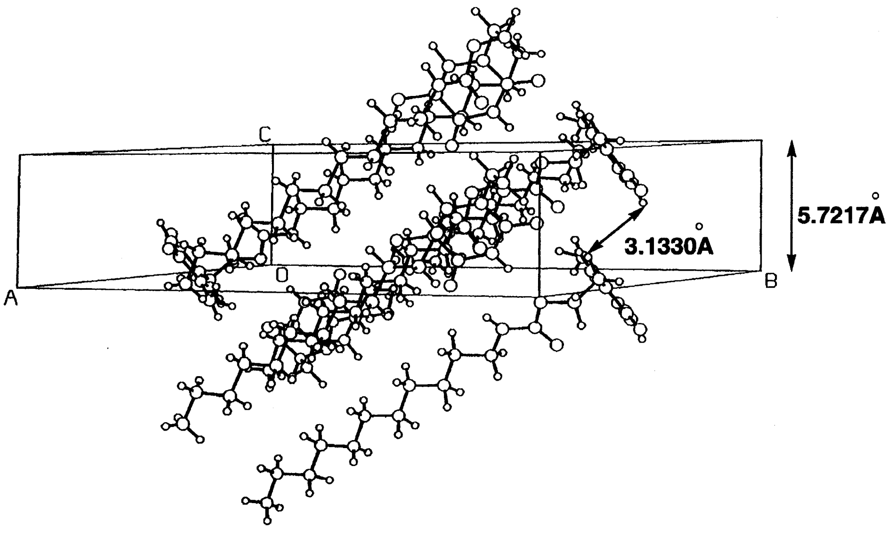


Fig. 12. Crystal structure of undecyl derivative (**3g**: C_{11}): short range.

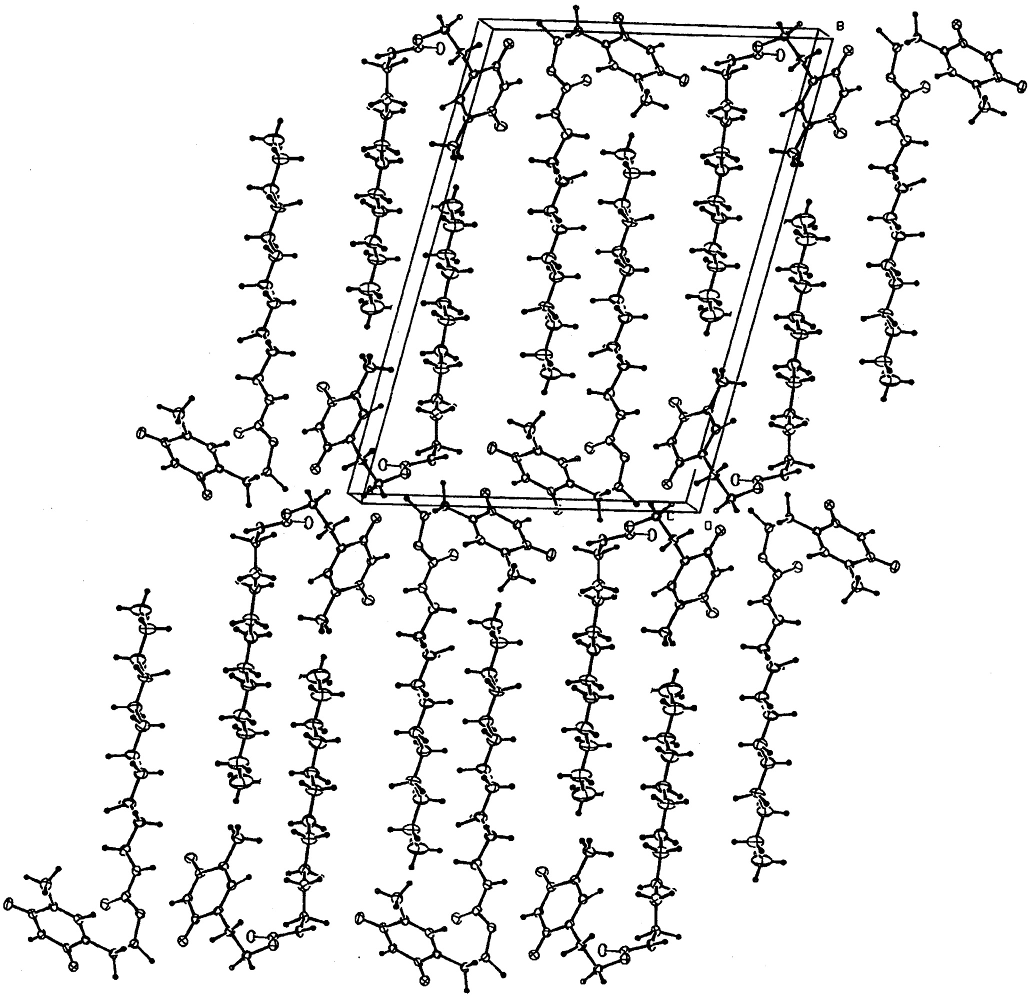


Fig. 13. Crystal structure of undecyl derivative (**3g**: C_{11}): long range.

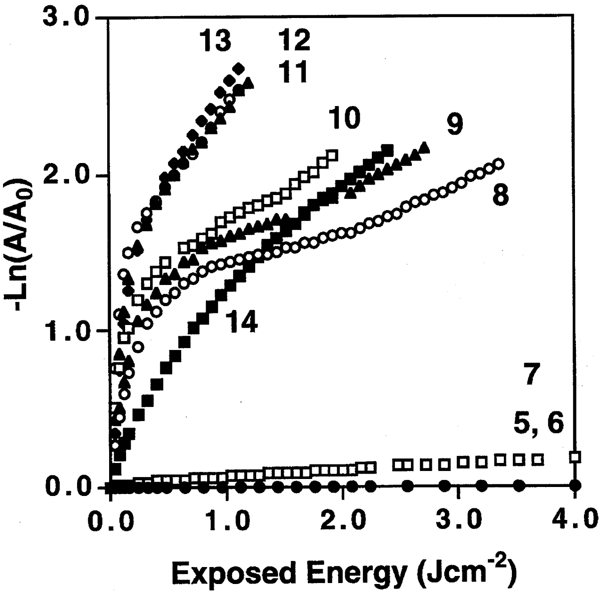


Fig. 14. The plots by fitting equation to first order kinetics for the spin-coated film (**A**). Numbers show the carbon number of the long alkyl chain.

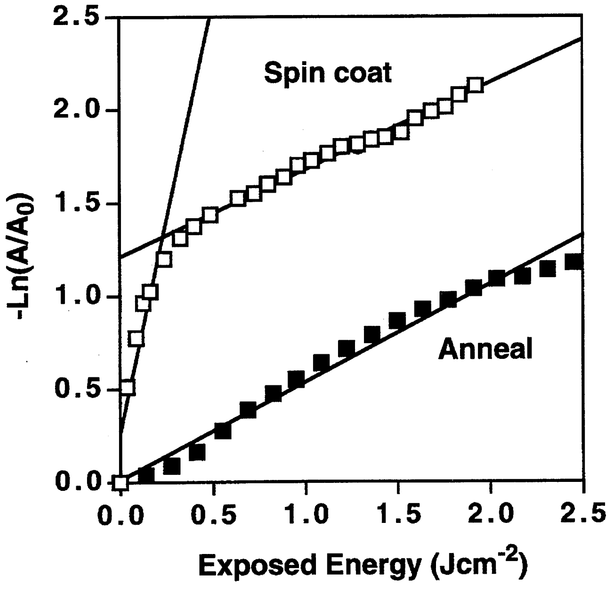


Fig. 15. The plots of decyl derivative (**3f**: C_{10}) by fitting equation to first order kinetics: (☐) spin-coated film (**A**), and (■) annealed film (**B**).

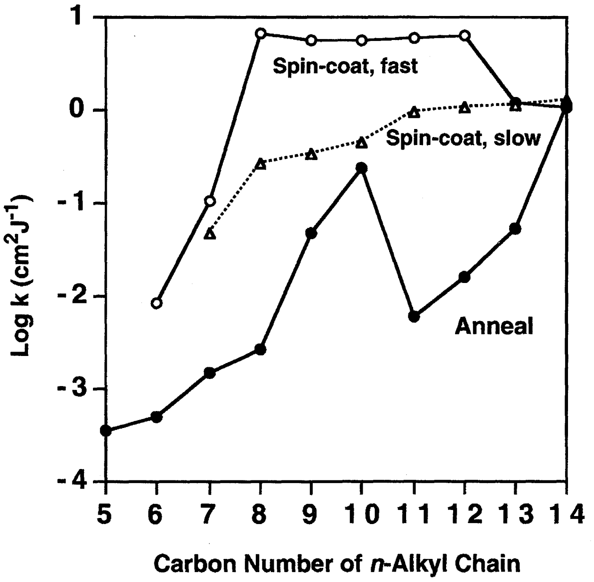


Fig. 16. The rate constants calculated from the slope in Fig. 15.

crystal. The determination of the structure of the photodimer, however, will be shown in the following paper.

In both decyl (**3f**) and undecyl derivatives (**3g**), each carbon–carbon double bond of adjacent thymine rings is far from suitable position for photodimerization. However, there are two layers in these crystals, one contains thymine bases and the other contains long alkyl chains (Fig. 10 and Fig. 13). In the layer structures of thymine, the photodimerization may be fast because of the high concentration of thymine base.

Photodimerization. The thin film of the thymine derivative obtained by spin-coating from chloroform solution was exposed to monochromatic UV light at 280 nm (13.6 mJ cm^{-2} s^{-1}). The photodimerizations were followed by monitoring the decrease in absorbance of thymine units (maximum absorption at 270 nm). Because the thymine photodimer has no absorption at 280 nm, thymine base units (T) give the photodimer (D) by irradiation of UV light at 280 nm (Eq. 1).[3,7—10] Therefore, the rate of the photodimerization of the thymine derivative can be derived as the Eq. 2, where E is exposed energy. Integration of Eq. 2 gives Eq. 3, which is expressed by absorption (A) of the thymine derivatives as Eq. 4. Then, the rate of the photodimerization (k) can be obtained from Eq. 4.

$$\mathrm{T} \xrightarrow{k} \mathrm{D} \tag{1}$$

$$-\frac{\mathrm{d}T}{\mathrm{d}E} = kT \tag{2}$$

$$\ln \frac{T_0}{T} = kE \tag{3}$$

$$\ln \frac{A_0}{A} = kE \tag{4}$$

Figure 14 shows the plot of the data for the thymine derivatives using Eq. 4. For **3a** (C_5) and **3b** (C_6), the rates of photodimerization were negligible under the condition in Fig. 14. The rate of the photodimerization was slow for the heptyl derivative (**3c**: C_7), and increased with increase of the length of the alkyl chain. For alkyl chains longer than C_{12}, the rate decreased again.

The effect of annealing of the film on the rate of photodimerization was studied. As shown in Fig. 15 for decyl derivative (**3f**: C_{10}), the initial rate of photodimerization of the spin-coated film **A** was fast, and became slow after the turning point. In the case of the annealed film **B** (100 °C for 5 min), the rate of photodimerization was slow without any turning point. The DSC data of the film suggested that annealing caused an increase of crystal part in the spin-coated film. Therefore, the slow reaction after the turning point for the spin-coated film proceeded probably in the crystal part.

The rate constants of photodimerization were calculated from the slope as shown in Fig. 15 to give Fig. 16. The rate of photodimerization in the annealed film increases with increase of carbon number, while a gap is present between C_{10} and C_{11}. No difference between even and odd carbon numbers in the photodimerization was observed, as was shown in DSC data. The fact indicates that the properties of the crystals did not strictly reflect on the reactivity, because the photodimerization was difficult to proceed from crystal.

The structure of the annealed film is similar to that of a single crystal, but the photodimerization of thymine units was found to occur in the annealed film. This fact suggested that the thymine units moved each other from positions in the crystal to form the photodimer. As mentioned above, thymine molecules in crystal from ethanol exist on the same plane forming hydrogen bonding, and give the photodimer only with difficulty. The planar orientation of thymine bases may collapse with increase of the carbon number of the alkyl chain. Then, the rate of photodimerization increased with increase of carbon number.

The gap between C_{10} and C_{11} may be caused by some extreme change of crystal structure. The thymine base of the decyl derivative (**3f**: C_{10}) (Fig. 9) in crystal may be able to move easily, because only one hydrogen bonding was observed in the crystal between thymine and carbamate. On the other hand, in the crystal of the undecyl derivative of thymine (**3g**: C_{11}) (Fig. 11), the thymine base finds it very hard to move because of four hydrogen bondings between thymines or between thymine and carbamate bond. Then, the reactivity of decyl derivative is higher than that of undecyl derivative.

The higher reactivity was obtained for the spin-coated film (fast) compared with the annealed film. The rates of the annealed film were slower than the slow reaction after turning point of the spin-coated film. The initial rate of photodimerization in the spin-coated film increased with increase of the chain length (C_6 to C_8), and decreased again (C_{12} to C_{14}) after a plateau (C_8 to C_{12}). Spin-coated film may be a mixture of micro crystal and amorphous state. Therefore, thymine bases in spin-coated film can move to a stacked orientation that is preferred for photodimerization. With increase of carbon number in alkyl chain, the degree of aggregation of thymine bases increased and the planar orientation of thymine units decreased to cause increasing rate of photodimerization. From C_8 to C_{12}, the rate may reach the ceiling, which would mean the maximum rate of the photodimerization of the thymine units.

The turning point was not clear for the curve of C_{14} in Fig. 14, and the rates of photodimerization were similar for the spin-coated and annealed films (Fig. 16). These results suggested that mobility of the thymine units in the film is restricted by strong interactions between the long alkyl chains. Decrease of the reactivity above C_{12}, therefore, may be caused by the interaction of the alkyl chain.

Conclusion

Thymine derivatives of long alkyl chain connected with carbamate bond gave transparent thin films by spin coat. Reactivity of the thymine in spin-coated film was fast, but decreased by annealing of the film. Thermal analyses and FT-IR spectra suggested that annealing caused increase of crystal parts. Crystal structure analyses suggested that thymine bases are apart each other. Therefore, thymine bases are required to move each other for efficient photodimerization reaction. Thymine bases in amorphous state are aggregated and can move easily. Thus, spin-coated film without annealing showed the highest reactivity for photodimerization.

Experimental

Material. 2-(Thymin-1-yl)ethyl *n*-Alkylcarbamate (3). Into a solution of 1-(2-hydroxyethyl)thymine (**4**)[4] (1.7 g, 10 mmol) in *N*,*N*-dimethylformamide (DMF, 50 ml), 1,1′-carbonyl diimidazole (CDI, 2.1 g, 13 mmol) was added. The mixture was stirred at room temperature for 48 h under nitrogen. The resulting mixture was evaporated to dryness and the residue was washed with dry tetrahydrofuran to remove unreacted CDI. The resulting compound (**5**) was dissolved in DMF (60 ml), and *n*-alkylamine (12 mmol) was added. The mixture was stirred at room temperature for 24 h under nitrogen. The resulting mixture was evaporated to dryness, and the crystalline residue was washed with dry ether and recrystallized from ethyl acetate to give **3**. The products were assigned as tabulated in Table 1.

Apparatus. The melting points were determined on a Yanaco micro melting point apparatus. Differential scanning calorimetric measurements were performed by a Seiko I&E DSC20 and a SSC/580 thermal controller. The ^{1}H NMR spectra (270 MHz) were measured on a JOEL GSX FT NMR spectrometer using tetramethylsilane as an internal standard. The elemental analyses were performed by the Analytical Center of Osaka University. The FT-IR spectra were measured on a Nicolet SDXC FT-IR spectrometer. X-ray analyses were carried out by single crystal X-ray crystallography. The structures were solved by direct method using MITHRIL program.

Photodimerization. Photodimerization was carried out by irradiation of UV light at 280 nm (13.6 mJ cm^{-2} s^{-1}) by a JASCO CRM-FA Spectro Irradiator. Photoreactions were followed by UV absorption at 270 nm determined on a MASCO UVIDEC-660.

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