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チミン塩基化合物の固相状態における可逆的光二量化反応と
その反応機構に関する研究

NORIMITSU TOHNAI
MATERIAL AND LIFE SCIENCE
GRADUATE SCHOOL OF ENGINEERING
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Preface

This studies was carried out under the direction of Proffessor Mikiji Miyata at Material and Life Science, Graduate School of Engineering, Osaka University, Japan, from 1993 to 1999. The interest of this study is focused on the relationship between structure, photoreactivity and mechanism of thymine derivatives.

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January, 1999

CONTENTS

Chapter.1

Reversible Photodimerization of Thymine Derivatives in Spin-Coat Thin Film
For Ester Derivatives of Thymine and 1-Alkylthymines

Chapter.2

Photodimerizatin of 1-Alkylthymine in Single Crystal ; from Ethyl Acetate

Chapter.3

Photoactive and Inactive Crystal of 1-Alkylthymine Derivatives

Chapter.4

Photodimerizatin of 1-Alkylthymine Crystallized from Acetonitrile Solution

GENERAL INTRODUCTION

The genetic information of DNA is quite stable judged from the germination of the 2000 years old lotus seed. Recently, skin cancer is taken up as a topic in Europe and United States. It is one of causes not to transmit the genetic information correctly being damaged DNA of the skin cell by UV light. The base parts of thymidine which is one of DNA are photodimerized when UV light is irradiated to the skin. The transmission of the genetic information is obstructed and the cancer generates as a result. These photodimers are cleavaged and restored by enzyme in vivo. But we clarified the reversible photoreaction could be controlled by the regulation of UV wave length. It is original that DNA, which is quite stable chemically and thermally, would be applied to rewritable photorecording system by UV light. It is a ultimately purpose to apply the transmission phenomenon of information in such nucleic acids to the rewritable photorecording device.

The advantage which the thymine base is used is to be easy the chemical modification of thymine, to be able to synthesize various thymine compounds, and not to lose photoreactivity after the chemical modification. The self-assembly of the molecule is promoted by modifying and the effectiveness of photoreaction can be raised. In the optical disk and the optical-magnet disk, the laser light in the visible light area is used as a heat source. Their systems are called heat mode. However, the recording density is limited by the size and the thermodiffusion of the laser spot. On the other hand, the photochromic compounds, which is expected as photon mode recording system, are actively researched in all over the world. This system might realize the wave length multiple recording. Thymine is photochromic compound and one of candidates for the system. The photoreaction of thymine in solid states is necessary for the photorecording device. So the author studied the reversible photodimerizations and their mechanisms for thymine compounds in solid states.

This thesis consists of following four chapters. Chapter 1 describes the photodimerizations in spin-coat film and in the annealed film. Chapter 2 deels with the reactivity and the mechanism of photodimerization for 1-octylthymine in solid state. In Chapter 3, the author shows the reactivity for the photodimerization of 1-octylthymine in the crystal obtained from ethanol solution. And Chapter 4 describes the photoreactivity of 1-alkylthymines in the crystals obtained from acetonitrile solution.

Chapter 1

Reversible Photodimerization of Thymine Derivatives in Spin-Coat Thin Film

For Ester derivatives of thymine and 1-*n*-Alkylthymines

Thymine compounds having long alkyl chain gave efficiently photodimer in spin coat film by irradiation at 280 nm UV light. As the photodimerization was reversible, repeating of the photodimerization and the photosplitting by irradiation at 240 nm occurred. The reversible photodimerization depended on the length of alkyl chain, and annealing of the film. Annealing of the film caused crystallization and deformation of the crystal. The structure of the thin film was estimated from powder X-ray analysis, thermal analysis, and isomer ratio of the photodimer. The photodimerization in thin film was related to the structure of the thin film.

1-1. INTRODUCTION

Thymine compounds give photodimer by irradiation of UV light at 280 nm . As this reaction is reversible, the photodimer give the original thymine compound by irradiation at 240 nm (Figure 1). Figure 2 shows typical repeated reversible photodimerization. Reversible

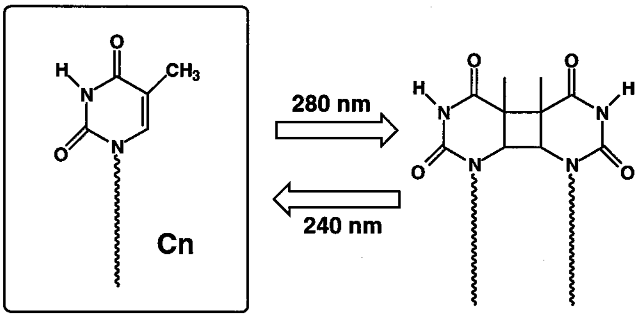


Figure 1

Reversible Photodimerization of the Thymine Derivatives.

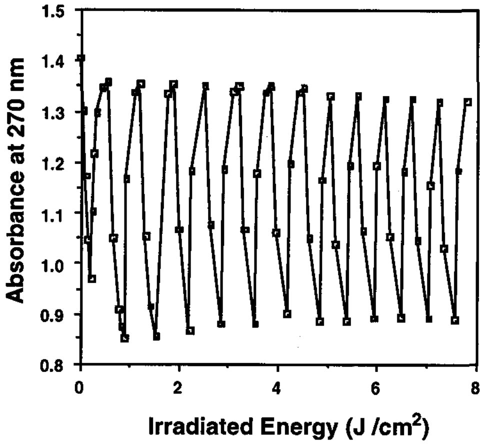


Figure 2

Typical Repeated Reversible Photodimerization

(1-*n*-Hexadecylthymine in spin-coated film)

photodimerization of thymine compounds must progress at high speed in order to apply the derivative to the optical record material.[1-2)] For the fast photodimerization, thymines should be in ordered orientation. For this purpose, thymine compounds having long alkyl chain were prepared such as 1-n-alkylthymine, ester derivatives and carbamate derivatives.[3-6)] The photodimerization of these compounds were studied in thin film, in polymer matrix and in single crystals.[7-11)] This paper deals with the reversible photodimerization of the ester derivatives of thymine and 1-*n*-

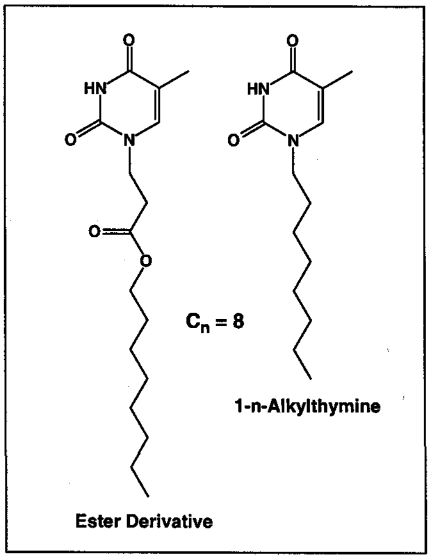


Figure 3

Ester Derivatives of Thymine and 1-*n*-Alkylthymines alkyl thymines in spin-coated thin film (Figure 3). Annealing of the film caused acceleration of the photodimerization, but prolonged annealing caused no photodimerization. In this paper, the structure of the thin film was estimated from powder X-ray analysis, thermal analysis, and isomer ratio of the photodimer. The photodimerization in thin film was related to the structure of the thin film.

1-2. EXPERIMENTAL

Materials

Ester derivatives of thymine

To pyridine solution (20 ml) of 1-(2-carboxyethyl)thymine (1.5 g, 7.5 mmol) and *n*-alkyl alcohol (C8-C13) (10 mmol), DCC (1.5 g, 7.5 mmol) was added at 0°C. The solution was stirred for 2 hr at 0°C, and 2 days at room temperature. The precipitated dicyclohexyl urea was removed by filtration. After evaporation of the solvent, the residue was washed twice with ethyl ether and recrystallized from benzene. Recrystallization from benzene was repeated to give pure product. Table 1 shows elementary analysis of the ester derivatives of thymine.

Compound	**Calcd.(%)**			**Found(%)**		
	H	**C**	**N**	**H**	**C**	**N**
T-E-9	8.70	62.94	8.63	8.66	63.18	8.56
T-E-10	8.93	63.88	8.28	8.83	63.70	8.56
T-E-11	9.15	64.15	7.95	9.18	65.00	7.90
T-E-12	9.35	65.54	7.64	9.41	65.50	7.91
T-E-13	9.54	66.28	7.36	9.49	66.27	7.37
T-E-14	9.71	66.91	7.10	9.18	66.86	7.21
T-E-15	9.87	67.61	6.86	9.89	67.47	7.17
T-E-16	10.02	68.21	6.63	10.14	68.41	6.58

Table 1

Elementary Analysis of Ester Derivatives of Thymine

Phtodimerization in thin film

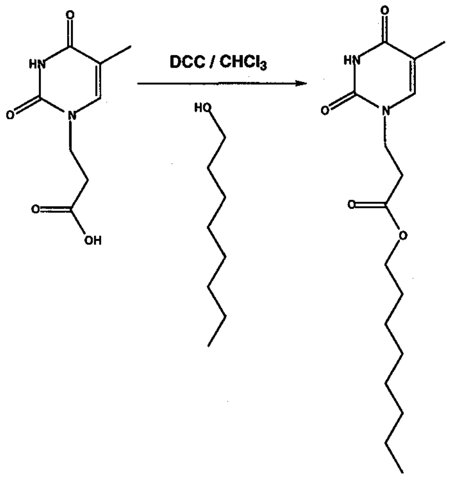
Thin film was obtained by spin coating on a quartz plate from chloroform solution, followed by drying overnight under reduced pressure. Irradiation of UV light was carried out by spectro irradiator (CRM-FA) at 280nm for dimerization and 240 nm for splitting reaction. The energy irradiated was 8.0 (mJ /count) at 280 nm, and 2.0 (mJ /count) at 240 nm. The photodimerization was followed by measuring UV spectra at 270 nm (Nihon Bunko UV/ VIS600). 1H-NMR Spectra were recorded with a Varian unity INOVA600 and JEOL GSX270. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) were measured by a Rigaku Thermo Plus TG8120 instrument. X-ray powder diffraction patterns were measured by Rigaku X-ray diffractometer RINT 2000 with Cu-$K\alpha$ radiation.

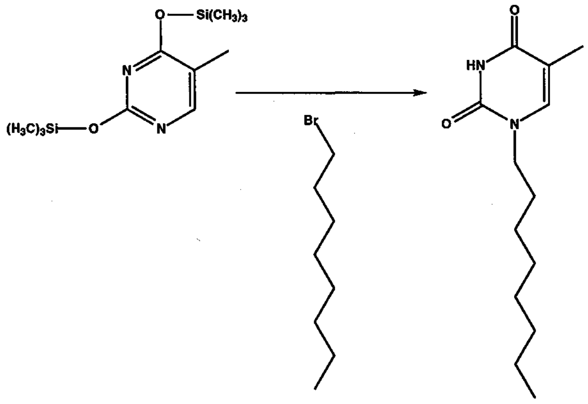
Photodimerization in polymer matrix

Chloroform solution of polyvinyl acetate (3 mmol) and the thymine derivative (1 mmol) was used for spin coating. The film was dried overnight in desiccator under reduced pressure.

1-3. RESULTS AND DISCUSSION

Synthesis of the thymine derivatives having long alkyl chain





Ester derivatives of thymine were prepared by condensation reaction using dicyclohexycarbodiimide (DCC) in chloroform solution (Scheme 1). 1-n-Alkylthymines were prepared by the reaction of 2, 4-bis (trimethylsilyl)-5-methylpyrimidine with n-alkyl bromide (Scheme 2).

Photodimerization of the ester derivative in Solution

Photodimerization of thymine in solution is known to occur from triplet state.[12-15)] The reaction, however, is very slow because efficiency of intersystem crossing is very low. Figure 4 shows the photodimerization of decyl derivative of 1-carboxyethylthymine (Cn=10) in chloroform solution by irradiation at 280 nm. The reaction was followed by UV spectra at 270 nm. The reaction was slow but give the photodimer quantitatively.

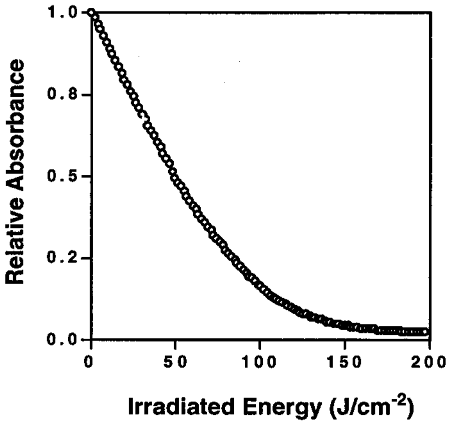


Figure 4

Photodimerization of Decyl Derivatives of 1-Carboxyethylthymine in Chloroform Solution

In the case of the photodimerization by monochromatic light at 280 nm, the thymine monomer gives the photodimer quantitatively with out by-product (Equation 1). As the energy of the irradiated light to thymine (E) is proportional to the reaction time, Equation 2 can be obtained, where A0 and At are UV absorption of the film at 270 nm at time=0, and t, respectively. The plots by Equation 2 shown in Figure 5 gave a straight line for the photodimerization in chloroform solution.

$$2M \xrightarrow{k} D$$

$$-\frac{d[M]}{dt} = k[M] \quad \text{..............................} (1)$$

$$\ln \frac{A_t}{A_0} = -k'E \quad \text{..............................} (2)$$

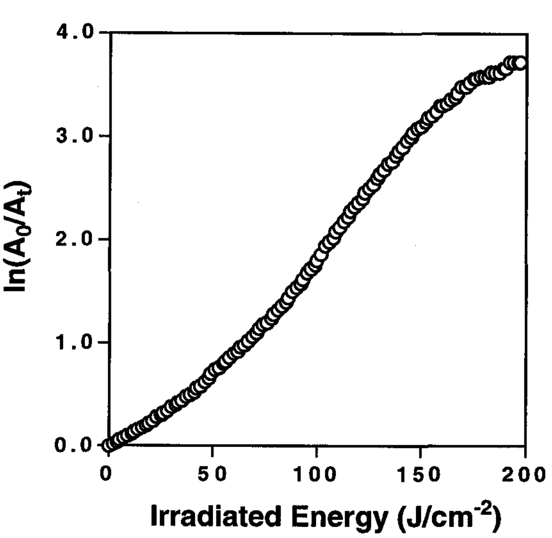


Figure 5

Rate of Photodimerization of Decyl Derivatives of 1-Carboxyethylthymine in Chloroform Solution

Photodimerization of the ester derivative in polymer matrix

Photodimerizations of the ester derivative of thymine (decyl, Cn=10) were fund to be reversible in polyvinyl acetate film. The photodimerization in polymer film was about 20 times faster than that in solution. The reason of the fast reaction should be that the photodimerization in polymer film was occurred in the aggregated thymines via singlet state.[16-18)] Figure 6 shows the plots using Equation 2 for the first photodimerization and the second photodimerization after splitting reaction at 240 nm. Both plots gave good linearity.

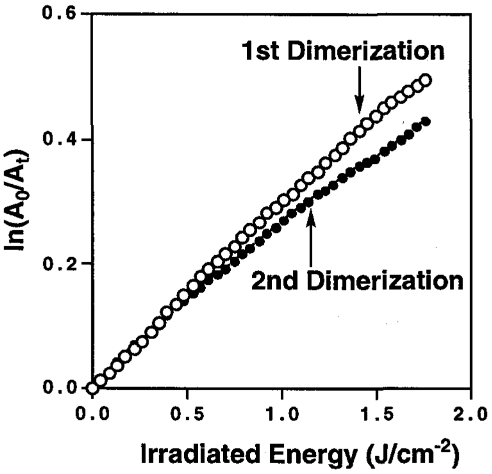


Figure 60,

First andSecond Rates of Photodimerization of Decyl Derivatives of 1-Carboxyethylthymine in Polymer Matrix

Photodimerization of the ester derivative in spin-coated film

Photodimerization in spin-coated film for the ester derivatives of thymine (tridecyl, Cn=13) gave excellent reversibility as shown in Figure 7. For the compounds Cn=9 (nonyl) and Cn=15 (pentadecyl), however, the reversible reactions decayed with repeat of reactions.

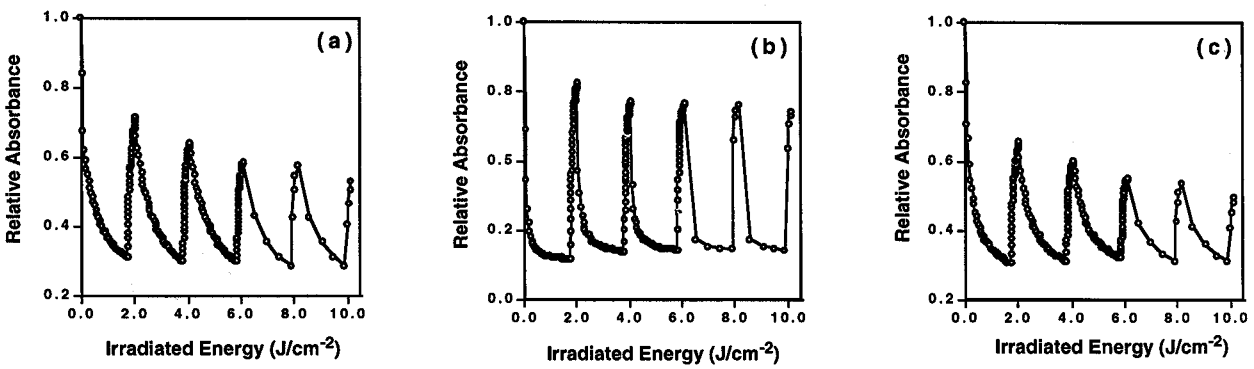


Figure 7

Photodimerization for Ester Derivatives of thymine in Spin-coated Film

a: Nonyl Ester Derivative (Cn=9)

b: Tridecy Ester Derivative (Cn=13)

c: Pentadecyl Ester Derivative (Cn=15)

The first, the second and the third photodimerization reactions were plotted in Figure 8. The first photodimerization of the spin-coated film of nonyl (Cn=9) and pentadecyl (Cn=15) derivatives was fast in the beginning of the reaction, followed by slow reaction after bending point. For the second and the third photodimerization, however, clear bending point was not observed. The photodimerization of the tridecyl derivative (Cn=13) was very fast and the bending point was observed even for the second and the third photodimerization. These findings suggested that there were two reactive sites in the spin-coated film: One site gave the fast reaction, and the other site gave the slow reaction. The photodimerization from the fast reaction site was 20 times faster than the reaction in polymer matrix.

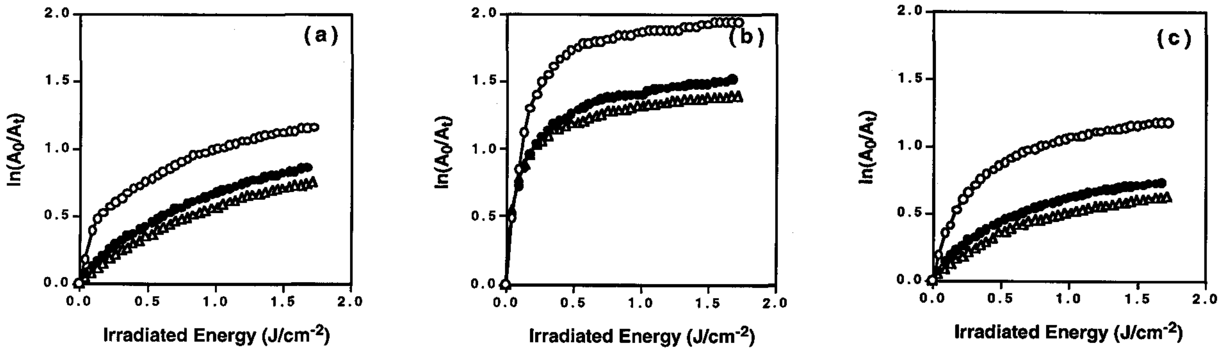


Figure 8

First, Second and Third Rates of Photodimerization for Ester Derivatives of thymine in Spin-coated Film

a: Nonyl Ester Derivative (Cn=9)

b: Tridecy Ester Derivative (Cn=13)

c: Pentadecyl Ester Derivative (Cn=15)

The first photodimerization reactions were plotted in Figure 9 for nonyl (Cn=9) to pentadecyl (Cn=15) ester derivatives of thymine. The rate of photodimerization increased with length of alkyl chain from nonyl (Cn=9) to tridecyl (Cn=13), and slow downed after tridecyl

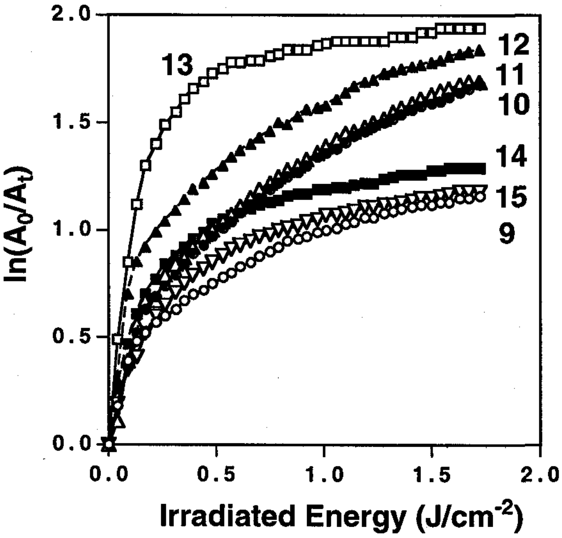


Figure 9

First Rate of Photodimerization for Nonyl (Cn=9) to Pentadecyl (Cn=15) Ester Derivatives of Thymine

(Cn=13) to pentadecyl (Cn=15). The fast rates of photodimerization in the beginning of the reaction and the slow reaction rates in the later were plotted against carbon number of the alkyl chains in Figure 10. For the compounds of dodecyl (Cn=12) and tridecyl (Cn=13), the fast reaction did not decay after repeated reactions. The slow reactions, however, did not depend on the length of the alkyl chain. The dependency of the photodimerization on the length of the alkyl chain may be caused by difference of the crystal structure in the spin-coated film.

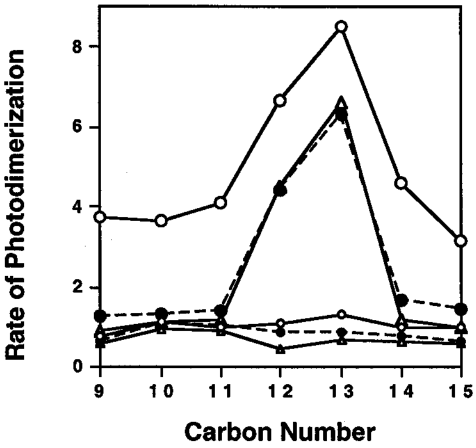


Figure 10

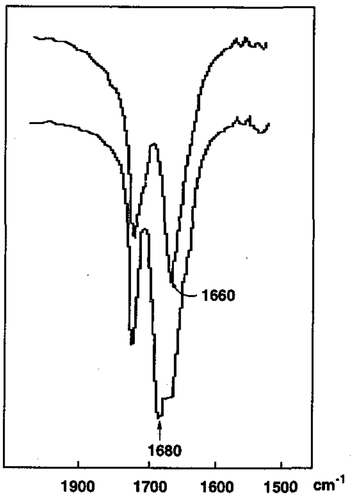
Plots of Rate of Photodimerization against Carbon Number of Alkyl Chains

○ ; First Rate of Splitting Reaction

● ; Second Rates of Splitting Reaction

△ ; Third Rates of Splitting Reaction

IR spectra of the ester compounds near 1700cm^{-1} were found to depend on the alkyl chain (Figure 11). The ratio of IR spectra, 1660/1680 cm^{-1}, of an odd numbered alkyl chain was higher than that of the even-numbered alkyl chain. These values were plotted with melting points against the carbon number of the alkyl chain for the ester derivatives in Figure 12. The difference in IR spectra may be caused by the interaction between thymine base and the ester bond, because such difference in IR spectra was not observed for 1-*n*-alkylthymines. The parity was observed for the carbamate derivatives of thymine having long alkyl chain. No relation, however, was observed between Figure 12 and the rate of photodimerization in Figure 9.



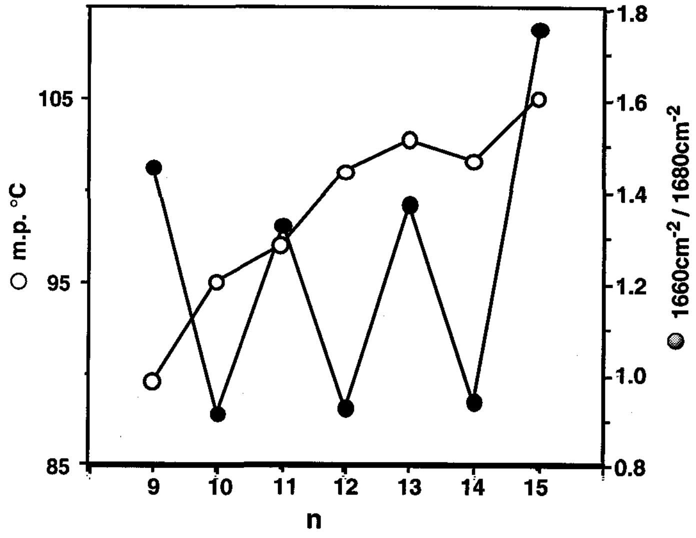


Figure 11

Two Kinds of IR Spectra of Ester Compounds neat 1700cm^{-1}

Figure 12

Relationship between Melting Points and IR Spectra

○ ;Melting Point against Carbon Number of Alkyl Chains

● ;IR Spectra against Carbon Number of Alkyl Chains

Figure 13 shows the reverse reactions for tridecyl (Cn=13) by irradiation of UV light at 240 nm. The first, the second and the third reverse reactions gave similar pattern, which is different from the results of photodimerization in Figure 8. The first reverse reactions are summarized in Figure 14. The reverse reaction of tridecyl (Cn=13) was also fastest as the case of the photodimerization.

The results of the reversible photodimerization for the ester derivatives of thymine indicated the presence of two or more reactive sites in the spin-coated film. These reactive sites may arise from different crystal structure. Unfortunately, single crystal of the ester derivatives for X-ray crystal analyses have not been obtained. Detailed mechanism of the photodimerization for the ester compound may become clear after X-ray crystal analyses of the crystal.

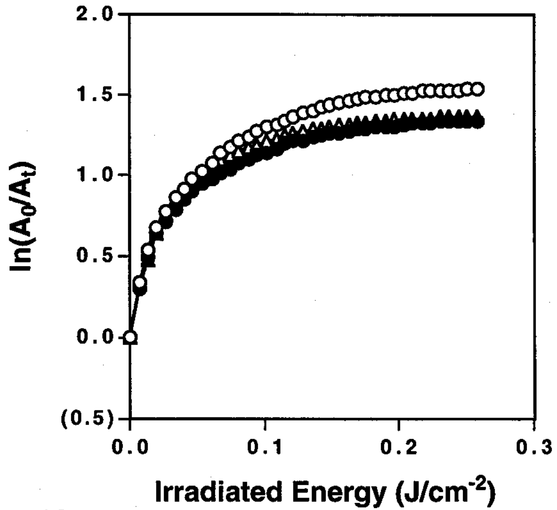


Figure 13

Rates of Splitting Reaction for Tridecy Ester Derivative (Cn=13)

○ ; First Rate of Splitting Reaction

● ; Second Rates of Splitting Reaction

△ ; Third Rates of Splitting Reaction

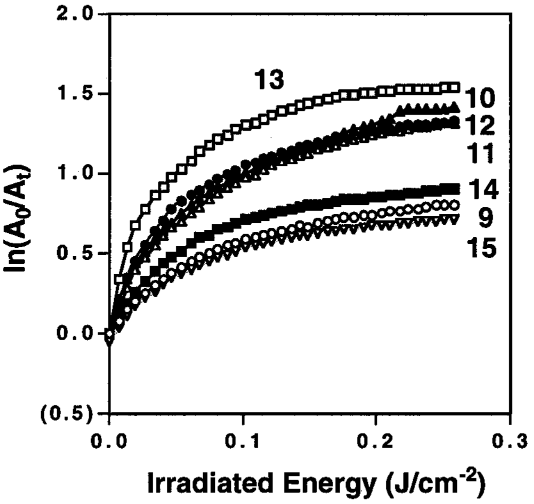


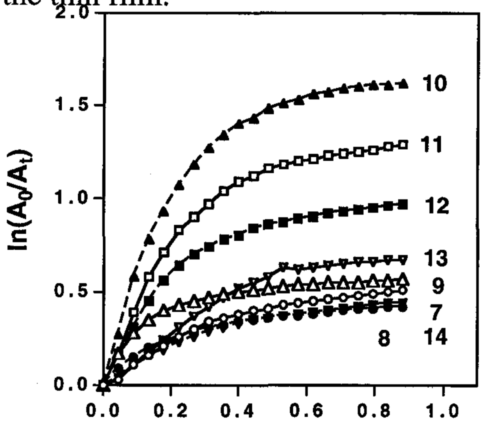
Figure 14

First Rates of Splitting Reaction for Nonyl (Cn=9) to Pentadecyl (Cn=15) Ester Derivatives of Thymine

Photodimerization of 1-*n*-alkylthymines in spin-coated film

Photodimerization of 1-*n*-alkylthymine depend also on the length of the alkyl chain. The first photodimerization was plotted in Figure 15. The reaction was fast in the beginning of the reaction, followed by slow reaction in the late reaction stage. In this case, decyl (Cn=10) compound had the fastest photodimerization reaction (Figure 16).

The photodimerization was found to depend on the kind of solvent for spin-coat as shown in Figure 17 (decyl, Cn=10). The solvent is known to remain after drying of the spin-coated film. The remaining solvent may affect on the ratio of the reactive sites and unreactive sites in the thin film.



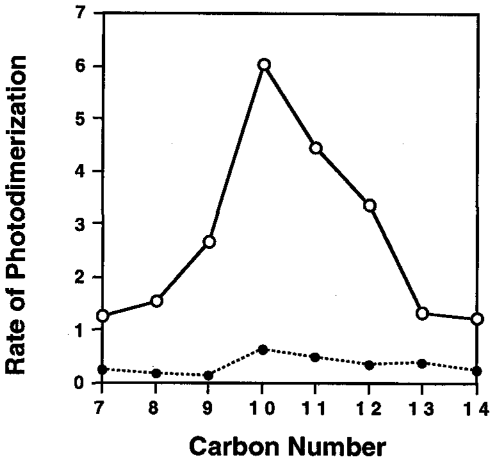


Figure 15

First Rates of Photodimerization for Heptyl (Cn=7) to Tetradecyl (Cn=14) Ester Derivatives of Thymine

Figure 16

First Rate Plots against Carbon Number of Alkyl Chains

○ ; Begining of Reaction

● ; Late Reaction Stage

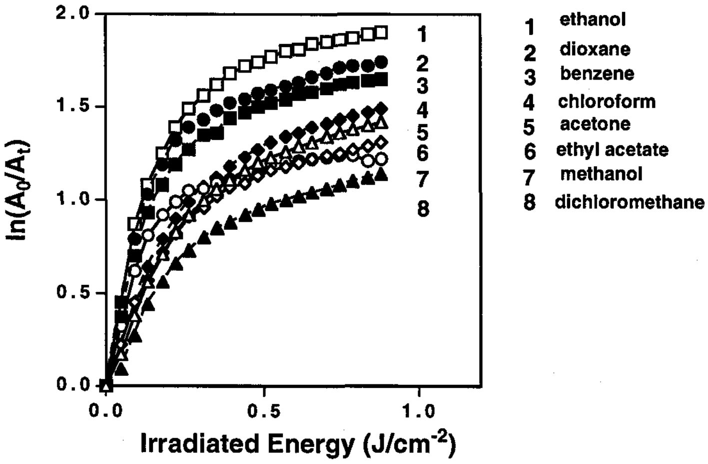


Figure 17

First Rates of Photodimerization for Decyl Ester Derivative (Cn=10) in Spin-coated Film with Several Solvents

Annealing of the thin film

Annealing of the spin-coat film was found to affect on the photodimerization of the 1-*n*-alkyl thymine (Figure 18). Figure 18 is the result of photodimerization of 1-*n*-tetradecylthymine (Cn=14) in thin film. Figure 19 shows the first photodimerization of the annealed film. Annealing for 1 min at 100°C below melting temperature (123°C) caused an acceleration of the fast photodimerization reaction in the initial reaction stage, but the conversion was decreased. The photodimerization could not occur for the film after annealing for 4 min. This finding suggests that the reactive site for the fast reaction in the film was increased by annealing for 1 min. Then, the reactive site changed to inactive site by annealing for 4 min.

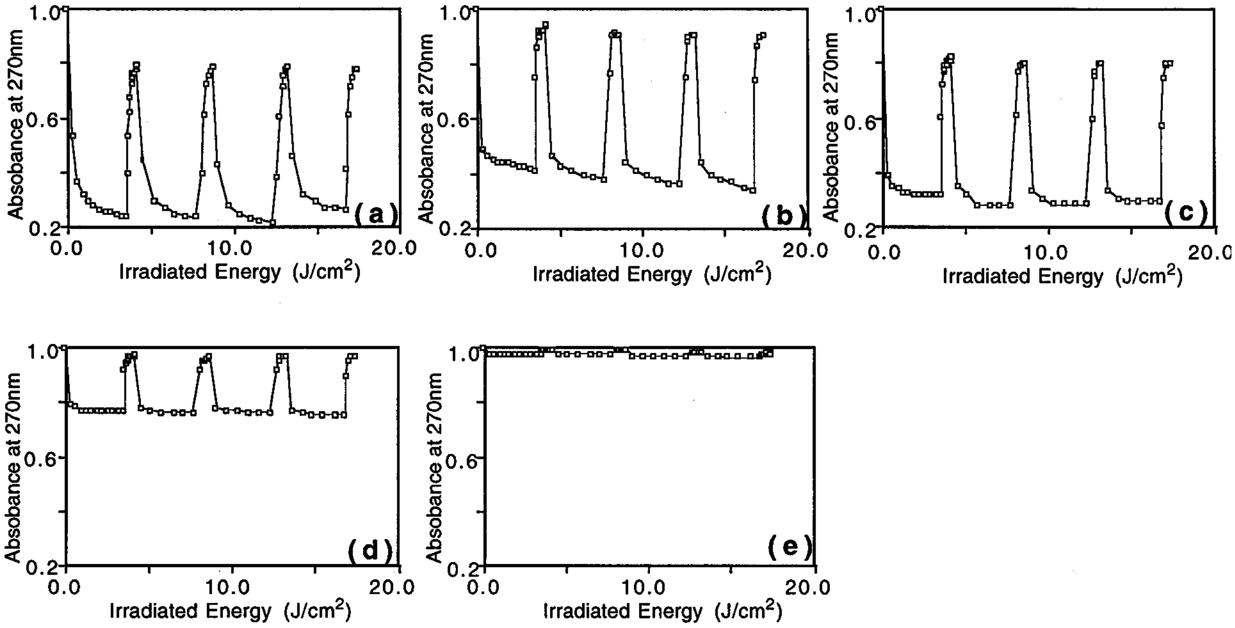


Figure 18

Reversible Photodimerization on Thin-Films in Several Annealing Times for 1-*n*-Tetradecylthymine

a: 0 min's annealing b: 1 min's annealing

c: 2 min's annealing d: 3 min's annealing

e: 4 min's annealing

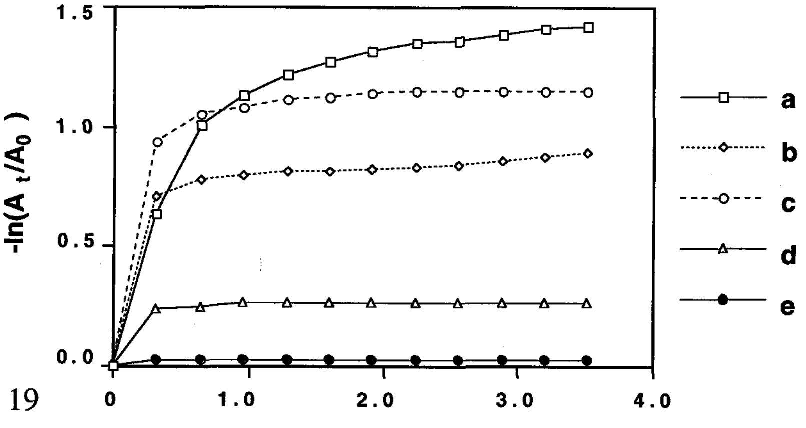


Figure 19

Rate of Photodimerization on Thin-Film in Several Annealing Times for 1-*n*-Tetradecylthymine

a: 0 min's annealing b: 1 min's annealing

c: 2 min's annealing d: 3 min's annealing

e: 4 min's annealing

Powder X-ray Diffraction of 1-*n*-Tetradecylthymine.

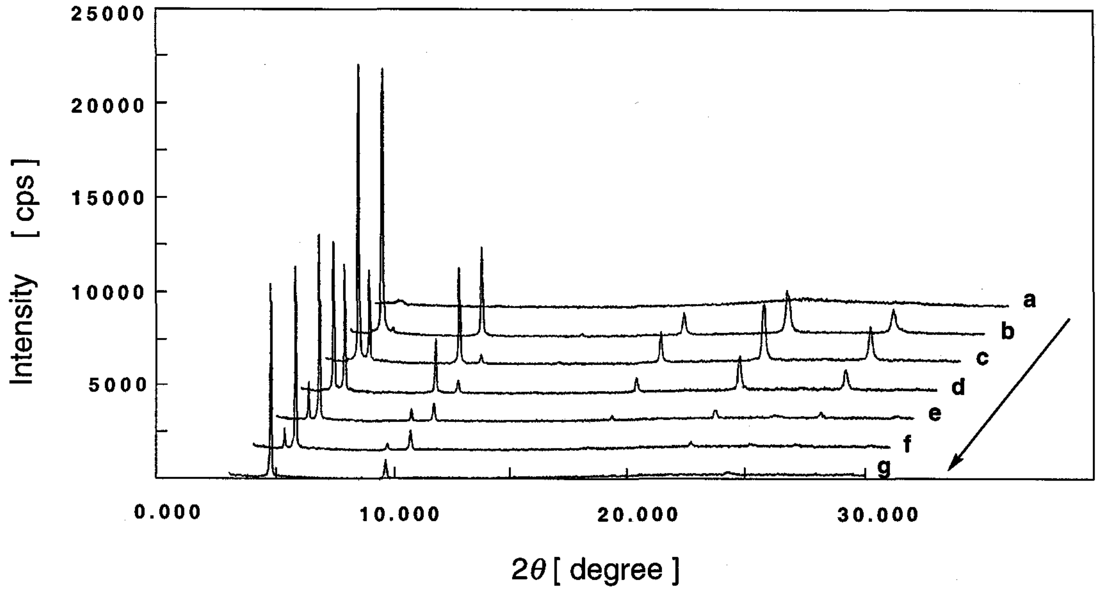


Figure 20

X-ray Powder Diffraction on Thin-Films in Several Annealing Times for 1-*n*-Tetradecylthymine

a: 0 min's annealing b: 1 min's annealing c: 2 min's annealing d: 3 min's annealing

e: 4 min's annealing f: 5 min's annealing g:10 min's annealing

The powder X-ray diffraction (XRD) was measured for the spin-coat film of 1-*n*-tetradecylthymine (Cn=14) and the annealed films (Figure 20). The spin-coat film had only broad peak (a), suggesting amorphous state of the film. New peaks were appeared by annealing of the film for 1 min (b), the big peak at $2\theta = 4.360°$ on low angle and small peaks at 8.660°, 17.320°, 21.680°, and 26.080° (Structure I). By additional annealing for 1 min, all peaks grew bigger and the crystallinity rose (c). Moreover, the new peaks at $2\theta = 4.800°$, 9.620° appeared. These new peaks indicated thin film already began to shift to next structure (Structure II) from Structure I. After annealing for 3 min, the first five peaks derived from Structure I became to be smaller and new two peaks grew bigger (d). For the annealed thin film for 4 min, the peak at $2\theta = 4.360°$ was quite small and other four peaks on higher angle went out gradually (e). At last the first five peaks went out completely, and the only two peaks at $2\theta = 4.800°$, 9.620° existed (f, annealing for 5 min). The structure of the thin film after annealing for 10 min (g) was defined as Structure II.

Annealing of the amorphous state of the spin-coat film caused crystallization of the thymine compound to give Structure I, which is very active for photodimerization. Prolonged annealing, however, caused deformation of the Structure I to Structure II that is inactive for the photodimerization.

Thermal Analysis of the Thin Films

The each transition point of amorphous state to Structure I and Structure I to Structure II was obtained by differential thermal analysis (DTA) study (Figure 21). Samples were prepared with coming off the quartz plate. The trace (a) shows a broad exothermic peak at around 56°C and a large endothermic peak at 123°C that is melting point. The peak at 56°C should be the crystallization point of Structure I. The thin film after annealing form 1 min (b) shows an exothermic peak at 72°C and the same endothermic peak at 123°C as the spin coat film (a). The exothermic peak at 72°C for (b) should be the deformation point from Structure I to Structure II.

Only endothermic peak at 123°C was observed for the thin film after annealing for 10 min (c), which is indicated Structure II from powder X-ray analysis in Figure 20.

Amorphous state shifted at very low temperature (56°C) because the amorphous state was very unstable. Structure I shifted to Structure II. Therefore, Structure II is more stable than Structure I. When the sample (b) was heated to 80°C and cooled to 50°C, the DTA trace for this sample was the same as sample (c). Then, Structure I transformed to Structure II at 72°C.

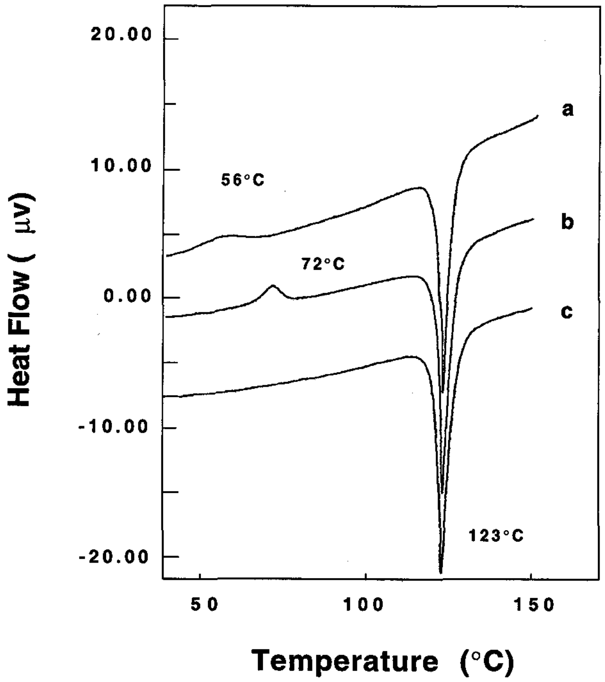


Figure 21

Differential Thermal Analysis of Thin-Film for 1-*n*-Tetradecylthymne in Several Annealing Times

a: 0 min (spin-coated) b: 2 min's annealing

c: 10 min's annealin

Isomers of the photodimers

There are four isomers for the photodimer of thymine compounds as shown in Figure 22. Irradiation of UV light on DNA gives only *cis-syn* photodimer.$^{19\text{-}20)}$ Photodimerization of the thymine derivatives in solution, however, gives four kinds of photodimer that were identified by NMR spectra (Table 2). The photodimerization of the spin-coat film from chloroform solution gave *trans-syn* and trans-anti photodimers with equal ratio. The same mixture of the photodimers was obtained by the photodimerization of needles from acetonitrile solution.[11] On the other hand, the photodimerization of the annealed film for 2 min gave only trans-anti photodimer. The plates from ethyl acetate solution gave only *trans-syn* photodimer.[9]

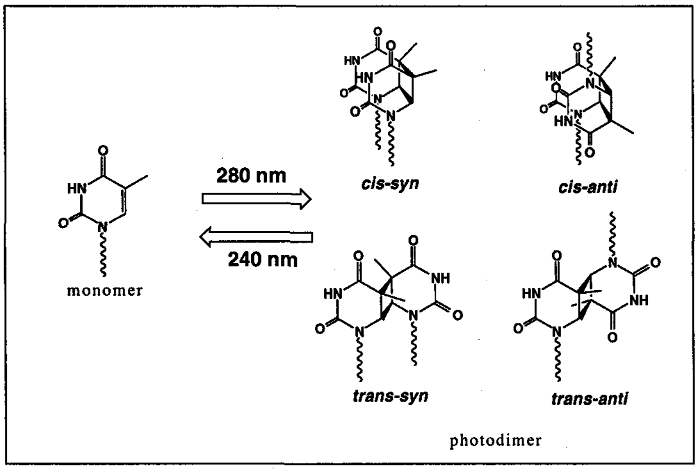


Figure 22

Four Stereo Isomers of 1-*n*-Alkylthymine Photodimer

	cis-syn	*cis-anti*	*trans-syn*	*trans-anti*
solution	**0.85**	**0.76**	**1.00**	**0.95**
spin-coated	**0.14**	**0.32**	**0.98**	**1.00**
2 min's annealled	**0.06**	**0.16**	**0.23**	**1.00**

Table 2

Rates of Photodimers for 1-*n*-Tetradecylthymine in Several States

Effect of chain length on the annealing time

Annealing of the spin coat film caused crystallization to Structure I and deformation to Structure II. The annealing time was found to depend on the length of alkyl chain. Figure 23 shows relation ship between the fast photodimerization rate in begging of the reaction and the annealing time. Change to the Structure I was fast for the compound having short alkyl chain (dodecyl, Cn=12), and slow for the compound having long alkyl chain (pentadecyl, Cn=15).

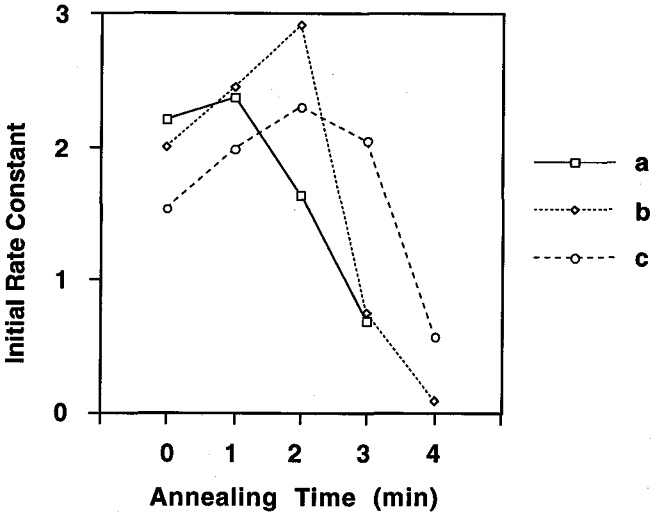


Figure 23

Initial Rate Constants of Photodimerization on Thin-Film in Several Annealing Times for 1-*n*-Alkylthymines

a: 1-*n*-Dodecylthymine

b: 1-*n*-Tetradecylthymine

c: 1-*n*-Pentadecylthymine

Prolonged annealing caused deformation of Structure I to photo-inactive Structure II, and the conversion of photodimer decreased. The photoactive Structure I was found stable for the thymine compound having long alkyl chain (Figure 24).

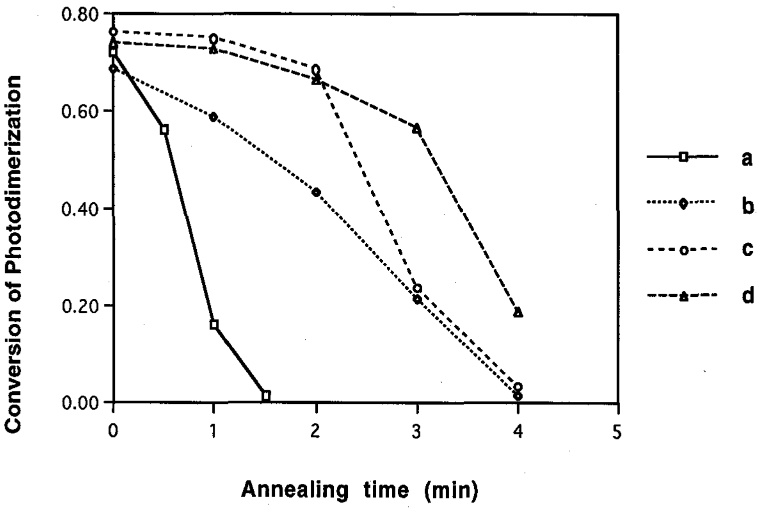


Figure 24

Conversion of Photodimerization on Thin-Film in Several Annealing Times for 1-*n*-Alkylthymines

a: 1-*n*-Octylthymine

b: 1-*n*-Dodecylthymine

c: 1-*n*-Tetradecylthymine

d: 1-*n*-Pentadecylthymine

Reverse reaction and annealing

Splitting of the photodimer by irradiation at 240 nm depended also on the length of the alkyl chain. Annealing of the spin-coat film caused an acceleration of the reverse reaction as shown in Figure 25. In the same Figure, the result of the reverse reaction was also plotted for the film that was prepared from the solution of photodimer. The re-prepared film gave slower reaction compared to the annealed film. Rotation of the thymines in crystal during photodimerization may cause strain in the crystal. The strain in the crystal may be the driving force for the reverse reaction. The strain in the crystal disappears by resolving the crystal.

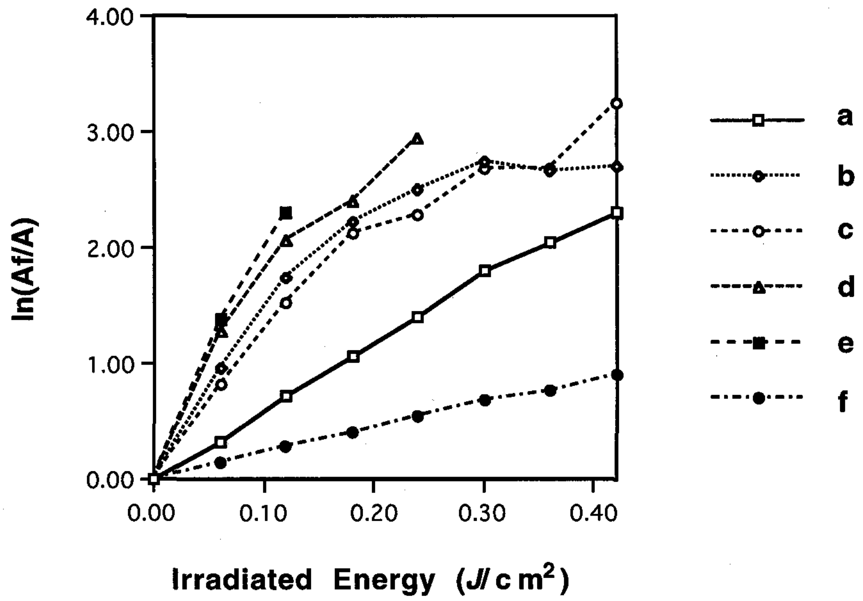


Figure 25

Splitting Rate of Photodimer on Thin-Film in Several Annealing Times

a: 0 min's annealing b: 1 min's annealing

c: 2 min's annealing d: 3 min's annealing

e: 4 min's annealing f: Spin-Coated Thin-Film for *trans-anti* dimer

Structure of the thin film formed by annealing

Alkyl derivatives of thymine have two sites for interaction; thymine base for hydrogen bonding interaction and alkyl group for hydrophobic interaction.[11)] When the alkyl chain is short, the hydrogen bonding of thymine bases is a main factor for interaction in preference to the hydrophobic interaction by the alkyl group. When the alkyl chain is long, on the contrary, the hydrophobic interaction is a main factor in preference to the hydrogen bonding. Therefore, the structure of thin film should be affected by length of the alkyl chain. The studies of photodimerization of 1-*n*-alkylthymine in single crystal revealed that the thymine bases rotated disrotatory in the crystal during photodimerization reaction.[9,11)] When the density of the crystal is high, the photodimerization could not occur because the rotation of thymine bases in crystal is inhibited.

Four kinds of crystal structure were found for the 1-n-alkylthymine from X-ray crystal analysis as tabulated in Table 3. Plates from ethyl acetate solution and needles from acetonitrile solution gave photodimers. The other crystals did not give photodimers. Rotation of the thymine base was concluded during the photodimerization in crystal. As the photoactive crystals are soft, rotation of thymine base in the crystal is possible. As the photo-inactive crystals are hard, rotation of thymine base is impossible.[9-11)]

crystal structure	solvent	shape	stability	inclusion	photpreaction	isomer
Form I	ethyl acetate, chloroform/*p*-xylene	plates	unstable	-	○	*trans-anti*
Form II	ethanol, methanol acetonitrile, acetone	plates	stable	-	x	-
Form III	acetonitrile	needles	unstable	○	○	*trans-anti* *trans-syn*
Form IV	DMF	plates	stable	-	x	-

Table 3

Summery of Four Kinds of Crystal Structures for 1-*n*-Alkylthymine

Structure of the thin film formed by annealing was estimated by the results of PXD, DTA, and isomer ratio of the photodimer. The structure of the spin-coat film and the annealed film were illustrated in Figure 26. The structure of spin-coated thin film was proved an amorphous form from powder X-ray analysis. The presence of crystal part in the spin-coat film, however, was indicated from the fast photodimerization reaction and the isomer ratio of the photodimer. The structure of the small crystal in the spin-coat film proved identical with the structure of needles obtained from acetonitrile solution as judged by the isomer ratio of the photodimer. Crystallization was occurred by annealing of the spin-coat film for a short time to give Structure I. The Structure I proved identical with the structure of plates obtained from ethyl acetate solution as judged by the isomer ratio of the photodimer and powder X-ray analysis. The Structure I changed to Structure II by annealing for long time. The Structure II could not give the photodimer, which is identical with the structure of plate obtained from ethanol solution.

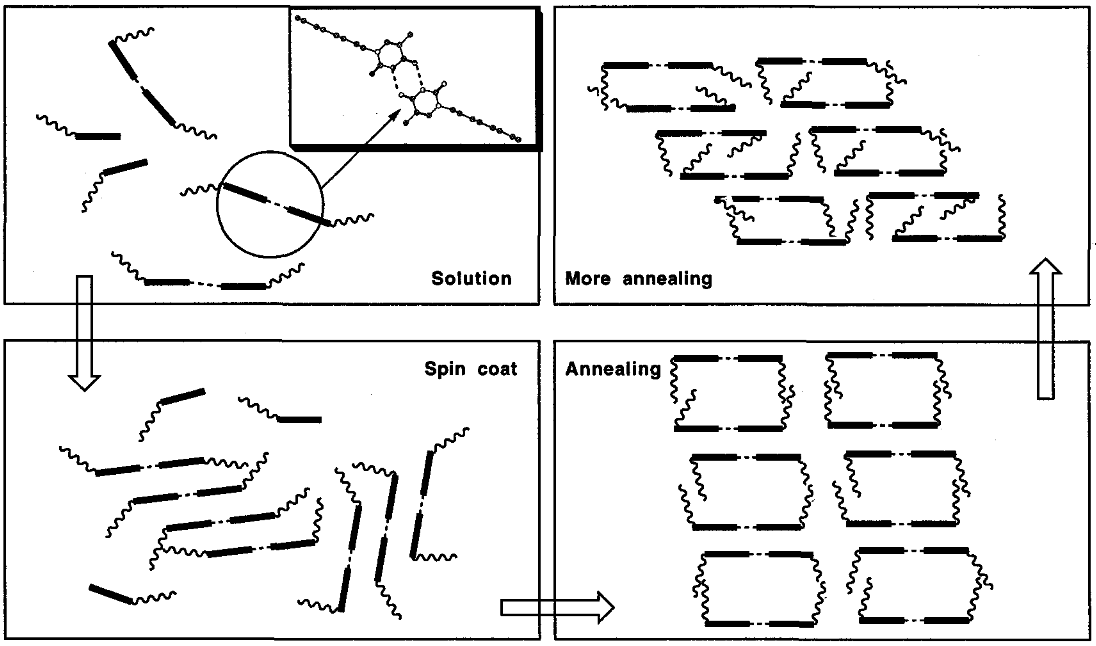


Figure 26

Illustration of Structure Transition

1-4. Conclusion

From these results, the photodimerizations in spin-coat film and in the annealed film can be concluded as follows. Reversible photodimerizations of thymine compounds having long alkyl chain were fast in spin-coat thin film where thymine bases aggregated feasibly for photodimerization. Annealing of the film caused an acceleration of the reaction because of crystallization of the thymine compound to Structure I that was just appropriate for photodimerization. Prolonged annealing, however, caused a deceleration of the photodimerization because the Structure I deformed to Structure II that is inactive for photodimerization. The highest reactivity of the photodimerization was observed for the thymine compounds having moderate chain length of alkyl group (tridecyl [Cn=13] for the ester compounds, and decyl [Cn=10] for 1-*n*-alkylthymines). In these compounds, the competitions between hydrogen bonding and hydrophobic interactions made the crystal unstable. Therefore, the thymines can rotate in these crystals during photodimerization.

The steric hindrance of the methyl group at 5-position is the main reason for the photo splitting of the thymine photodimer by irradiation at 240 nm. The reverse photodimerization did not occur for the photodimer of uracil that has no methyl group. The strain should be generated during the photodimerization of the thymine compound in crystal because the photodimerization accompany the rotation of the thymine bases. The reverse photodimerization in crystal, consequently, was a fast reaction releasing the strain in the crystal.

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Chapter.2

Photodimerizatin of 1-Alkylthymine in Single Crystal
; from Ethyl Acetate

Thymine derivative of long alkyl chain showed a very high photoreactivity in crystal state and gave only one isomer of photodimer though the photodimerization in solution gave the four isomers. The crystal structure determined by the results of X-ray analysis suggested the formation of the *trans-syn* photodimer. The photodimer obtained, however, was identified to be the *trans-anti* isomer from the NMR spectrum. The *trans-anti* photodimer was concluded to be formed by disrotatory motion of the thymine in the crystal.

2-1. INTRODUCTION

Thymine derivatives are known to give photo-dimers upon irradiation to UV light near the λmax (280 nm) of thymine. The photodimerization is reversible reaction and the photodimer splits to afford the original thymines very efficiently upon irradiation at a shorter wavelength (240 nm)(Fig. 1).

A variety of thymine derivatives were synthesized and the photoreactivity has been studied in the film state and in the polymer matrix[1-4]. The increase and the decrease in the absorbance at 270 nm are repeated as shReversibl photodimerization of the thymine derivative.UV spectra of original thymine derivatives and photodimers.Figure 2 Figure 1ows in Fig. 2 because of the formation and the cleavage of this photodimer.

It was necessary to make the reacting thymine derivatives aggregate and always make the thymines approach for the effective photoreaction in the solid phase. The movement of the thymine molecules in the solid state is restricted in the same situation as the crystal state. Therefore, the photodimerization of thymine derivatives should be studied in the crystal state. This paper deals with the crystal structure analysis and photodimerization in the crystal state of the thymine com-

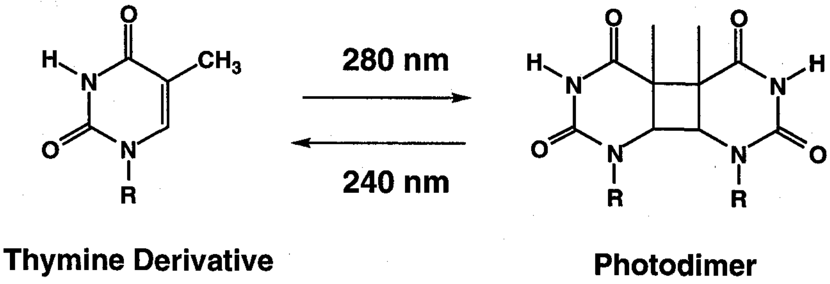


Figure 1

Reversibl photodimerization of the thymine derivative.

pound having long alkyl chain. The photodimerization in the crystal gave only one stereo isomer (*trans-anti*) of the photodimers, though the reaction in solution gave four isomers. The mechanism of the selective formation of the *trans-anti* isomer will be discussed considering the crystal structure of the thymine derivative.

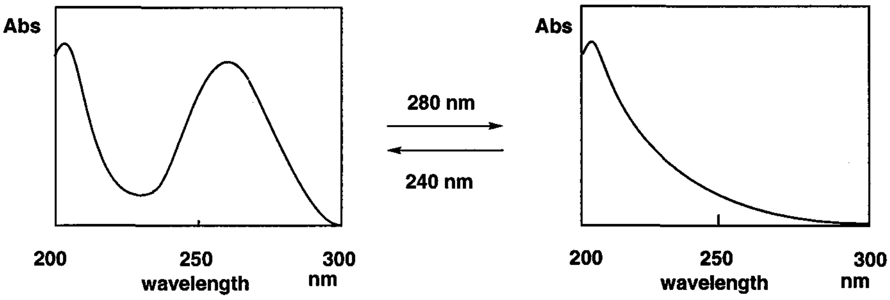


Figure 2

UV spectra of original thymine derivatives and photodimers.

2-2. EXPERIMENTALS

Synthesis of 1-Octyl Thymine (2)

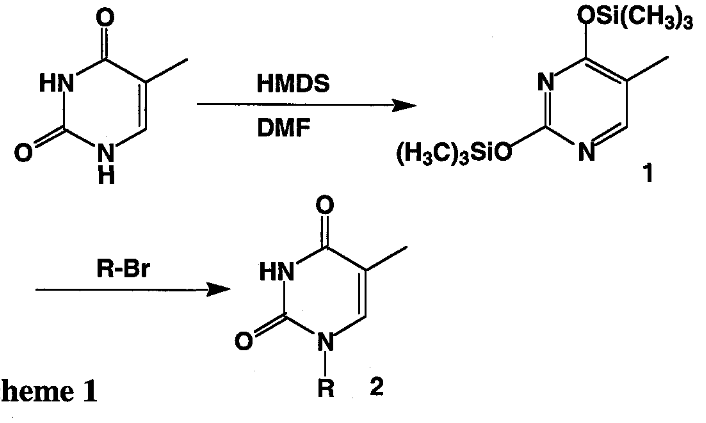
Thymine (31.5 g, 0.25 mol) in hexamethyldi-silazane (HMDS) (250 ml, 1.70 mol) was refluxed for 24 hours at 160° C with 10 ml of *N, N*-dimethylformamide (DMF) as a catalyst. After the reaction, DMF and HMDS were removed at 40 ° C under reduced pressure. By the distillation under reduced pressure (13 mmHg), 5-methyl-2, 4-bis-(trimethylsiloxy)-pyrimidine (**1**) was obtained (123-125 ° C, yield 98.7%).

A mixture of 1-octyl bromide (27.5 g, 0.142 mol) and 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine (23.8 g, 0.088 mol) was stirring for 10 days at 60 ° C. After the reaction, methyl alcohol (200 ml), 6N HCl (20 ml), and water (100 ml) were added to the obtained oil. The mixture was heated and the precipitate was filtered. After removing the solvents under reduced pressure, the residue was extracted with water/chloroform. Chloroform was evaporated and the residue was washed with petroleum ether and recrystallized with benzene to give **2** (nearly quantitative yield). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.04 (1H, s, NH), 6.98 (1H, s, C6-H), 3.69 (2H, t, N-CH_2), 1.92 (3H, s, C5-CH_3), 1.67 (2H, m, N-C-CH_2), 1.25 (10H, m, CH_2), 0.88 (3H, t, C-CH_3).

Crystal Structure Analysis

Crystal structure data for 1-octyl thymine (**2**) : $C_{26}H_{44}O_4N_4$, triclinic, space group P1, a = 17.08(1), b = 17.415(5), c = 11.756(3)Å, α= 89.97(2)°, β = 110.02(6)°, γ= 110.27(4)°, V = 3053(3) Å^3, r calc = 1.04 g cm^{-3}, Z = 8, R = 0.139, Rw = 0.077.

Intensity data of 1-octyl thymine was collected by Rigaku RAXIS-CS imaging plate two-dimensional area detector with graphite-monochromatized Mo-Kα radiation (λ = 0.71070Å) at 15±1°C. Their crystals showed 4455 unique reflections (2θmax = 59.6°). For further calculations, [|F0|>3s|F0|] reflections was used after Lorenz and polarization corrections. The structure was solved by direct methods (SAPI91), and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were located in the calculated positions.



Scheme 1

Synthesis of thymine derivatives having long alkyl chain.

The positions of hydrogen atoms attached to oxygen and nitrogen atoms were obtained from difference Fourier syntheses. All calculations were performed by using TEXSAN crystallographic software package of the Molecular Structure Corporation.

Photodimerization

Photodimerizations in crystal state were carried out by SUPER CURE-203S UV LIGHT SOURCE SAN-EI ELECTRIC (280 nm).

For the photodimerization in acetone solution, HALÕS P1H-500 C/S60 EIKOSHA was used. The obtained four isomers were separated by recrystallization. The first crystal was obtained from methanol, and was identified as *trans-syn* from NMR spectra (Table 1). The second crystal (*trans-syn*) was obtained from acetonitrile, and the third crystal (*cis-syn*) was obtained from ethyl acetate. The last crystal (*cis-anti*) was obtained from ethyl ether/petroleum ether (1/9, v/v). The NMR data for the photodimer were identical with the data of dimethylthymine except *trans-syn* dimer[5].

Table 1. Chemical shifts of four stereo isomeric photodimers (δ in $CDCl_3$).

	$C\text{-}CH_3$ 6H, t	$\text{-}CH_2\text{-}$ 20H, m	$5\text{-}CH_3$ 6H, s	$N\text{-}CH_2$ 2H, m	6-H 2H, s	$N\text{-}CH_2$ 2H, m	N-H 2H, s
trans-anti	0.87	1.27	1.43	2.84	3.78	3.90	7.82
trans-syn	0.87	1.27	1.44	2.87	3.52	3.87	7.92
cis-syn	0.87	1.26	1.50	2.53	3.79	4.01	8.63
cis-anti	0.87	1.26	1.59	2.99	3.34	3.92	8.26

2-3. RESULTS and DISCUSSION

Crystal Structure

Figure 3 shows a unit cell (a) and the plane structure (b) of the crystal of 1-octyl thymine. The unit cell contains eight molecules. The crystal is a layer structure consisted of the hydrophilic layer of thymine bases and the hydrophobic layer of long alkyl groups (Fig. 4). The distance between the two planes formed by thymine bases was almost 3.3Å . The van der Waals radius of the thymine base might be touched. Moreover, the long alkyl chain groups aggregate and form the hydrophobic layer.

The thymine bases are in the same plane (Fig. 3b), and associated by hydrogen bonding on the plane (Fig. 5). The thymine molecule faces another thymine in opposite plane with head to head (Fig. 6). As shown in the Figure 6, two thymine bases on the opposite plane were in the position of *trans-syn*. Therefore, the distance and the orientation of two thymine bases in this crystal suggest that the *trans-syn* photodimer should be obtained dominantly by photodimerization.

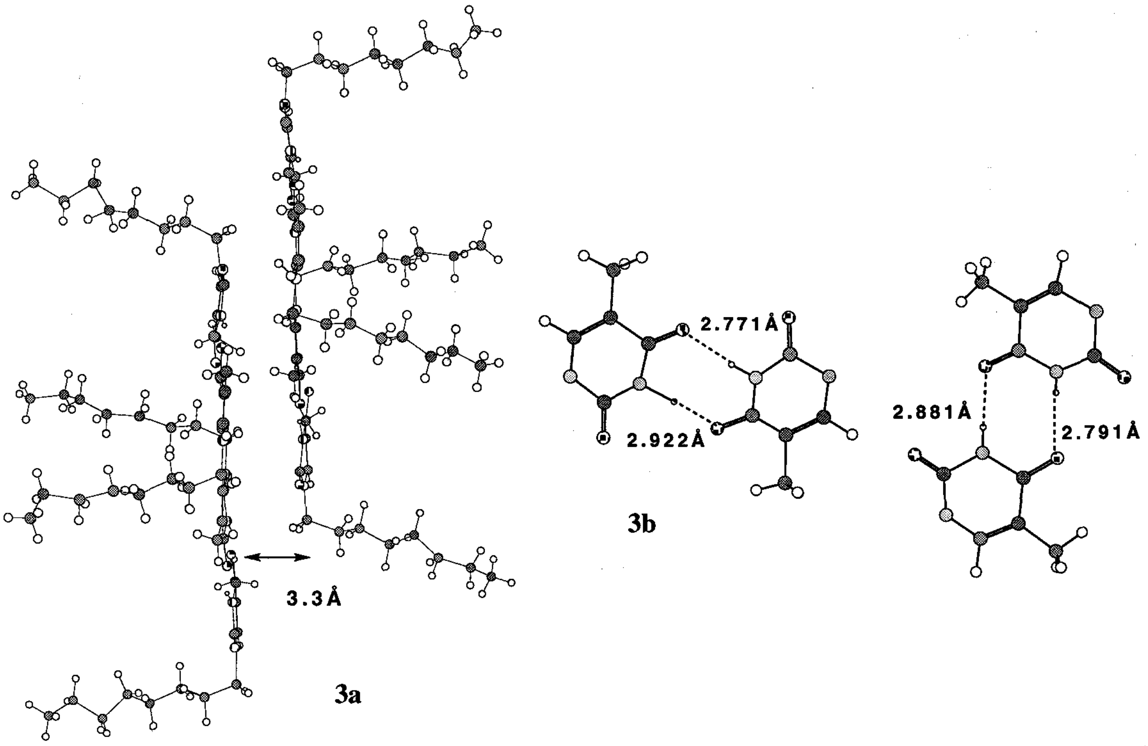


Figure 3

Crystal structure of 1-octyl thymine rerystallized from ethyl acetate.

(a) Unit cell consisted of eight molecules

(b) Plane structure and hydrogen bondings.

Photodimerization

UV light was irradiated to the plate crystal which was obtained by recrystallization from ethyl acetate. The process of the photoreaction was confirmed from UV, IR and NMR spectra. The conversion was calculated by the NMR spectra in $CDCl_3$ from the peaks of 6-H of photodimers and original thymine. After UV irradiation of the plate crystal for 3 hours, the photodimerization proceeded in yield of 98.3%.

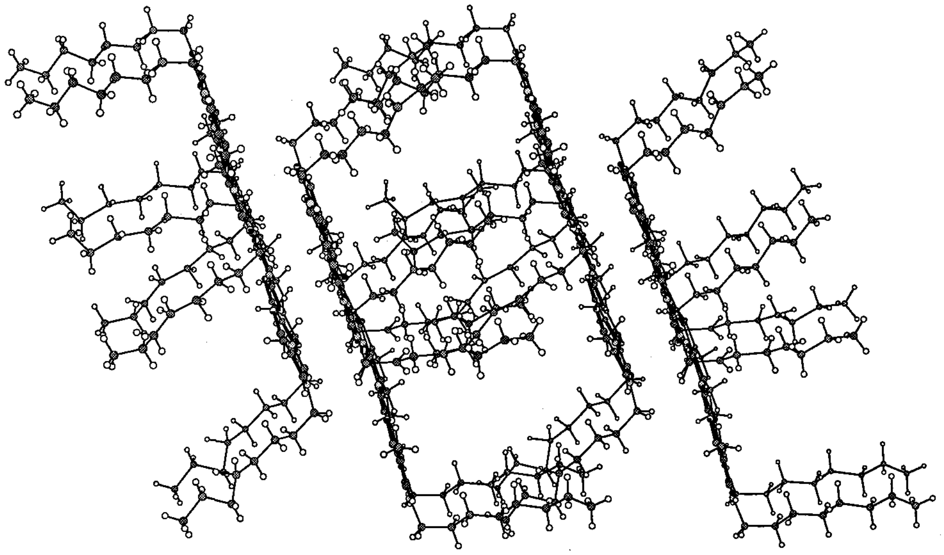


Figure 4

Lamella structure of thymine derivative having long alkyl chain.

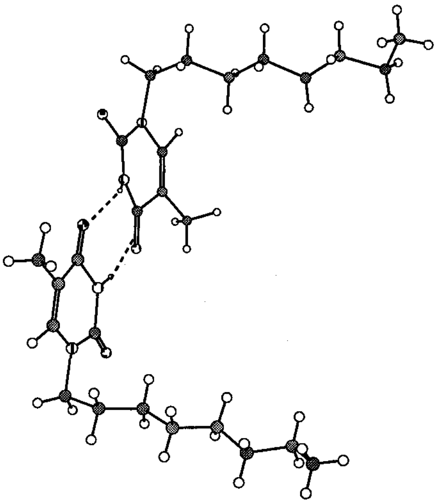


Figure 5

Two thymine derivatives associated with hydrogen bondings.

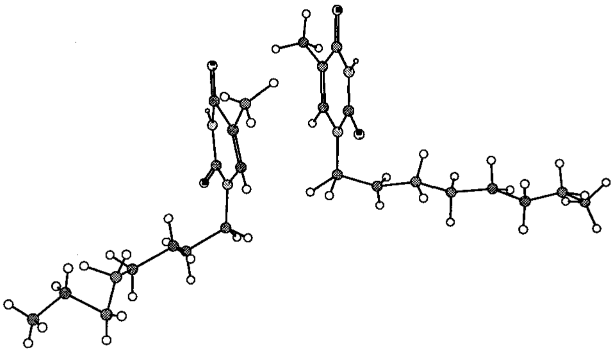


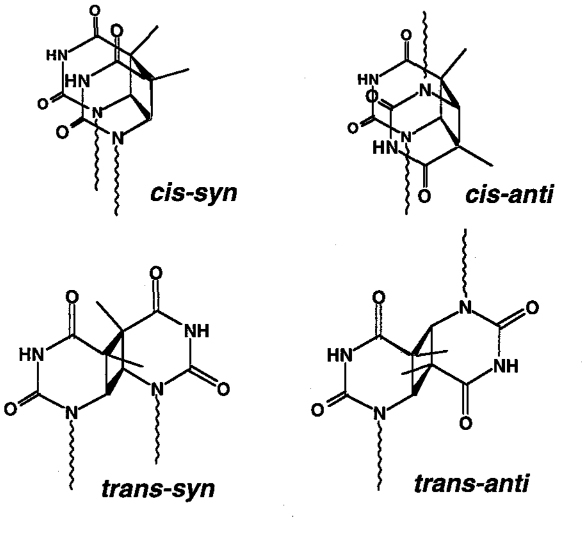
Figure 6

Two oppsite thymine derivatives in the position of *trans-syn.*

There are four stereoisomeric dimers possible by linkage of two thymines to form a cyclobutane ring across their 5, 6 double bonds: *cis-syn*, *cis-anti*, *trans-syn*, and *trans-anti* (Fig. 7). The *cis-syn* photodimer is known to be formed by UV irradiation on DNA.

The photodimerization of 1-octyl thymine hardly occurred in solution, where triplet state was the precursor[6-9]. However, the photodimerization gave all isomers in acetone which was the triplet sensitizer. The isomers were isolated by recrystallization and identified from NMR (Tab. 1). In the solution reaction, the *trans-anti* dimer was a main product and the other isomers were generated with an almost equal ratio (Tab. 2).

Only one isomer was obtained from the UV irradiation of the plate crystal from ethyl acetate.



cis-syn

cis-anti

trans-syn

trans-anti

Figure 7 Four photodimer structures of 1-alkyl thymine derivatives.

The dimerization was fast because the reaction proceeded through the singlet state [10-12]. The isomer was identified as *trans-anti* from chemical shifts of 5-CH and 6-H of the NMR spectra. This isomer is different from the *trans-syn* isomer predicted from the crystal structure.

	Solution	Crystal
cis-syn	0.5	-
cis-anti	0.6	0.07
trans-syn	0.4	0.05
trans-anti	1	1

Table 2.
Relative photodimer distributions

The nearest neighbor thymine bases in the crystal are picked out from Fig. 4 to give Fig. 8. The distance between thymines in the plane is short, but the formation of the photodimer is difficult because the interaction of double bonds is necessary for the photodimerization.

Two stacked thymines in Fig. 8 are illustrated in Fig. 9. The cyclobutane photodimer can be formed by the reaction between two double bonds of C5 and C6. When the first bond is formed between C5 and C5', the *syn* type photodimer should be formed after formation of the second bond between C6 and C6'. On the other hand, when the first bond is formed between C5 and C6', the *anti* type photodimer should be formed after formation of the second bond between C6 and C5'. The

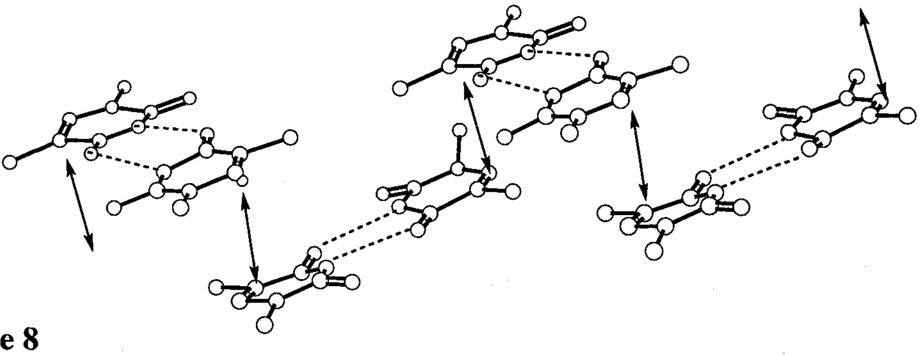


Figure 8

Hydrogen bonding network and photoreacting base pairs on the opposite plane.

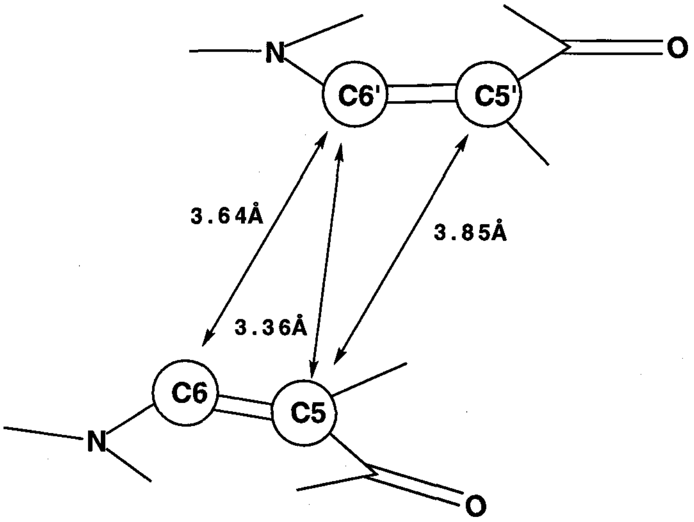


Figure 9

Photoreacting sites of the nearest neighbor thymine bases in crystal.

crystal data suggested that the nearest carbons are C5' and C6 in the distance of 3.36Å as suggested in Fig. 9. Therefore, the photodimer formed by UV irradiation in crystal should be the *anti* type isomer.

If the photodimerization occurs face to face between the stacked thymines, the photodimer should be the *cis-anti* isomer. However, the photodimer obtained was the *trans-anti* isomer, suggesting another mechanism of photodimerization. The photocyclization of a diene compound is known to occur by disrotatory motion, although the thermal cyclization occurs by conrotatory motion. If the photodimerization of thymine bases in crystal occurred by disrotatory motion, the product should be the *trans-anti* isomer. This mechanism of disrotation may be possible because the motion of the molecule is fixed in the crystal by the interaction of the long alkyl chain.

The probable mechanism of the photodimeriz-ation is illustrated in Fig. 10. When the thymine bases in crystal rotate disrotatory (path a), the first bond is formed between C5 and C6' in *cis* conformation. After rotation of the thymine on the plane, the second bond is formed between C6 and C5' giving the *trans-anti* photodimer. By the conrotatory motion of thymine bases (path b), however, the *cis-anti* photodimer should be formed through the *trans* type intermediate.

Though the *trans-anti* isomer is the main product of the photodimerization in crystal, small

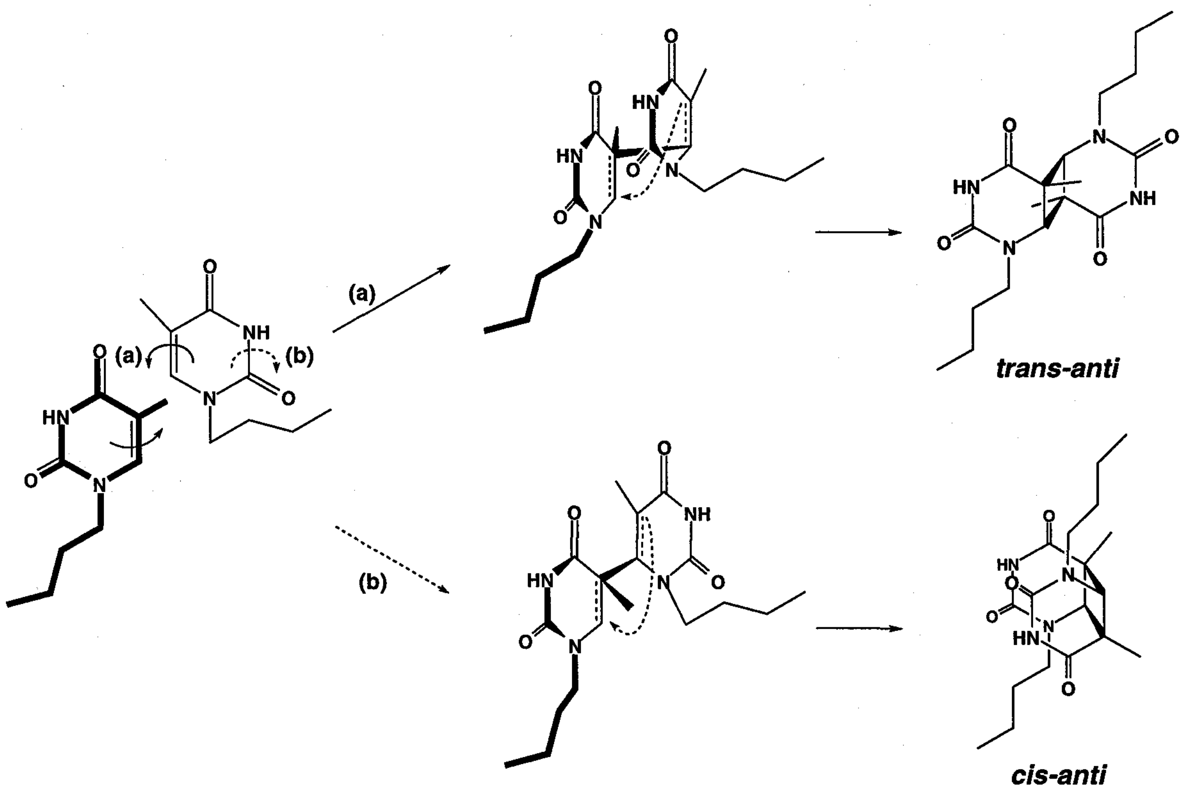


Figure 10

Probable mechanism of photodimerization of thymine derivatives having long alkyl chain in crystal state from two opposite thymine derivatives in the position of *trans-syn.*

amounts of another isomer (*cis-anti* and *trans-syn*) are formed (Tab. 2). These minor isomers may be formed from collapsed crystal. The powder X-ray diffraction suggested that the sharp peak observed at the beginning of the reaction became a broad peak at the end of reaction (Fig. 11). The formation of the *trans-anti* photodimer may accompany collapse of the crystal structure. The transparent crystal was observed to become cloudy as the progress of the reaction. The minor isomers obtained were concluded to be formed from the collapsed crystal at the end of reaction.

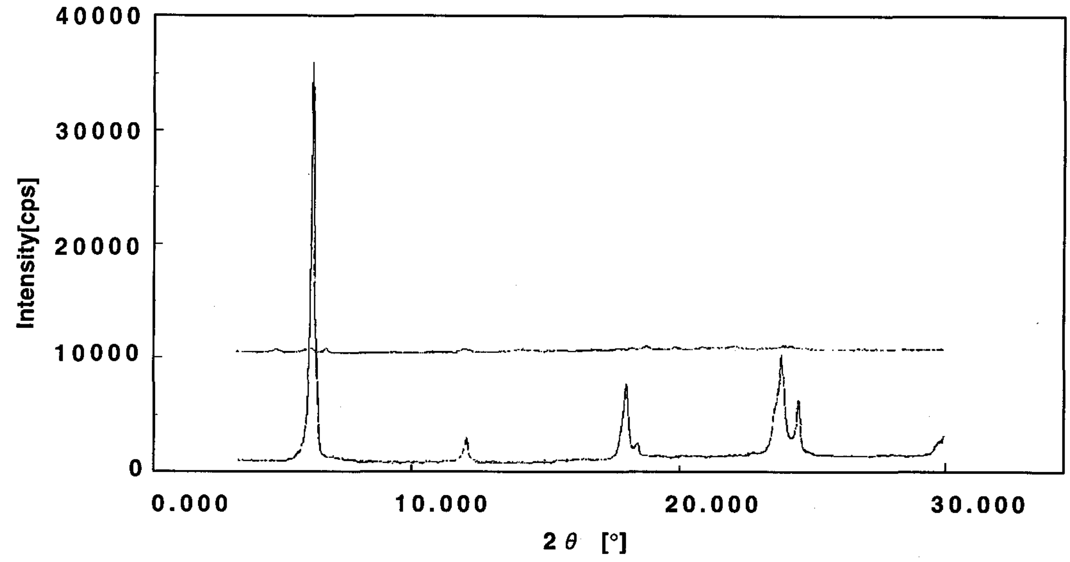


Figure 11

X-ray diffraction patterns of thymine derivatives having long alkyl chain recrystallized from ethyl acetate with different photoreacttion conversion.

[a] conversion= 0%, [b] conversion= 98.7%

2-4. CONCLUSION

The plate crystal of 1-octyl thymine recrystallized from ethyl acetate showed a very high photoreactivity and gave only one isomer of photodimer. The crystal structure suggested the formation of the *trans-syn* photodimer. The photodimer obtained, however, was identified to be the *trans-anti* isomer from the NMR spectrum. The *trans-anti* photodimer was concluded to be formed by disrotatory motion of the thymine in the crystal. The mechanism of the intermolecular photodimerization of thymines in crystal was found to be the same as the intramolecular photocycloaddition of dienes because the thymine derivative was fixed with the alkyl group in the crystal.

2-5. Crystal Data of 1-Octylthymine from Ethyl Acetate

Table 1. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms and hydrogen atoms.

atom	x	y	z	B(eq)
O(1)	0.6991	0.2163	-0.0502	8.8287
O(2)	0.6878	0.3951	0.1699	8.0640
O(3)	0.6986	0.2800	0.3751	9.4516
O(4)	0.6963	0.1036	0.1441	8.2522
N(1)	0.6951	0.4098	-0.0535	6.2540
N(2)	0.6937	0.3093	0.0584	6.6245
H(1)	0.6972	0.2407	0.0900	-78.9568
N(3)	0.6966	0.0867	0.3732	6.0176
N(4)	0.6963	0.1891	0.2601	6.3368
H(3)	0.6918	0.2592	0.2300	-78.9568
C(1)	0.6962	0.3058	-0.0177	6.2033
C(2)	0.6900	0.4044	0.1014	5.7197
C(3)	0.6889	0.5107	0.0601	5.6958
C(4)	0.6913	0.5079	-0.0144	5.7280
H(2)	0.6929	0.5750	-0.0400	-78.9568
C(5)	0.6855	0.6185	0.1028	8.2350
H(5)	0.6523	0.6190	0.1000	-78.9568
H(6)	0.6967	0.6150	0.1600	-78.9568
H(7)	0.6880	0.6754	0.0800	-78.9568
C(6)	0.6971	0.1911	0.3389	6.2857

C(7)	0.6970	0.0940	0.2145	5.6901
C(8)	0.6987	-0.0130	0.2554	5.8254
C(9)	0.6980	-0.0104	0.3315	6.1078
H(4)	0.6986	-0.0784	0.3600	-78.9568
C(10)	0.7013	-0.1199	0.2114	8.8356
H(8)	0.6780	-0.1226	0.1800	-78.9568
H(9)	0.7206	-0.1185	0.1800	-78.9568
H(10)	0.7007	-0.1775	0.2400	-78.9568
C(11)	0.6968	0.4157	-0.1362	9.2948
H(11)	0.7053	0.4799	-0.1500	-78.9568
H(12)	0.7020	0.3514	-0.1500	-78.9568
C(12)	0.6952	0.0806	0.4566	7.8672
H(13)	0.7020	0.1441	0.4800	-78.9568
H(14)	0.7068	0.0129	0.4800	-78.9568
C(13)	0.6517	0.4192	-0.2036	13.2802
H(13A)	0.6388	0.4909	-0.1965	-78.9568
H(13B)	0.6573	0.4274	-0.2539	-78.9568
C(14)	0.6499	0.0858	0.4544	12.1579
H(14A)	0.6385	0.0095	0.4404	-78.9568
H(14B)	0.6541	0.0961	0.5119	-78.9568
C(15)	0.6188	0.3441	-0.2205	13.8986
H(15A)	0.6121	0.3336	-0.1721	-78.9568
H(15B)	0.6302	0.2710	-0.2314	-78.9568
C(16)	0.5772	0.3670	-0.2910	18.7267
H(16A)	0.5670	0.4430	-0.2828	-78.9568
H(16B)	0.5836	0.3729	-0.3405	-78.9568

C(17)	0.5386	0.2978	-0.3142	23.7229
H(17A)	0.5289	0.2916	-0.2669	-78.9568
H(17B)	0.5457	0.2208	-0.3247	-78.9568
C(18)	0.4976	0.3304	-0.3859	26.8782
H(18A)	0.4826	0.3920	-0.3701	-78.9568
H(18B)	0.5058	0.3570	-0.4304	-78.9568
C(19)	0.4685	0.2390	-0.4130	28.7159
H(19A)	0.4606	0.2088	-0.3690	-78.9568
H(19B)	0.4816	0.1790	-0.4344	-78.9568
C(20)	0.4278	0.2914	-0.4816	33.2904
H(20A)	0.4049	0.2349	-0.5035	-78.9568
H(20B)	0.4364	0.3191	-0.5248	-78.9568
H(20C)	0.4166	0.3531	-0.4593	-78.9568
C(21)	0.6150	0.1481	0.4139	13.6386
H(21A)	0.6120	0.1516	0.3571	-78.9568
H(21B)	0.6227	0.2265	0.4355	-78.9568
C(22)	0.5712	0.1239	0.4142	21.1976
H(22A)	0.5630	0.0515	0.3873	-78.9568
H(22B)	0.5761	0.1116	0.4719	-78.9568
C(23)	0.5332	0.1885	0.3834	26.6396
H(23A)	0.5304	0.2104	0.3282	-78.9568
H(23B)	0.5402	0.2586	0.4155	-78.9568
C(24)	0.4883	0.1608	0.3737	31.2144
H(24A)	0.4757	0.1114	0.3261	-78.9568
H(24B)	0.4897	0.1177	0.4218	-78.9568
C(25)	0.4590	0.2509	0.3638	32.9002

H(25A)	0.4681	0.2979	0.4130	-78.9568
H(25B)	0.4565	0.2975	0.3167	-78.9568
C(26)	0.4179	0.1926	0.3504	36.0610
H(26A)	0.3952	0.2467	0.3474	-78.9568
H(26B)	0.4223	0.1412	0.3953	-78.9568
H(26C)	0.4088	0.1509	0.2996	-78.9568
C(27)	0.6187	0.4898	-0.2153	13.2026
H(27A)	0.6284	0.5655	-0.2212	-78.9568
H(27B)	0.6116	0.4888	-0.1661	-78.9568
C(28)	0.5782	0.4672	-0.2873	19.2968
H(28A)	0.5855	0.4486	-0.3333	-78.9568
H(28B)	0.5642	0.3970	-0.2750	-78.9568
C(29)	0.5427	0.5402	-0.3143	23.7845
H(29A)	0.5568	0.6164	-0.3237	-78.9568
H(29B)	0.5349	0.5632	-0.2669	-78.9568
C(30)	0.5021	0.5219	-0.3855	28.4888
H(30A)	0.5094	0.5175	-0.4341	-78.9568
H(30B)	0.4894	0.4495	-0.3795	-78.9568
C(31)	0.4703	0.6043	-0.3979	30.7432
H(31A)	0.4775	0.6741	-0.4195	-78.9568
H(31B)	0.4644	0.6198	-0.3487	-78.9568
C(32)	0.4343	0.5407	-0.4601	35.4774
H(32A)	0.4076	0.5859	-0.4798	-78.9568
H(32B)	0.4288	0.4721	-0.4360	-78.9568
H(32C)	0.4428	0.5223	-0.5053	-78.9568
C(33)	0.6176	0.0071	0.4135	11.7025

H(33A)	0.6292	-0.0681	0.4330	-78.9568
H(33B)	0.6117	0.0104	0.3551	-78.9568
C(34)	0.5743	0.0204	0.4257	20.9038
H(34A)	0.5788	0.0191	0.4824	-78.9568
H(34B)	0.5606	0.0944	0.4024	-78.9568
C(35)	0.5422	-0.0652	0.3811	23.2658
H(35A)	0.5523	-0.1384	0.4066	-78.9568
H(35B)	0.5406	-0.0689	0.3248	-78.9568
C(36)	0.4965	-0.0420	0.3796	31.1376
H(36A)	0.4974	-0.0519	0.4351	-78.9568
H(36B)	0.4893	0.0369	0.3647	-78.9568
C(37)	0.4615	-0.1090	0.3258	33.2883
H(37A)	0.4680	-0.1892	0.3361	-78.9568
H(37B)	0.4559	-0.0924	0.2685	-78.9568
C(38)	0.4219	-0.0734	0.3476	42.4203
H(38A)	0.3953	-0.1120	0.3119	-78.9568
H(38B)	0.4175	0.0070	0.3404	-78.9568
H(38C)	0.4279	-0.0930	0.4040	-78.9568
C(39)	0.6517	0.4192	-0.2036	13.2802
H(39A)	0.6576	0.4244	-0.2538	-78.9568
H(39B)	0.6393	0.3447	-0.2040	-78.9568
C(40)	0.6499	0.0858	0.4544	12.1579
H(40A)	0.6524	0.0866	0.5114	-78.9568
H(40B)	0.6379	0.1596	0.4315	-78.9568

Table 2. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.1659	0.0527	0.0849	0.0001	0.0676	-0.0110
O(2)	0.1575	0.0458	0.0663	0.0041	0.0625	0.0033
O(3)	0.1858	0.0464	0.0794	0.0098	0.0645	-0.0072
O(4)	0.1613	0.0453	0.0686	0.0004	0.0638	0.0019
N(1)	0.1099	0.0530	0.0627	0.0016	0.0485	0.0011
N(2)	0.1241	0.0355	0.0667	0.0023	0.0502	0.0015
N(3)	0.1094	0.0471	0.0569	0.0020	0.0384	0.0016
N(4)	0.1175	0.0370	0.0644	0.0002	0.0426	0.0017
C(1)	0.1091	0.0481	0.0656	-0.0017	0.0459	-0.0051
C(2)	0.1018	0.0388	0.0622	0.0030	0.0384	0.0017
C(3)	0.0998	0.0384	0.0646	0.0013	0.0411	0.0030
C(4)	0.0965	0.0414	0.0690	-0.0008	0.0400	0.0046
C(5)	0.1559	0.0405	0.0818	0.0080	0.0609	0.0053
C(6)	0.1169	0.0437	0.0586	0.0056	0.0389	-0.0005
C(7)	0.1002	0.0422	0.0614	-0.0013	0.0406	-0.0018
C(8)	0.1039	0.0388	0.0635	-0.0007	0.0410	-0.0001
C(9)	0.1108	0.0396	0.0641	-0.0013	0.0388	0.0080
C(10)	0.1724	0.0420	0.0781	0.0067	0.0596	-0.0007
C(11)	0.1735	0.0744	0.0770	-0.0025	0.0831	0.0000
C(12)	0.1475	0.0654	0.0613	0.0160	0.0538	0.0052
C(13)	0.1869	0.2153	0.0599	-0.0177	0.0615	-0.0005
C(14)	0.1627	0.1898	0.0930	0.0315	0.0777	0.0260

C(15)	0.1680	0.2333	0.1015	-0.0525	0.0592	-0.0084
C(16)	0.1840	0.3504	0.1101	-0.0430	0.0357	-0.0199
C(17)	0.1743	0.4147	0.2616	-0.0130	0.0243	-0.0589
C(18)	0.1741	0.5042	0.2512	-0.0689	-0.0097	-0.0317
C(19)	0.2011	0.4940	0.3352	-0.0269	-0.0281	0.0133
C(20)	0.1697	0.6329	0.3224	0.0323	-0.0687	0.1009
C(21)	0.1502	0.2233	0.1308	0.0160	0.0567	0.0220
C(22)	0.1577	0.3692	0.2347	0.0471	0.1259	0.0673
C(23)	0.1523	0.4498	0.3405	0.0466	0.0802	0.0382
C(24)	0.1506	0.5530	0.3747	0.0991	0.1436	0.0545
C(25)	0.1593	0.5444	0.4463	0.0617	0.0743	0.0150
C(26)	0.1258	0.6743	0.3941	-0.0453	0.0651	-0.0163
C(27)	0.1969	0.1782	0.1155	0.0798	0.0619	0.0282
C(28)	0.2261	0.3332	0.1305	0.0762	0.0147	-0.0159
C(29)	0.1939	0.4167	0.2470	0.0777	0.0173	0.0443
C(30)	0.1832	0.5449	0.2452	0.0770	0.0246	0.0171
C(31)	0.1903	0.5542	0.3339	0.0140	0.0365	0.0303
C(32)	0.1821	0.6961	0.2966	0.0068	-0.0028	0.1110
C(33)	0.1699	0.1536	0.1159	-0.0121	0.0614	-0.0053
C(34)	0.1726	0.3604	0.2249	-0.0514	0.1160	-0.0284
C(35)	0.1579	0.3987	0.2768	-0.0527	0.0878	0.0184
C(36)	0.1572	0.5516	0.3708	-0.0648	0.1170	-0.0226
C(37)	0.1607	0.5685	0.4292	-0.0562	0.0782	-0.0057
C(38)	0.1521	0.8102	0.4316	0.0239	0.1059	0.0993
C(39)	0.1869	0.2153	0.0599	-0.0177	0.0615	-0.0005
C(40)	0.1627	0.1898	0.0930	0.0315	0.0777	0.0260

2-6. References

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Chapter 3

Photoreactive and Inactive Crystals of 1-Alkyl-Thymine Derivatives.

Two kinds of crystal structures were found for 1-*n*-octylthymine from X-ray structure analysis: Structure I was obtained from Crystal I recrystallized from ethyl acetate, and Structure II was obtained from Crystal II recrystallized from ethanol. Crystal I had the high reactivity of thymine base for photodimerization. Crystal II, however, was inactive for the photodimerization of thymine bases. Thymine derivatives having long alkyl chain (1-*n*-octylthymine) showed very high photoreactivities in the spin-coated thin films. However, photoreaction did not occur when the film was annealed. Powder X-ray diffraction study revealed that the crystal structure of the spin-coated thin film was photoreactive Structure I, and the crystal structure of the annealed thin film was photoinactive Structure II.

3-1. INTRODUCTION

Thymine bases, one of the nucleic acid bases, convert to photodimers upon irradiation with UV light near 280 nm (Fig. 1). This reaction is known to cause damage of DNA by solar UV light.[1-2] The photodimerization is a reversible reaction and the photodimers split to afford the original thymines very efficiently upon irradiation at a shorter wavelength 240 nm. The absorbance at 270 nm of thymine decreases with the formation of the photodimer, and increases with the cleavage of photodimer (Fig. 2). Therefore, the photoreaction of thymine bases can be followed by monitoring the decrease and increase in absorbance at 270 nm, respectively. The reversible photodimerization of thymine derivatives can be applied to negative or positive type photoresist materials[3-5] and the photorecording system by controlling wavelength of irradiating UV light.[6-7]

For applications of the thymine derivatives to the photochemical systems, it is necessary to investigate the reactivity of thymine derivatives in thin film state. It was found that photoreaction of thymine is dependent on the kind of excited state (singlet or triplet).[8-14] the association of the molecules (solutions, thin films, and crystals), [15-17] and the substitution isomers (N^1 or N^3 substituted thymine).[18] We have also reported that the rates of photodimerization in solid thin film are dependent on the length of alkyl chain of the thymines having long alkyl chain. The study of the photodimerization of 1-*n*-octylthymine in single crystal suggested that the thymine base rotated in the single crystal during photodimerization.[19]

The photodimerization and the reverse reaction of the thymine derivatives in thin films were found to depend on annealing. The reactivity of the spin-coated film was high, but decreased remarkably by annealing. This paper reveals the crystal structure of 1-*n*-octylthymine crystallized from ethanol determined by X-ray crystal structure analysis. The single crystal from ethanol (Crystal II) did not give the photodimer. The single crystal from ethyl acetate (Crystal I), however, gave the photodimer[19]. Powder X-ray diffraction study revealed that the crystal structure of the spin-coated thin film was the same as that of the single crystal from ethyl acetate (Structure I). On the other hand, the crystal structure of the annealed thin film was the same as that of the single crystal from ethanol (Structure II). In this paper, discussions will be focused on the relationship between the molecular orientation of the thymine bases in the single crystals and

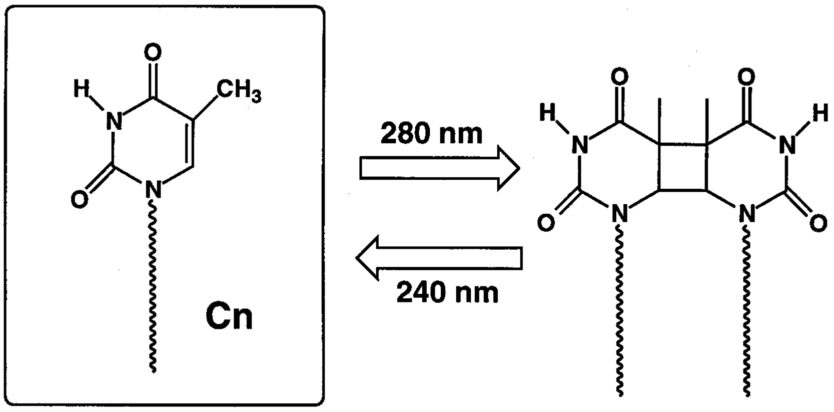

Figure 1

Reversible Photodimerization of the Thymine Derivatives.

the reactivity of the thymine base for photodimerization.

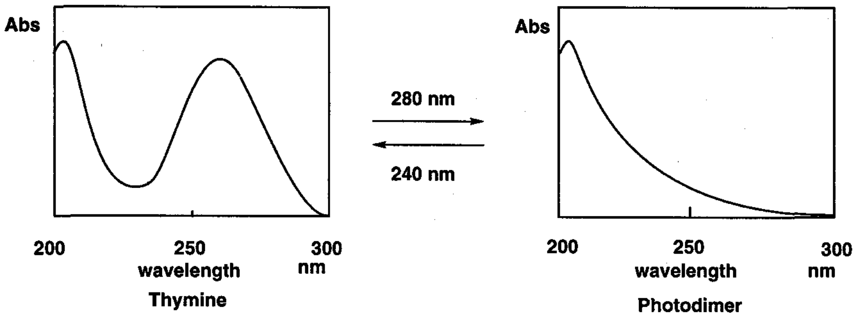

Figure 2

UV Spectra of Original Thymine Derivatives and Photodimers

3-2. EXPERIMENTAL

Preparation of 1-*n*-Octylthymine

The alkylthymine derivative was prepared according to method reported in the literature.[19)] Thymine was reacted with hexamethyldisilazane to give 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine. A mixture of 1-*n*-octyl bromide and 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine was stirring for 10 days at 60°C to afford 1-*n*-octyl thymine.

Preparation of Thin Films

Chloroform (0.5 ml) solution of 1-*n*-octyl thymine (10 mg) gives clear thin films by spin-coating onto a quartz plate. Annealing of the spin-coated film was carried out by heating at 100-110°C below melting point (122°C) for various seconds, followed by cooling to room temperature.

Photodimerization

Photodimerizations in single crystal were carried out by SUPER CURE-203S UV LIGHT SOURCE SAN-EI ELECTRIC. For the photodimerization in the thin films, JASCO CRM-FA was used. ^{1}H-NMR Spectra were recorded with a Varian unity INOVA600 and JEOL

GSX270. UV Spectra were recorded with a JASCO UVIDEC 660. IR Spectra were recorded with a JASCO IR-810 infrared spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) were measured by a Rigaku Thermo Plus TG8120 instrument. X-ray powder diffraction patterns were measured by Rigaku X-ray diffractometer RINT 2000 with Cu-Kα radiation.

Crystal Structure Analysis

Data of X-ray diffraction for 1-*n*-octyl thymine were collected by Rigaku RAXIS-CS imaging plate two-dimensional area detector using graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71070Å) at 15±1°C. Unique reflections of 2364 were measured up to 2θ of 60.0°. For further calculations, $[|F_o|>3\sigma(F_o)]$ reflections were used after Lorenz and polarization corrections. Crystal structure was solved by the direct methods (SHELXS-97), and refined by the full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were located in the calculated positions. The positions of hydrogen atoms attached to nitrogen atoms were obtained from the difference Fourier syntheses. All the crystallographic calculations were performed by using TEXSAN software package of the Molecular Structure Corporation.

3-3. RESULTS AND DISCUSSION

Photodimerization of 1-*n*-Octylthymine in Thin Film

The thin film of 1-*n*-octylthymine gave the photodimer by irradiation of UV light at 280 nm. Figure 3 (curve **a**) shows decrease of absorbance at 270 nm under irradiation of UV light (280 nm). Irradiation of UV light at 240 nm to the photodimer causes splitting to give the original thymine derivative with increase of absorbance as shown in Fig. 3 (curve **a**). The formation of the photodimer and the splitting of the photodimer were confirmed by NMR spectra.19)

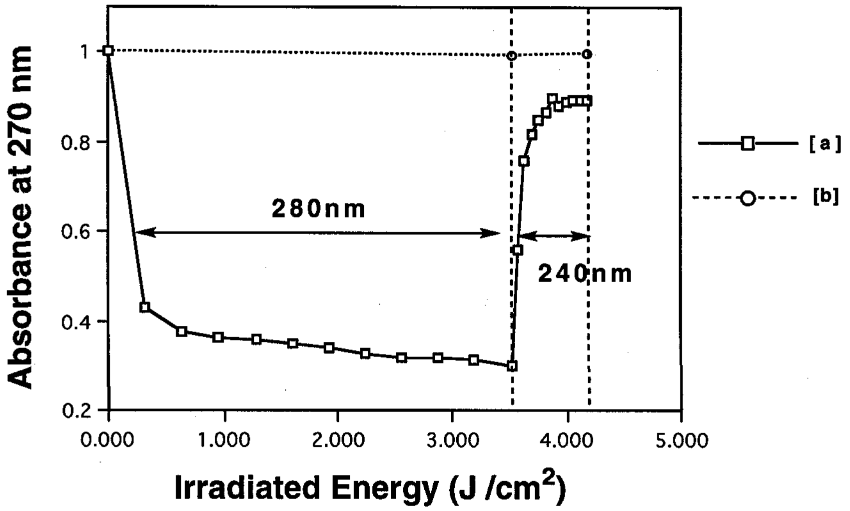

Figure 3

Effect of Annealing for Reversible Photodimerization of 1-*n*-Octylthymine (spin-coated thin film).

[a]; Before annealing.

[b]; After annealing for 90 sec.

The photodimerization, however, hardly occurred after annealing of the thin film as shown in Fig. 3 (curve **b**). The photoreactive thin film was obtained by spin-coating on a quartz plate from chloroform solution of 1-*n*-octylthymine, followed by drying under reduced pressure at room temperature. The annealing process was done at 100° to 110°C below the melting point of thymine derivative (122°C). The annealing times had been varied with 0, 10, 20, 30, 60, and 90 sec. The appearances of thin films and UV spectra were not changed by annealing.

Powder X-ray Diffraction of 1-*n*-Octylthymine

The powder X-ray diffraction studies were employed to clear the crystal structure of the thin film. Figure 4 shows the powder X-ray diffraction patterns of 1-*n*-octylthymine thin film at various annealing times. The spin-coated thin film (**a** in Fig. 4) was not a glassy state but had the crystal structure. The peak at $2\theta = 5.700°$ disappeared, and the new peak at $2\theta = 5.740°$ appeared during annealing of the thin film when the annealing time was made longer. Moreover, the peaks at $2\theta = 11.640°$, $17.600°$, and $23.600°$ went out gradually and newly the peaks at $2\theta = 17.980°$, $24.160°$ resulted on respectively. After annealing for 90 sec, the original crystal structure shifted almost completely.

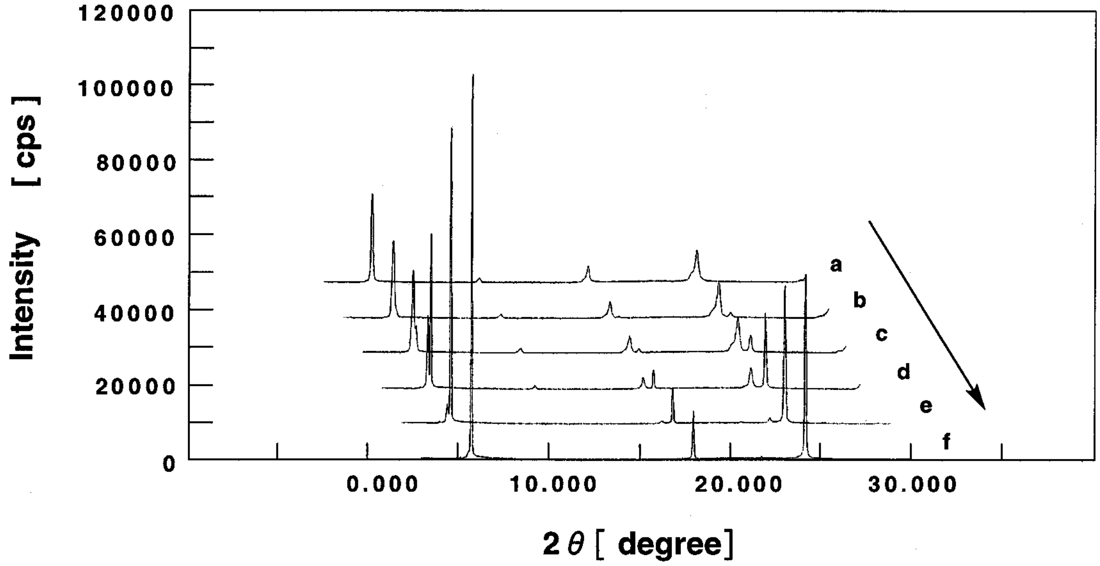

Figure 4

Effect of Annealing on Powder X-ray Diffraction Pattern of 1-*n*-Octylthymine Thin Film. Annealing time [a] 0 sec, [b] 10 sec, [c] 20 sec, [d] 30 sec, [e] 60 sec, [f] 90 sec. Annealing at 100-110°C.

The pattern of powder X-ray diffraction for the spin-coated thin film (0 sec annealing time, **b** in Fig. 5) coincided with the pattern of the plate crystal from ethyl acetate (Crystal I) (**a** in Fig. 5).[19] On the other hand, the pattern of powder X-ray diffraction for the annealed thin film (90 sec annealing time, **d** in Fig. 5) coincided with the pattern of the plate crystal from ethanol (Crystal II) (**c** in Fig. 5)

Crystal Structure of 1-*n*-Octylthymine

The crystal structure of 1-*n*-octylthymine crystallized from ethyl acetate (Structure I) was reported previously.[19)] In this paper, the crystal structure of the compound crystallized from ethanol (Structure II) will be reported.

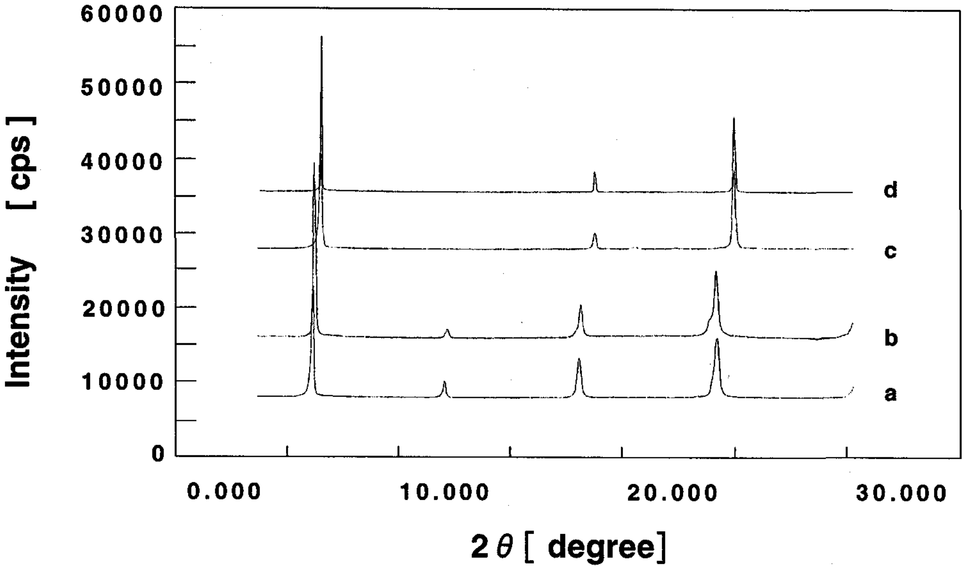

Figure 5

Powder X-ray Diffraction Pattern of 1-*n*-Octylthymine.

[a]; Crystal I (ethyl acetate), [b]; Thin film before annealing

[c]; Crystal II (ethanol), [d]; Thin film after annealing for 90 sec.

Crystal data for 1-*n*-octyl thymine (from ethanol): $C_{13}H_{22}O_2N_2$, monoclinic, space group $P2_1/c$, $a = 15.11(1)$, $b = 12.115(4)$, $c = 16.471(5)$ Å, $\beta = 106.35(5)°$, $V = 2893(2)$ Å^3, Dcalc = 1.09 g cm^{-3}, $Z = 8$, $R = 0.138$, Rw = 0.104. The final R and Rw indices are rather high because of the disordered structure for the long alkyl chains judged from the anisotropic temperature factors. Thus, it was difficult to locate the end of long alkyl group accurately. The thymine base part, which played an important role for photoreaction, however, was located effectively.

Figure 6 shows a molecular packing structure of 1-*n*-octyl thymine crystallized from ethanol (Crystal II). The unit cell contains eight molecules. The crystal is a double layer structure consisted of the hydrophilic layer of thymine bases and the hydrophobic layer of long alkyl groups (Fig. 7). The distance between the two planes formed by thymine bases was about 3.4Å.

The van der Waals radius of the thymine base might be touched. Moreover, the long alkyl chain groups aggregate weekly and form the hydrophobic layer. Therefore, hydrogen bonding and van der Waals forces of thymine bases were main driving forces to form the crystal. The lamella structure was a peculiar structure to thymine derivatives having long alkyl chain and whole crystal structure of Crystal II was the same as that of Crystal I.

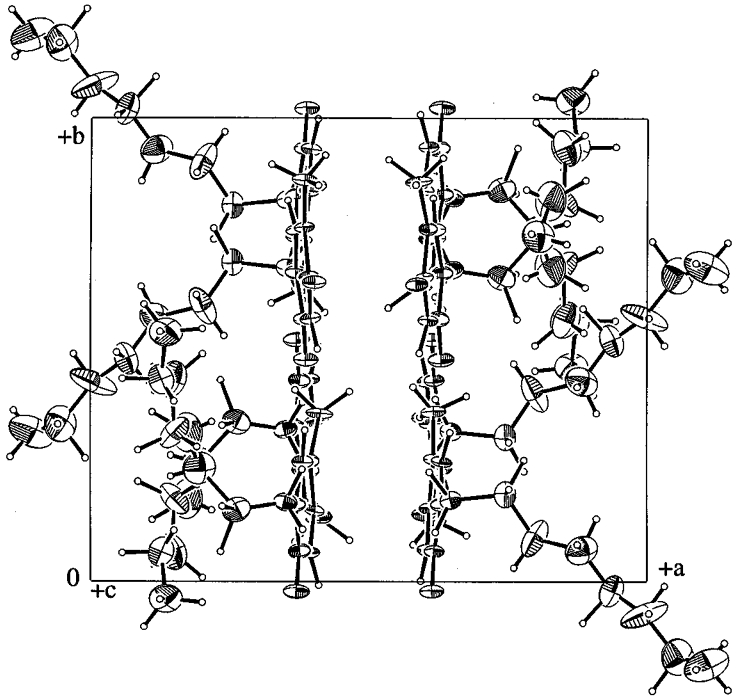

Figure 6

Molecular Packing Structure of 1-*n*-Octylthymine Crystallized from Ethanol (Crystal II).

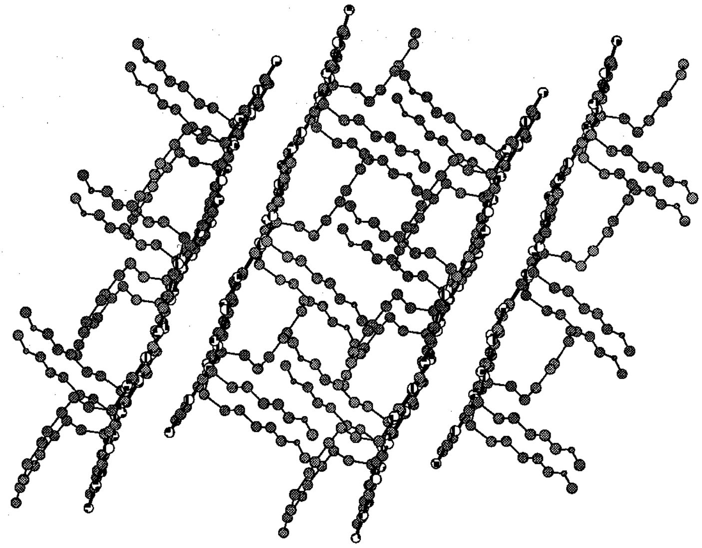

Figure 7

Lamella Structure of 1-*n*-Octylthymine Crystallized from Ethanol (Crystal II)

Structural Comparison between Two Forms of Crystals

Figure 8a shows the plane structure in Structure II (ethanol). The orientation of the thymine bases in Fig. 8a is the same as that of Structure I (ethyl acetate) (Fig. 8b) .[19] Moreover, the distances of hydrogen bonding are almost equal for both structures. It should be noted that the plain structure formed by hydrogen bonding in Structure II was almost identical to that of Structure I.

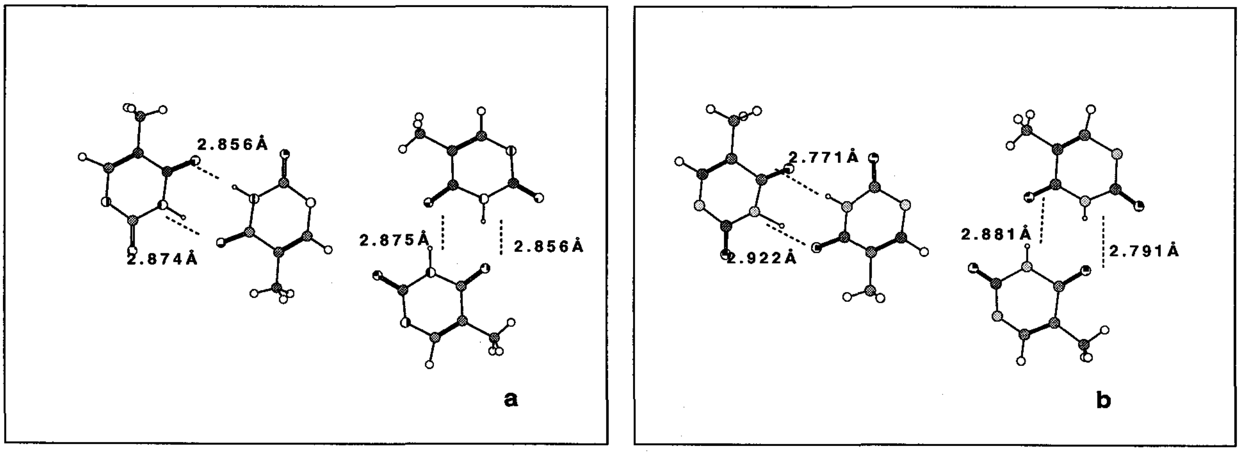

Figure 8

Plane Structures and Hydrogen Bondings of 1-*n*-Octylthymine.

[a]; Crystal II (ethanol) [b]; Crystal I (ethyl acetate)

Figures 9a and 9b show the orientation of thymine bases for two planes. In the photoreactive Crystal I (ethyl acetate) (Fig. 9b), the two double bonds (C5 and C6 of thymine) overlapped with each other. This orientation of thymine ring is suitable for the photodimerization. In the inactive Crystal II (ethanol) (Fig. 9a), however, thymine rings were arranged alternatively to avoid the steric hindrance between two opposite planes. Therefore, the double bonds did not overlap in Crystal II. Consequently, the packing form of the plane structures in Crystal II is different from that of Crystal I, though the orientation of the thymine bases in the plane had no difference between two crystals.

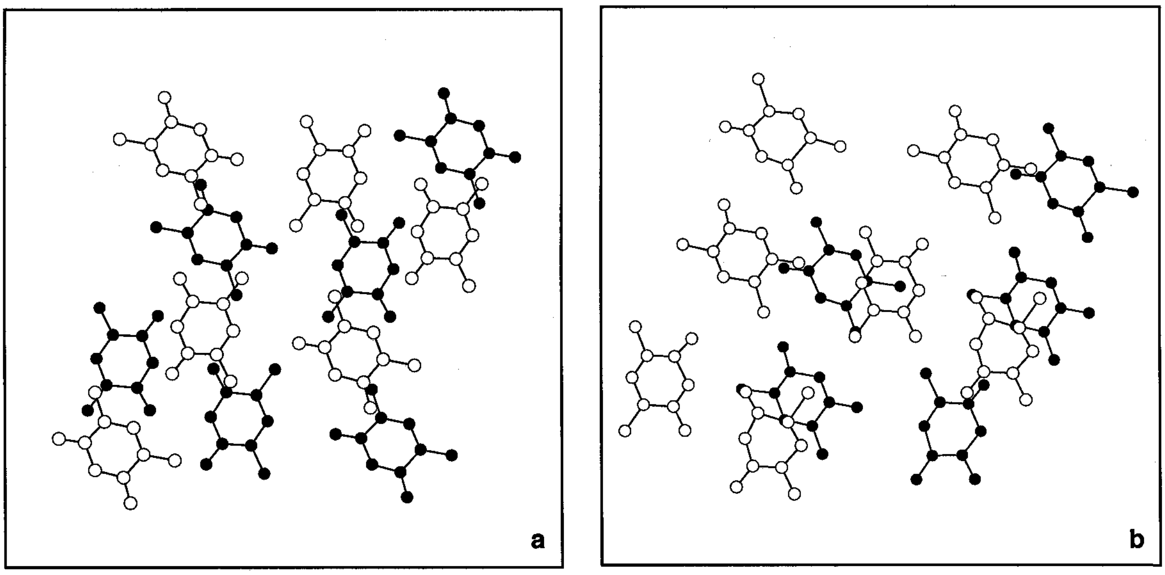

Figure 9

Orientations of Thymine Bases in Two Layers.

White circles are on this side, and black circles are on the inside.

[a]; Crystal II (ethanol)

[b]; Crystal I (ethyl acetate)

Photodimerization of 1-*n*-Octylthymine in Single Crystals

Irradiation of UV light (280 nm) to Crystal I (ethyl acetate) gave the photodimer with 98.7% conversion.[19)] On the other hand, Crystal II (ethanol) gave no photodimers under the same condition. These results of the photodimerization in single crystals were corresponding to the results of photoreaction in the thin film. Structure I of the spin-coated film gave the photodimer, but the Structure II formed by annealing gave no photodimer. The differences of these photoreactivities will be clarified by the molecule orientation in the crystal structure obtained from X-ray structure analysis studies.

Two facing thymines in Crystal I and Crystal II are shown in Figures 10a and 10b. In Crystal I (Fig. 10b), the distance between two planes of the thymines was about 3.3 Å, and the distance between the nearest carbon atoms of the double bond (C6 and C51) was 3.362 Å. This distance of 3.362 Å for Crystal I was suitable for photodimerization. In Crystal II (Fig. 10a), on the other hand, the distance between two planes of the thymines was about 3.4 Å, and the distance between the nearest carbon atoms of the double bond (C5 and C61) was 4.344 Å. The distance of 4.344 Å for the Crystal II was too far for the photodimerization.

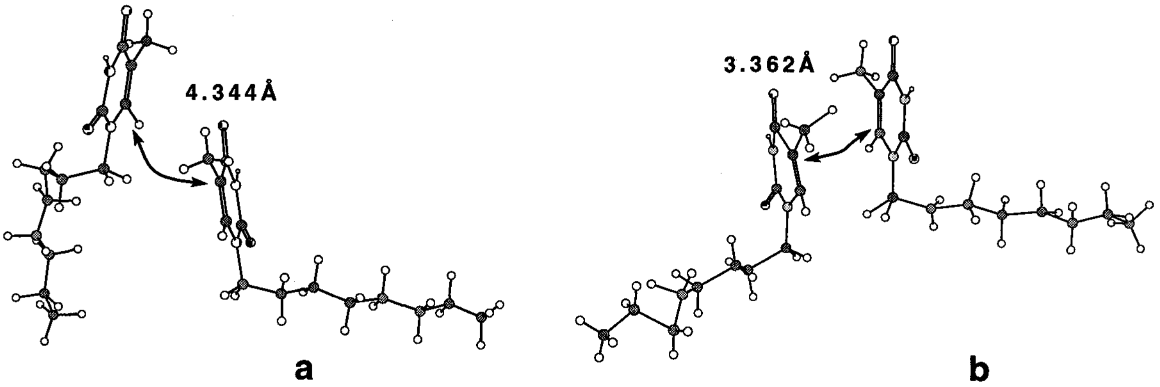

Figure 10

Two Facing Thymine Derivatives in the Nearest Position.

[a]; Crystal II (ethanol)

[b]; Crystal I (ethyl acetate)

Both crystals formed lamella structures, and the molecules in the crystals were fixed by the long alkyl chains. Therefore, it was thought that moving of the molecules in the crystal was impossible even if UV light was irradiated. In the case of Crystal I, however, rotation of the thymine ring during the photodimerization was suggested from the conformational analysis of the photodimer.[19)] Different from Crystal I, the crystal structure of Crystal II indicates that the molecules locate closely, then the rotation of the thymine bases in the crystal is impossible. Therefore, the thymine bases in Crystal II were not suitable for photodimerization.

Thermal Analysis of the Crystals

The transition points of the Structure I to Structure II were obtained by differential thermal analysis (DTA) study (Figure 11). On the trace of Crystal I (ethyl acetate), a small endothermic peak was found at 106°C and an exothermic peak was found at 111°C (Fig. 11b). A large endothermic peak at 122°C should be melting point. On the trace of Crystal II (ethanol), a broad endothermic peak was shown at 100°C and a large endothermic peak was shown at 122°C (Fig. 11a).

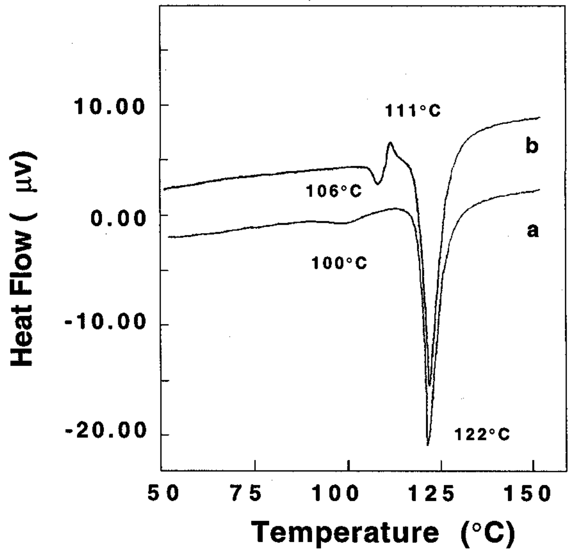

Figure 11

DTA traces of 1-*n*-Octylthymine. Scanning rate was 5K/ min.

[a]; Crystal II (ethanol) [b]; Crystal I (ethyl acetate)

The small endothermic peaks at around 100°C can be assigned to the melting of the *n*-octyl chain. The differences of temperature between two crystals may be caused by the difference of assembly for each long alkyl chain (Fig. 12). Long alkyl chains cross each other in Crystal II (Fig. 12a), but the chains are parallel in Crystal I (Fig. 12b). To make sure that the peaks at 106° and 111°C for Crystal I are the transition point, DTA was measured for the annealed crystal. Crystal I was heated to 110°C and cooled to 50°C. The DTA trace for the annealed crystal showed the quite similar DTA trace to Crystal II as shown in Figure 11a. This result indicated that Structure I (ethyl acetate) transformed to Structure II (ethanol).

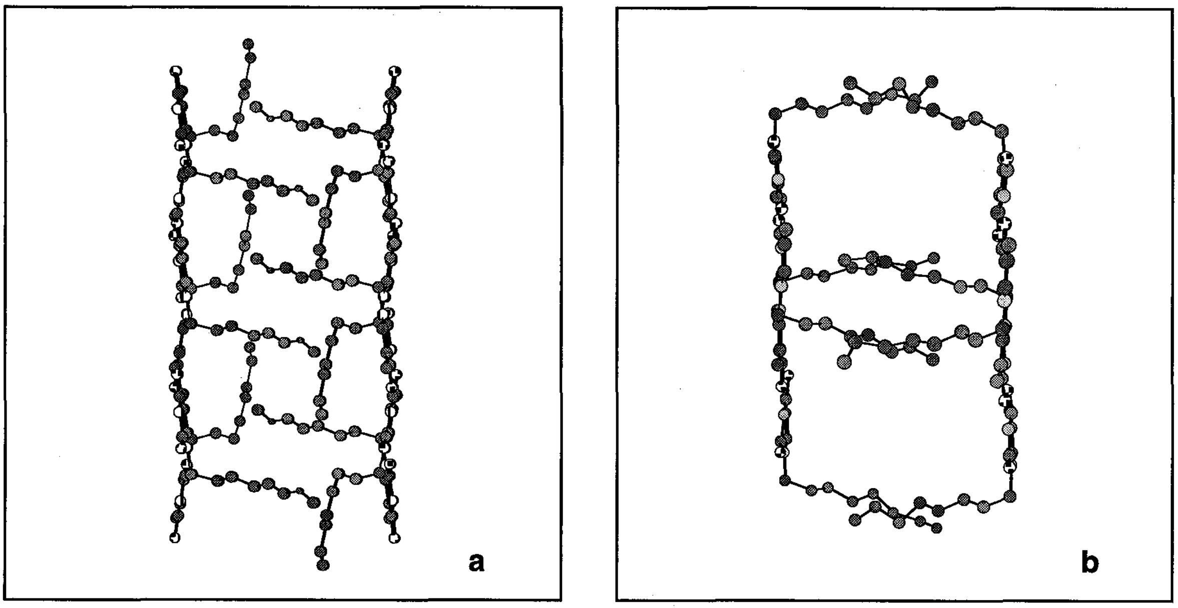

Figure 12

Packing of Long Alkyl Chains in Crystals.

[a]; Crystal II (ethanol)

[b]; Crystal I (ethyl acetate)

The thymine bases associated strongly with two hydrogen bonds on the plane as shown in Fig. 8. Therefore, both crystals showed the same melting point at 122°C. The *n*-octyl groups in Crystal I melted at 106°C with keeping the plane structures by hydrogen bonding as shown in Fig. 8. This plane of Crystal I moved to more packed structure of Crystal II as shown in Fig. 9.

Then, the plane structure by hydrogen bonding of Structure II melted at 122°C. This phenomenon of the crystal structure transition should be caused by annealing of the spin-coated thin film.

Photoreactive and Inactive Crystals

Figure 13 shows an illustration of photoreactive and inactive crystals from the above results. In this Figure, rectangles present the plane of molecule formed by hydrogen bonding shown in Fig. 8. Photodimerizations of the thymine bases occurs between the planes, but can not occur in the some plane. Photoreactive crystal obtained from ethyl acetate (Crystal I) has the

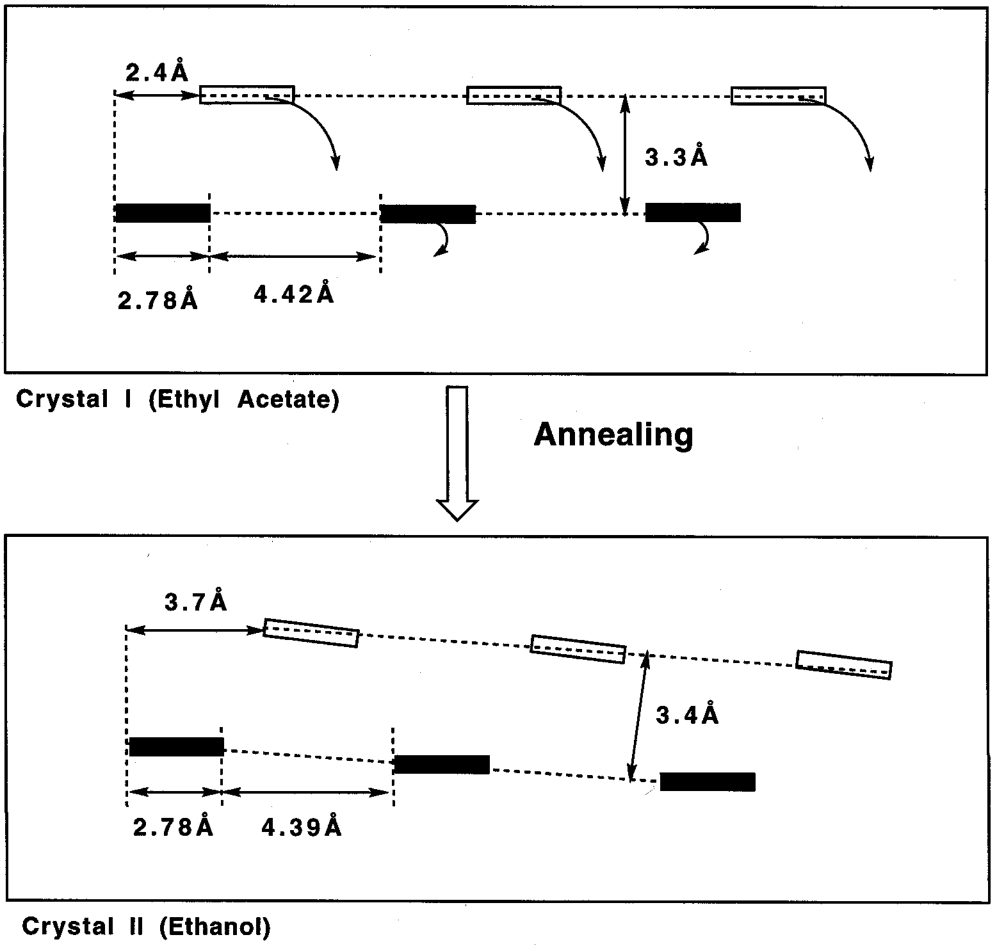

Figure 13

Transformation of Structure by Annealing (Illustration).

Structure I where the planes overlap each other with slight deviation (2.4 Å). The planes of the photoreactive crystals slide by annealing to give the Structure II of the photo-inactive crystal crystallized from ethanol (Crystal II). The Structure II has the space of 3.4 Å between planes that is longer than 3.3 Å of the Structure I, and no overlapping of the thymine bases.

For effective photodimerization of thymines, overlapping of the thymine bases should be required. Structure I with overlapping of the thymine bases have been found for the thymine derivatives having longer alkyl chain than *n*-octyl group. The results will be presented in a subsequent paper.

3-4. CONCLUSION

Reactivity for the photodimerization of 1-*n*-octyl thymine in the spin-coated thin film was very high. The photoreactivity, however, was disappeared by annealing at 100-110°C. The crystal structure of the thin film before annealing corresponded to Structure I for photoreactive Crystal I crystallized from ethyl. The crystal structure of the thin film after annealing corresponded to Structure II of inactive Crystal II recrystallized from ethanol. The powder X-ray diffraction and the differential thermal analysis indicated that the annealing of the thin film caused the transformation of Structure I to Structure II with keeping the plane structure by the hydrogen bonding.

3-5. CRYSTAL DATA OF 1-OCTYLTHYMINE FROM ETHANOL

Table 1. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms and hydrogen atoms.

atom	x	y	z	B(eq)
O(1)	0.6991	0.2163	-0.0502	8.8287
O(2)	0.6878	0.3951	0.1699	8.0640
O(3)	0.6986	0.2800	0.3751	9.4516
O(4)	0.6963	0.1036	0.1441	8.2522
N(1)	0.6951	0.4098	-0.0535	6.2540
N(2)	0.6937	0.3093	0.0584	6.6245
H(1)	0.6972	0.2407	0.0900	-78.9568
N(3)	0.6966	0.0867	0.3732	6.0176
N(4)	0.6963	0.1891	0.2601	6.3368
H(3)	0.6918	0.2592	0.2300	-78.9568
C(1)	0.6962	0.3058	-0.0177	6.2033
C(2)	0.6900	0.4044	0.1014	5.7197
C(3)	0.6889	0.5107	0.0601	5.6958
C(4)	0.6913	0.5079	-0.0144	5.7280
H(2)	0.6929	0.5750	-0.0400	-78.9568
C(5)	0.6855	0.6185	0.1028	8.2350
H(5)	0.6523	0.6190	0.1000	-78.9568
H(6)	0.6967	0.6150	0.1600	-78.9568
H(7)	0.6880	0.6754	0.0800	-78.9568
C(6)	0.6971	0.1911	0.3389	6.2857

C(7)	0.6970	0.0940	0.2145	5.6901
C(8)	0.6987	-0.0130	0.2554	5.8254
C(9)	0.6980	-0.0104	0.3315	6.1078
H(4)	0.6986	-0.0784	0.3600	-78.9568
C(10)	0.7013	-0.1199	0.2114	8.8356
H(8)	0.6780	-0.1226	0.1800	-78.9568
H(9)	0.7206	-0.1185	0.1800	-78.9568
H(10)	0.7007	-0.1775	0.2400	-78.9568
C(11)	0.6968	0.4157	-0.1362	9.2948
H(11)	0.7053	0.4799	-0.1500	-78.9568
H(12)	0.7020	0.3514	-0.1500	-78.9568
C(12)	0.6952	0.0806	0.4566	7.8672
H(13)	0.7020	0.1441	0.4800	-78.9568
H(14)	0.7068	0.0129	0.4800	-78.9568
C(13)	0.6517	0.4192	-0.2036	13.2802
H(13A)	0.6388	0.4909	-0.1965	-78.9568
H(13B)	0.6573	0.4274	-0.2539	-78.9568
C(14)	0.6499	0.0858	0.4544	12.1579
H(14A)	0.6385	0.0095	0.4404	-78.9568
H(14B)	0.6541	0.0961	0.5119	-78.9568
C(15)	0.6188	0.3441	-0.2205	13.8986
H(15A)	0.6121	0.3336	-0.1721	-78.9568
H(15B)	0.6302	0.2710	-0.2314	-78.9568
C(16)	0.5772	0.3670	-0.2910	18.7267
H(16A)	0.5670	0.4430	-0.2828	-78.9568
H(16B)	0.5836	0.3729	-0.3405	-78.9568

C(17)	0.5386	0.2978	-0.3142	23.7229
H(17A)	0.5289	0.2916	-0.2669	-78.9568
H(17B)	0.5457	0.2208	-0.3247	-78.9568
C(18)	0.4976	0.3304	-0.3859	26.8782
H(18A)	0.4826	0.3920	-0.3701	-78.9568
H(18B)	0.5058	0.3570	-0.4304	-78.9568
C(19)	0.4685	0.2390	-0.4130	28.7159
H(19A)	0.4606	0.2088	-0.3690	-78.9568
H(19B)	0.4816	0.1790	-0.4344	-78.9568
C(20)	0.4278	0.2914	-0.4816	33.2904
H(20A)	0.4049	0.2349	-0.5035	-78.9568
H(20B)	0.4364	0.3191	-0.5248	-78.9568
H(20C)	0.4166	0.3531	-0.4593	-78.9568
C(21)	0.6150	0.1481	0.4139	13.6386
H(21A)	0.6120	0.1516	0.3571	-78.9568
H(21B)	0.6227	0.2265	0.4355	-78.9568
C(22)	0.5712	0.1239	0.4142	21.1976
H(22A)	0.5630	0.0515	0.3873	-78.9568
H(22B)	0.5761	0.1116	0.4719	-78.9568
C(23)	0.5332	0.1885	0.3834	26.6396
H(23A)	0.5304	0.2104	0.3282	-78.9568
H(23B)	0.5402	0.2586	0.4155	-78.9568
C(24)	0.4883	0.1608	0.3737	31.2144
H(24A)	0.4757	0.1114	0.3261	-78.9568
H(24B)	0.4897	0.1177	0.4218	-78.9568
C(25)	0.4590	0.2509	0.3638	32.9002

H(25A)	0.4681	0.2979	0.4130	-78.9568
H(25B)	0.4565	0.2975	0.3167	-78.9568
C(26)	0.4179	0.1926	0.3504	36.0610
H(26A)	0.3952	0.2467	0.3474	-78.9568
H(26B)	0.4223	0.1412	0.3953	-78.9568
H(26C)	0.4088	0.1509	0.2996	-78.9568
C(27)	0.6187	0.4898	-0.2153	13.2026
H(27A)	0.6284	0.5655	-0.2212	-78.9568
H(27B)	0.6116	0.4888	-0.1661	-78.9568
C(28)	0.5782	0.4672	-0.2873	19.2968
H(28A)	0.5855	0.4486	-0.3333	-78.9568
H(28B)	0.5642	0.3970	-0.2750	-78.9568
C(29)	0.5427	0.5402	-0.3143	23.7845
H(29A)	0.5568	0.6164	-0.3237	-78.9568
H(29B)	0.5349	0.5632	-0.2669	-78.9568
C(30)	0.5021	0.5219	-0.3855	28.4888
H(30A)	0.5094	0.5175	-0.4341	-78.9568
H(30B)	0.4894	0.4495	-0.3795	-78.9568
C(31)	0.4703	0.6043	-0.3979	30.7432
H(31A)	0.4775	0.6741	-0.4195	-78.9568
H(31B)	0.4644	0.6198	-0.3487	-78.9568
C(32)	0.4343	0.5407	-0.4601	35.4774
H(32A)	0.4076	0.5859	-0.4798	-78.9568
H(32B)	0.4288	0.4721	-0.4360	-78.9568
H(32C)	0.4428	0.5223	-0.5053	-78.9568
C(33)	0.6176	0.0071	0.4135	11.7025

H(33A)	0.6292	-0.0681	0.4330	-78.9568
H(33B)	0.6117	0.0104	0.3551	-78.9568
C(34)	0.5743	0.0204	0.4257	20.9038
H(34A)	0.5788	0.0191	0.4824	-78.9568
H(34B)	0.5606	0.0944	0.4024	-78.9568
C(35)	0.5422	-0.0652	0.3811	23.2658
H(35A)	0.5523	-0.1384	0.4066	-78.9568
H(35B)	0.5406	-0.0689	0.3248	-78.9568
C(36)	0.4965	-0.0420	0.3796	31.1376
H(36A)	0.4974	-0.0519	0.4351	-78.9568
H(36B)	0.4893	0.0369	0.3647	-78.9568
C(37)	0.4615	-0.1090	0.3258	33.2883
H(37A)	0.4680	-0.1892	0.3361	-78.9568
H(37B)	0.4559	-0.0924	0.2685	-78.9568
C(38)	0.4219	-0.0734	0.3476	42.4203
H(38A)	0.3953	-0.1120	0.3119	-78.9568
H(38B)	0.4175	0.0070	0.3404	-78.9568
H(38C)	0.4279	-0.0930	0.4040	-78.9568
C(39)	0.6517	0.4192	-0.2036	13.2802
H(39A)	0.6576	0.4244	-0.2538	-78.9568
H(39B)	0.6393	0.3447	-0.2040	-78.9568
C(40)	0.6499	0.0858	0.4544	12.1579
H(40A)	0.6524	0.0866	0.5114	-78.9568
H(40B)	0.6379	0.1596	0.4315	-78.9568

Table 2. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.1659	0.0527	0.0849	0.0001	0.0676	-0.0110
O(2)	0.1575	0.0458	0.0663	0.0041	0.0625	0.0033
O(3)	0.1858	0.0464	0.0794	0.0098	0.0645	-0.0072
O(4)	0.1613	0.0453	0.0686	0.0004	0.0638	0.0019
N(1)	0.1099	0.0530	0.0627	0.0016	0.0485	0.0011
N(2)	0.1241	0.0355	0.0667	0.0023	0.0502	0.0015
N(3)	0.1094	0.0471	0.0569	0.0020	0.0384	0.0016
N(4)	0.1175	0.0370	0.0644	0.0002	0.0426	0.0017
C(1)	0.1091	0.0481	0.0656	-0.0017	0.0459	-0.0051
C(2)	0.1018	0.0388	0.0622	0.0030	0.0384	0.0017
C(3)	0.0998	0.0384	0.0646	0.0013	0.0411	0.0030
C(4)	0.0965	0.0414	0.0690	-0.0008	0.0400	0.0046
C(5)	0.1559	0.0405	0.0818	0.0080	0.0609	0.0053
C(6)	0.1169	0.0437	0.0586	0.0056	0.0389	-0.0005
C(7)	0.1002	0.0422	0.0614	-0.0013	0.0406	-0.0018
C(8)	0.1039	0.0388	0.0635	-0.0007	0.0410	-0.0001
C(9)	0.1108	0.0396	0.0641	-0.0013	0.0388	0.0080
C(10)	0.1724	0.0420	0.0781	0.0067	0.0596	-0.0007
C(11)	0.1735	0.0744	0.0770	-0.0025	0.0831	0.0000
C(12)	0.1475	0.0654	0.0613	0.0160	0.0538	0.0052
C(13)	0.1869	0.2153	0.0599	-0.0177	0.0615	-0.0005
C(14)	0.1627	0.1898	0.0930	0.0315	0.0777	0.0260

C(15)	0.1680	0.2333	0.1015	-0.0525	0.0592	-0.0084
C(16)	0.1840	0.3504	0.1101	-0.0430	0.0357	-0.0199
C(17)	0.1743	0.4147	0.2616	-0.0130	0.0243	-0.0589
C(18)	0.1741	0.5042	0.2512	-0.0689	-0.0097	-0.0317
C(19)	0.2011	0.4940	0.3352	-0.0269	-0.0281	0.0133
C(20)	0.1697	0.6329	0.3224	0.0323	-0.0687	0.1009
C(21)	0.1502	0.2233	0.1308	0.0160	0.0567	0.0220
C(22)	0.1577	0.3692	0.2347	0.0471	0.1259	0.0673
C(23)	0.1523	0.4498	0.3405	0.0466	0.0802	0.0382
C(24)	0.1506	0.5530	0.3747	0.0991	0.1436	0.0545
C(25)	0.1593	0.5444	0.4463	0.0617	0.0743	0.0150
C(26)	0.1258	0.6743	0.3941	-0.0453	0.0651	-0.0163
C(27)	0.1969	0.1782	0.1155	0.0798	0.0619	0.0282
C(28)	0.2261	0.3332	0.1305	0.0762	0.0147	-0.0159
C(29)	0.1939	0.4167	0.2470	0.0777	0.0173	0.0443
C(30)	0.1832	0.5449	0.2452	0.0770	0.0246	0.0171
C(31)	0.1903	0.5542	0.3339	0.0140	0.0365	0.0303
C(32)	0.1821	0.6961	0.2966	0.0068	-0.0028	0.1110
C(33)	0.1699	0.1536	0.1159	-0.0121	0.0614	-0.0053
C(34)	0.1726	0.3604	0.2249	-0.0514	0.1160	-0.0284
C(35)	0.1579	0.3987	0.2768	-0.0527	0.0878	0.0184
C(36)	0.1572	0.5516	0.3708	-0.0648	0.1170	-0.0226
C(37)	0.1607	0.5685	0.4292	-0.0562	0.0782	-0.0057
C(38)	0.1521	0.8102	0.4316	0.0239	0.1059	0.0993
C(39)	0.1869	0.2153	0.0599	-0.0177	0.0615	-0.0005
C(40)	0.1627	0.1898	0.0930	0.0315	0.0777	0.0260

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Chapter 4

Photodimerization of 1-Alkylthymines Crystallized from Acetonitrile Solution

Crystallization of 1-*n*-octylthymine from acetonitrile solution gave needles and plates. The plates did not give the photodimer because rotation of thymines hardly occurred in the crystal. In the case of the needles, the rotation of thymines in the crystal was possible because the crystal contains acetonitrile. Therefore, the needles can give photodimer. There are two pairs of thymine, which form the photodimer in the needles of 1-*n*-octylthymine. In both pairs, thymine rotated disrotatory during phtodimerization reaction to give *trans-anti* and *trans-syn* isomers, respectively. When alkyl group became long, the formation of *trans-syn* photodimer decreased because strong interaction of the alkyl group inhibited moving of molecules. The photodimerization of 1-*n*-alkylthymine was concluded to occur when the rotation of the thymine is possible in the crystal.

4-1. INTRODUCTION

Thymine, one of the nucleic acid bases, converts to photodimers upon irradiation with UV light near 280 nm (Figure 1). This reaction is known to cause damage of DNA by solar UV light.[1-2] The photodimerization is a reversible reaction and the photodimers split to afford the original thymines very efficiently upon irradiation at a shorter wavelength (240 nm). The reversible photodimerization of thymine derivatives can be applied to negative or positive type photoresist materials[3-5] and the photorecording system by controlling wavelength of irradiating UV light.[6-7]

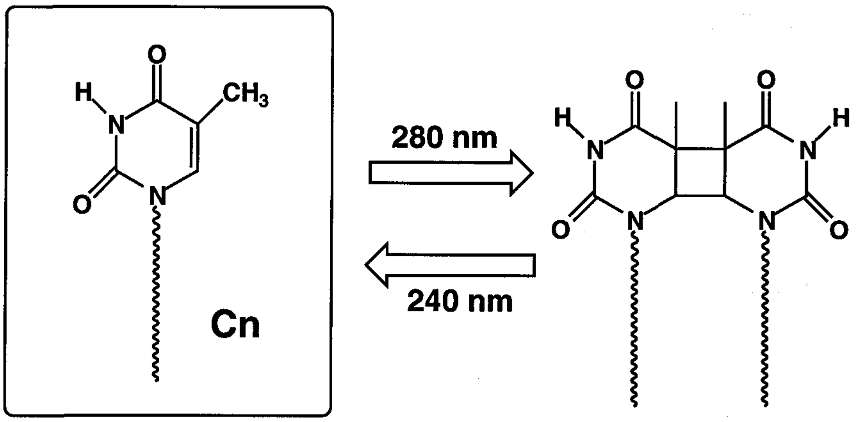
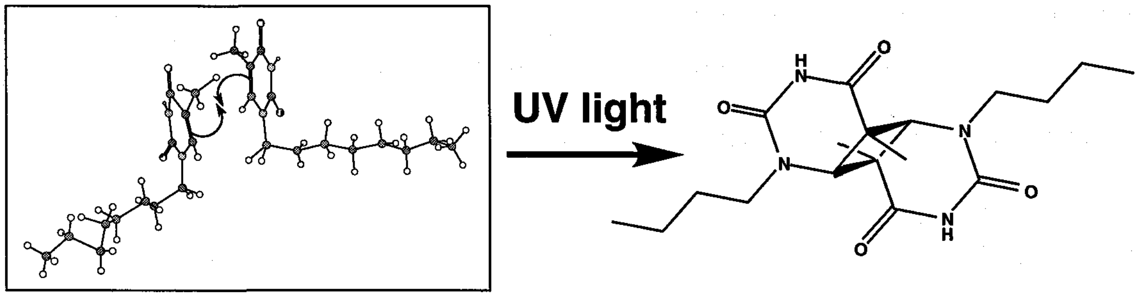


Figure 1

Reversible Photodimerization of Thymine Derivatives.

For applications of the thymine derivatives to the reversible photochemical systems, it is necessary to investigate the reactivity of thymine derivatives in solid state.8-11) In order to clear the mechanism of photodimerization of thymines in solid state, the photodimerization reactions were studied for single crystals. The single crystal of 1-*n*-octylthymine from ethyl acetate was found to give the photodimer.12) The plate crystal obtained from ethanol, however, did not give the photodimer.13) The study of the photodimerization of 1-*n*-octylthymine in single crystal suggested that the thymine base rotated in the single crystal during photodimerization (Figure 2).

Crystallization of 1-*n*-octylthymine from acetonitrile solution gave two kinds of crystals, needles and plates. The needles were found to give photodimers by irradiation of ultraviolet



trans-syn **orientation in single crystal**

trans-anti **photodimer**

Figure 2

Photodimerization of 1-*n*-Octylthymine in Crystal from Ethyl Acetate Solution.12) light at around 280 nm, but the plates could not give the photodimer. This paper deals with the structure of two 1-*n*-alkylthymine crystals obtained from acetonitrile solution, with photodimerization of these crystals, and effects of length of alkyl group on the photodimerization.

4-2. EXPERIMENTAL

Preparation of 1-*n*-Octylthymine

The alkylthymine derivatives were prepared according to the method reported in the literature.[12] Thymine was reacted with hexamethyldisilazane to give 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine. A mixture of 1-*n*-octyl bromide and 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine was stirring for 10 days at 60°C to afford 1-*n*-octyl thymine.

Photodimerization

Photodimerizations in single crystal were carried out by SUPER CURE-203S UV LIGHT SOURCE SAN-EI ELECTRIC. 1H-NMR Spectra were recorded with a Varian unity INOVA600 and JEOL GSX270. UV Spectra were recorded with a JASCO UVIDEC 660. Thermogravimetric analysis (TGA) and differential thermal analyses (DTA) were measured by a Rigaku Thermo Plus TG8120 instrument. X-ray powder diffraction patterns were measured by Rigaku X-ray diffractometer RINT 2000 with Cu-$K\alpha$ radiation.

Crystal Structure Analysis

Data of X-ray diffraction for 1-*n*-octyl thymine were collected by Rigaku RAXIS-IV imaging plate two-dimensional area detector using graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71070$Å) at 15 ± 1°C. Data of X-ray diffraction for 1-*n*-undecylthymine were collected by Rigaku RAXIS-CS imaging plate two-dimensional area detector using graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda= 0.71070$Å) at 15 ± 1°C. Unique reflections of 1807 and

2150 were measured up to 2θ of 51.7° and 60.1°, respectively. For further calculations, $[|F_o|>3\sigma(F_o)]$ reflections were used after Lorenz and polarization corrections. Crystal structures were solved by the direct methods (SIR-88 and SHELXS-97), and refined by the full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were located in the calculated positions. The positions of hydrogen atoms attached to nitrogen atoms were obtained from the difference Fourier syntheses. All the crystallographic calculations were performed by using TEXSAN software package of the Molecular Structure Corporation.

4-3. RESULTS AND DISCUSSION

Crystal Structure of 1-*n*-Octylthymine Crystallized from Acetonitrile Solution

Needles of 1-*n*-octylthymine were obtained by crystallization from acetonitrile solution. When the solvent was evaporated gradually, plates were obtained. The crystal data of needles of 1-*n*-alkylthymines are shown in Table 1.

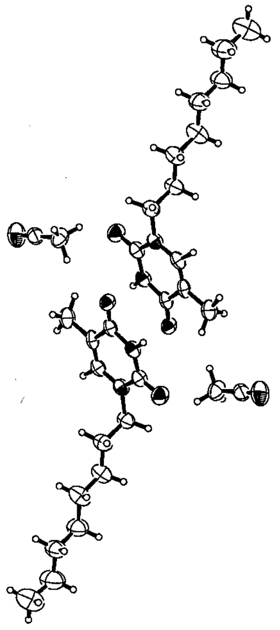


Figure 3

Molecular Packing Structure of 1-*n*-Octylthymine in Needles from Acetonitrile Solution.

Compound		1-*n*-Octylthyumine	1-*n*-Nonylthymine	1-*n*-Decylthymine	1-*n*-Undecylthymine
Alkyl Chain Number		8	9	10	11
Empirical Formula		$C_{15}H_{25}N_3O_2$	$C_{16}H_{27}N_3O_2$	$C_{17}H_{29}N_3O_2$	$C_{18}H_{31}N_3O_2$
Formula Weight		279.38	293.41	307.44	321.46
Crystal Color, Habit		colorless, needle	colorless, needle	colorless, needle	colorless, needle
Crystal System		triclinic	triclinic	triclinic	triclinic
Spaca Group		$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Lattice Parameter;	a/ Å	9.200(5)Å	9.31(5)Å	9.151(7)Å	9.265(6)Å
	b/ Å	18.80(1)Å	20.26(2)Å	21.30(2)Å	22.39(2)Å
	c/ Å	5.027(1)Å	5.003(6)Å	5.026(2)Å	4.981(8)Å
	α/ °	94.33(5)°	92.2(3)°	94.62(5)°	90.61(8)°
	β/ °	99.94(4)°	100.1(3)°	99.81(4)°	99.78(7)°
	γ/ °	84.52(3)°	84.2(8)°	80.28(6)°	79.88(6)°
	V/ Å^3	851.0(7)Å^3	920(8)Å^3	950(1)Å^3	1002(1)Å^3
z Value		2	2	2	2
R, Rw		0.073, 0.068	0.090, 0.103	-	0.075, 0.116
D_{calcd}/gcm^{-3}		1.090 gcm^{-3}	1.059 gcm^{-3}	1.074 gcm^{-3}	1.065 gcm^{-3}
F_{000}		304.00	320.00	336.00	352.00
μ(Mo-$K\alpha$)/cm^{-1}		0.73cm^{-1}	0.71cm^{-1}	0.71cm^{-1}	0.70cm^{-1}

Table 1

Data of X-ray Structure Analysis for 1-*n*-Alkylthymine Having Different Length of Alkyl Group in Needles from Acetonitrile Solution.

The form of the needles was greatly different from those of crystals obtained from ethyl acetate and ethanol solutions. Figure 3 shows a molecular packing structure of 1-*n*-octylthymine. The crystal contained acetonitrile in the cavity at the molar ratio of 1:1 (thymine: acetonitrile). As the z value was 2, one unit cell includes two thymine molecules and two acetonitrile molecules. Figure 4 showed the arrangement of the *ab* and *cb* planes. The crystal had the cumulated bilayer structure with the cavity where acetonitrile was included. Thymine bases stacked for c axis but did not completely overlap. The hydrogen bonding modes of thymine bases in the hydrophilic layer were shown in Figure 5. The lamella structure is consisted of the hydrophilic and

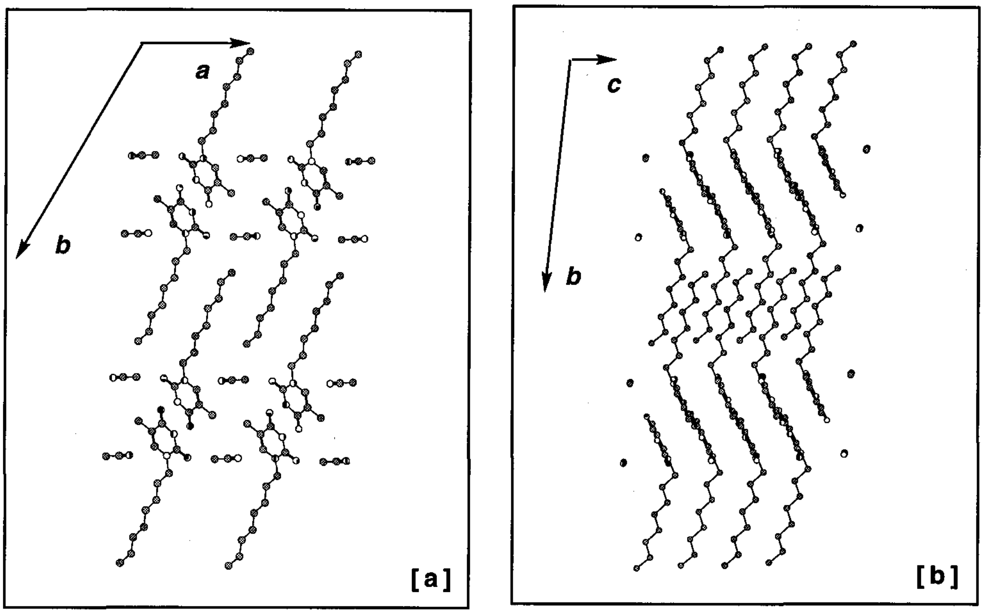


Figure 4

Molecular Arrangement of 1-*n*-Octylthymine in Needles.

[a] *ab* Plane, [b] *bc* Plane

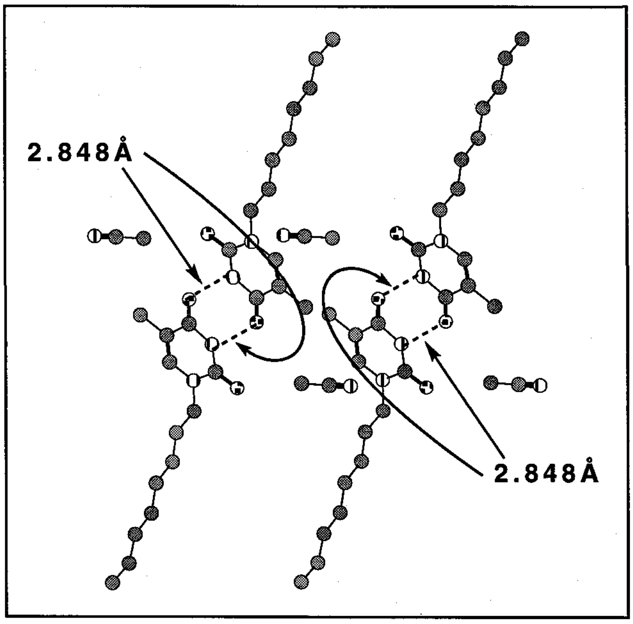


Figure 5

Hydrogen Bonding Modes of 1-*n*-Octylthymine in Needles.

hydrophobic layers. The hydrophilic layer was composed of thymine bases and acetonitrile, and the hydrophobic layer was composed of the long alkyl chain part. Two layers were conjugated by that hydrogen bonding and they contributed to the stability of the hydrophilic layer.

The plates of 1-*n*-ocytlthymine obtained by slow evaporation of acetonitrile gave the same form as the plates from ethanol solution reported in previous paper (Figure 6).

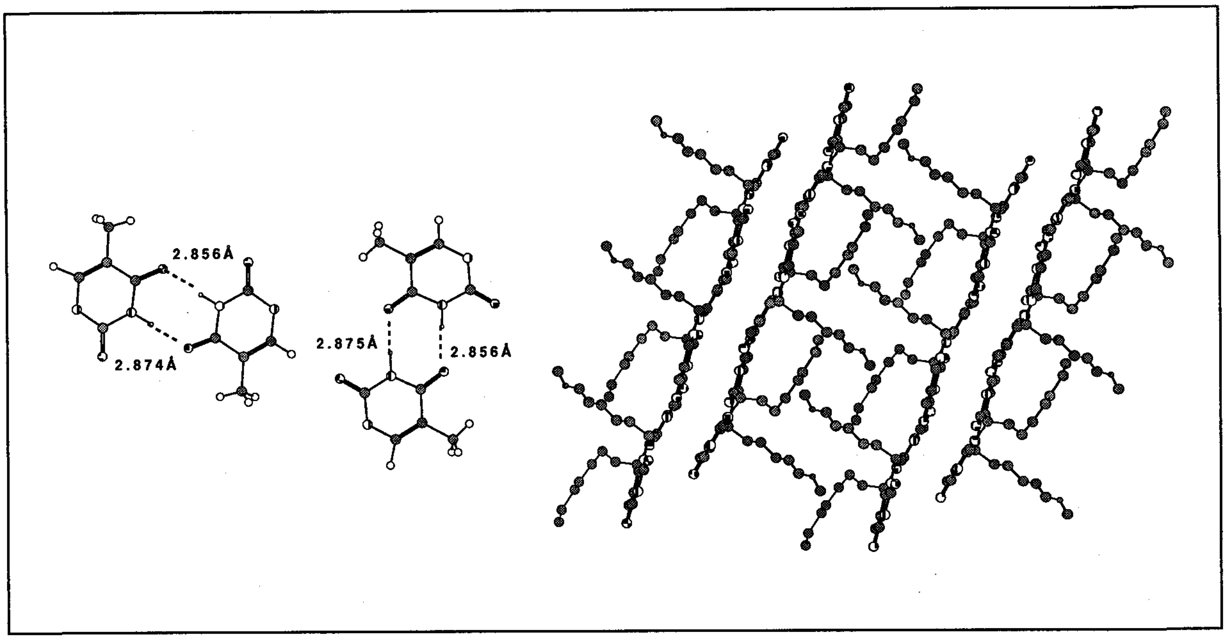


Figure 6

Hydrogen Bondings and Lamella Structure of 1-*n*-Octylthymine in Plates from Ethanol Solution.[13)]

Thermal Analysis of the Crystals

Inclusion of acetonitrile in the crystal of 1-*n*-octylthymine was supported by differential thermal analysis (DTA) and thermogravimetry (TGA) (Figure 7). The DTA of the needles in Figure 7 shows two peaks at 65 and 123°C. The peak of 65°C corresponds to the decrease of TGA, indicating release of acetonitrile from the crystal at this temperature. The melting point was 123°C, where the hydrogen bonds between thymines broken down.

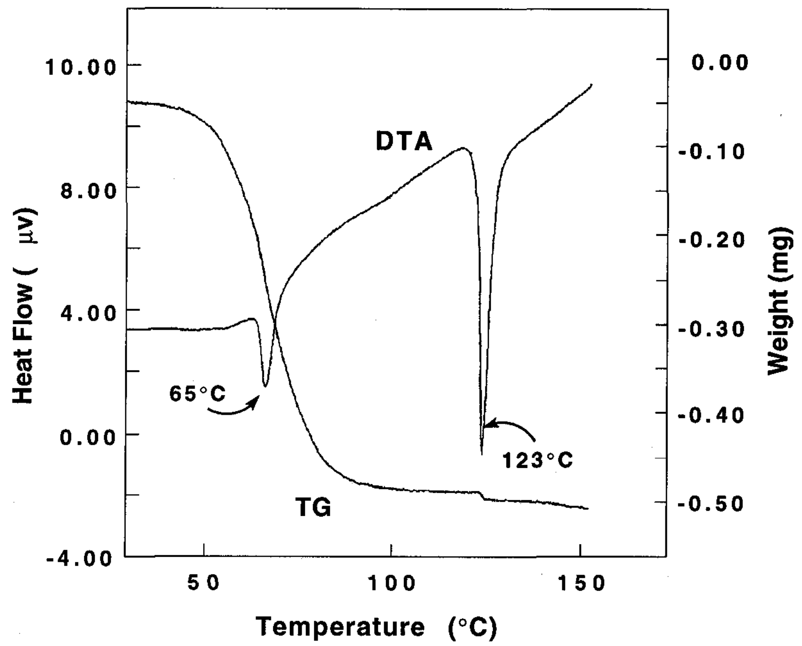


Figure 7

Differential Thermal Analysis and Thermogravimetry Studies of 1-*n*-Octylthymine in Needles. Scanning rate was 5K/ min.

X-ray Powder Diffraction of 1-*n*-Octylthymine

The X-ray powder diffraction was measured to clear the crystal structure before and after release of acetonitrile at 65°C. The data in Figure 8 suggest that the needles containing acetonitrile (**a**) gave (**b**) by release of acetonitrile at 100°C. It was reported that the density of the plates from ethanol solution was higher than that of the plates from ethyl acetate solution[13)]. The X-ray powder data in Figure 8 suggest that the density of the crystal without acetonitrile is higher than the crystal from ethanol. The value of 2θ (6.560°) for the annealed crystal (**b**) was higher than the value of plates from acetonitrile (**c**: 5.740°) or the plates from ethyl acetate (**d**: 5.700°).

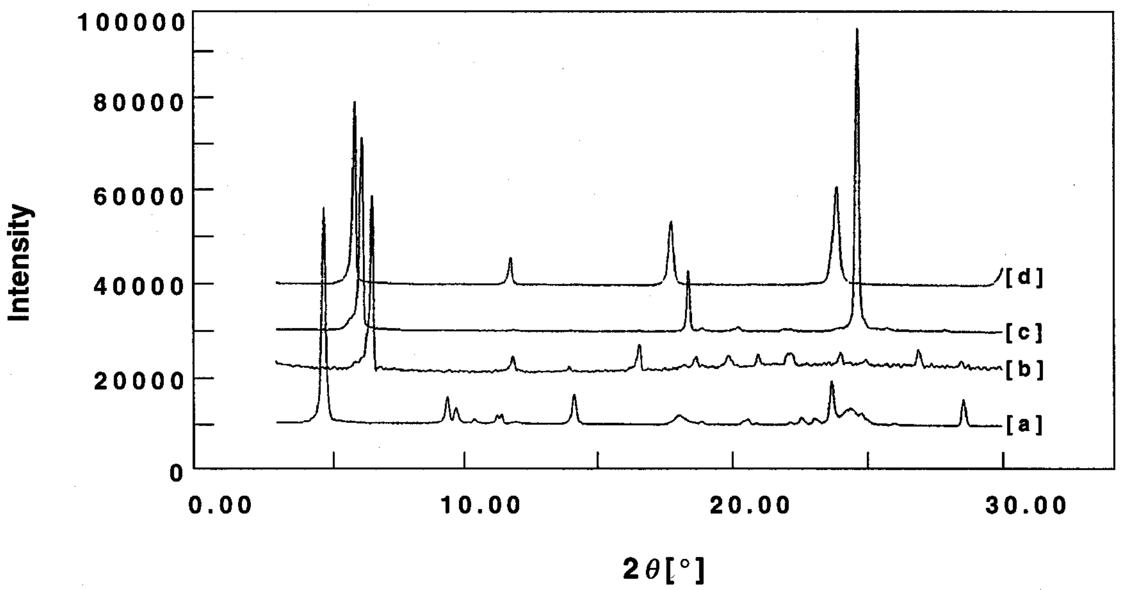


Figure 8

Powder X-ray Diffraction Patterns of 1-*n*-Octylthymine.

[a] Needles from acetonitrile solution.

[b] Annealing of the needles at 100°C (after releasing of acetonitrile).

[c] Crystals from ethanol solution.

[d] Crystals from ethyl acetate solution.

Photodimerization of 1-*n*-Octylthymine

Irradiation of UV light around 280 nm on the needles obtained from the acetonitrile solution gave the photodimer. However, the plates didn't show photochemical reactivity as in the case of the plates obtained from the ethanol solution.

Photodimerization of the 1-*n*-alkylthymines in solution with acetone as a sensitizer gave four kinds of isomers (Figure 9)[14-17). The crystal from ethyl acetate, however, gave only *trans-anti* isomer by irradiation of UV light. Irradiation of UV light on the needles from acetonitrile also gave the photodimers that were identified by NMR spectra. NMR spectrum in Figure 10 suggests the formation of two kinds of photodimers by photodimerization of the needle of 1-*n*-

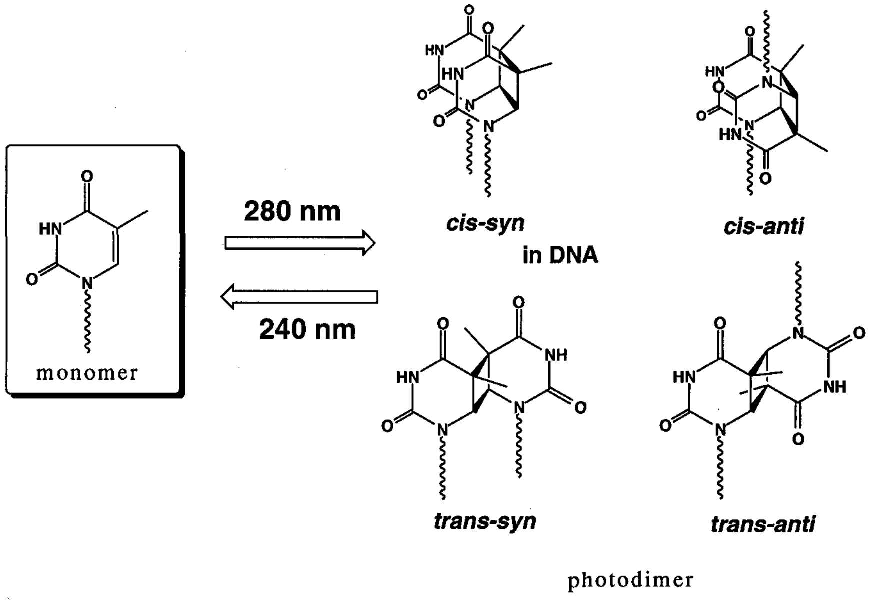


Figure 9

Four Stereo Isomers of 1-*n*-Alkylthymine Photodimer.

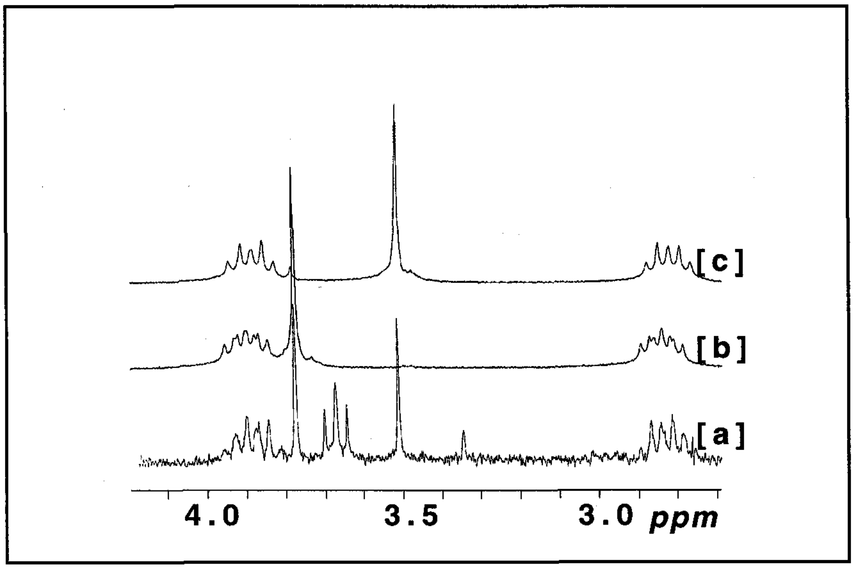


Figure 10

NMR Spectra of Photodimers in $CDCl_3$.

[a] Photodimerization products of 1-*n*-octylthymine in needles including unreacted compound (*t*, 3.68 ppm).

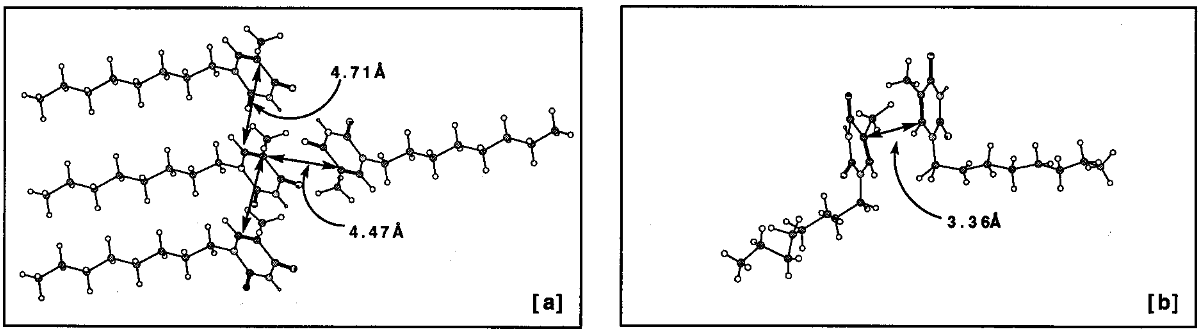
[b] Isolated*trans-anti* Isomer.12)

[c] Isolated*trans-syn* Isomer.12)

octylthymine ([**a**]). The two isomers were identified as *trans-anti* ([**b**], peak at 3.78 ppm) and *trans-syn* ([**c**], peak at 3.52 ppm) isomers comparing the NMR spectra of the isolated photodimers.[12)]

Mechanism of Photodimerization

Mechanisms of the formation of two kinds of photodimers were estimated from the form of the needles. In the plates from ethyl acetate, the pair of thymine which forms the photodimer exists in *trans-syn* orientation (Figure 11b), but gave *trans-anti* photodimer by rotation of the thymines during photodimerization reaction. On the other hand, there are two orientations of the thymine pairs that form photodimer in the needles from acetonitrile solution (Figure 11a).



Acetonitrile (Needles) **Ethyl Acetate (Plates)**

Figure 11

Arrangement of Reacting Thymine Derivatives in Crystals.

[a] Needles from acetonitrile solution. [b] Plates from ethyl acetate solution.[12)]

One is the *trans-anti* orientation. As shown in Figure 12, thymines in *trans-anti* orientation rotate for the reaction between C5 and C51, and rotate again for the formation of photodimer, giving *trans-syn* isomer. The disrotatory motion of thymines is illustrated in detail

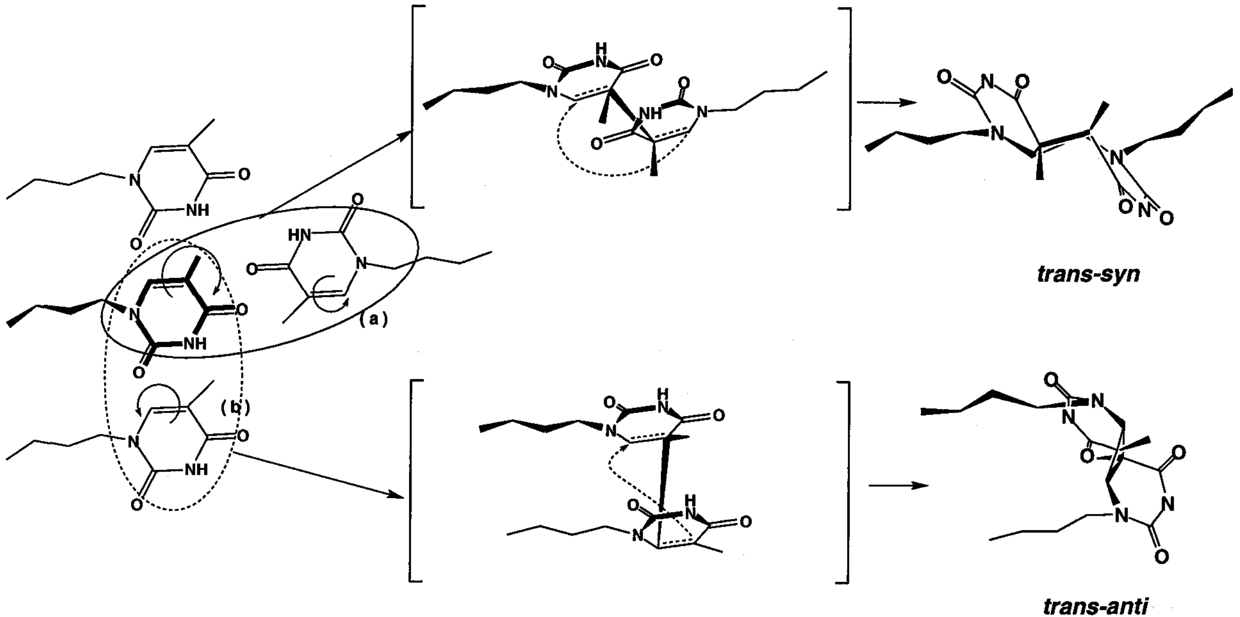


Figure 12

Mechanisms of Photodimerization for 1-*n*-Octylthymine in Needles.

[a] Orientation of *trans-anti* giving *trans-syn* photodimer.

[b] Orientation of *cis-syn* giving *trans-anti* photodimer.

(Figure 13).

The other orientation is *cis-syn*, and gives the *trans-anti* photodimer by rotation of thymines during the photodimerization reaction. As illustrated in Figure 14, the thymines rotate outside to give *cis-syn* orientation of the intermediate that give the *trans-anti* photodimer by reaction between C6 and C51 with internal rotation. If the thymines rotate inside, the photodimer should be *cis-anti*. The rotation inside, however, may be inhibited by steric hindrance of methyl groups of thymine. Therefore, only small amounts of *cis-anti* photodimer were obtained (as shown in NMR at 3.34 ppm in Figure 10)12).

In both pairs, the thymines gave the photodimers by disrotatory motion in the crystals during the photodimerization reaction. If conrotatory motion was occurred during the photodimerization, another isomers could be obtained. No photodimerization in the plates may be caused by difficulty of rotation of thymines in the crystals.

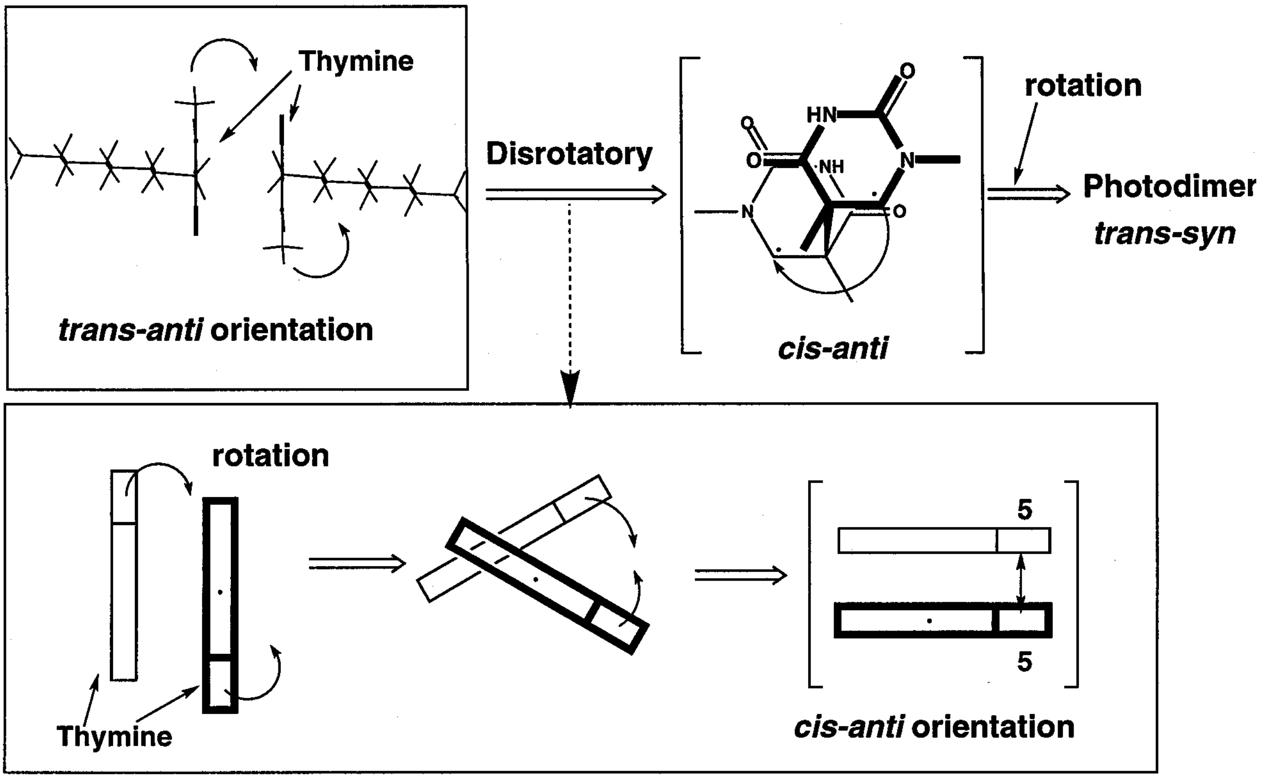


Figure 13

Illustration of Disrotatory Motion from *trans-anti* Orientation to *cis-anti* Intermediate.

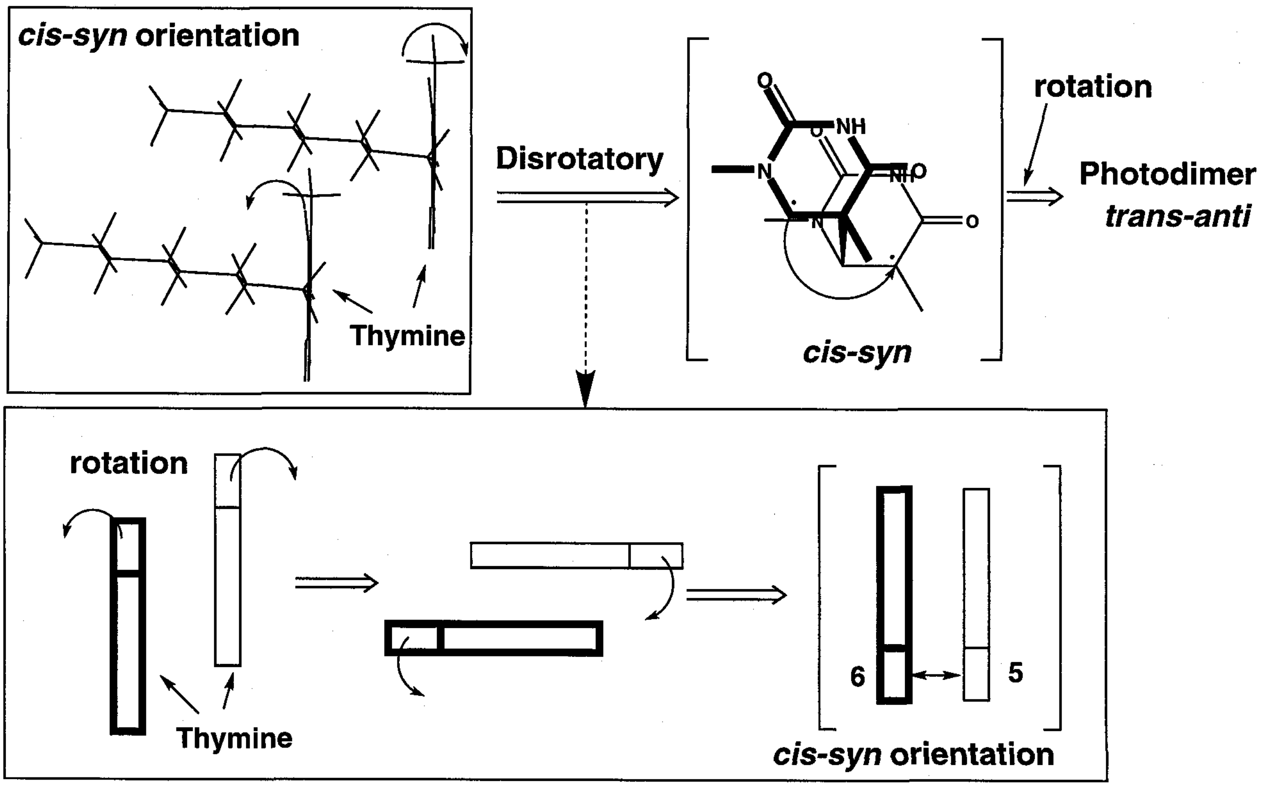


Figure 14

Illustration of Disrotatory Motion from *cis-syn* Orientation to *cis-syn* Intermediate.

Effect of the Alkyl Chain Length on the Photodimerization

When the length of the alkyl group in the 1-*n*-alkylthymines changes, the result of the photodimerization changes. The structures of the photodimers were determined by NMR spectra for the needles of 1-*n*-alkylthymine having different length of the alkyl group (Figure 15). The NMR spectra show that the formation ratio of the isomer varies according to the length of the alkyl group. The peak identified to *trans*-*syn* isomer (3.52 ppm) observed for 1-*n*-octylthymine ([**a**]) decreased with increase of alkyl chain length ([**b**]: 1-*n*-nonylthymine, [**c**]: 1-*n*-undecylthymine), and disappeared for 1-*n*-hexadecylthymine ([**d**]).

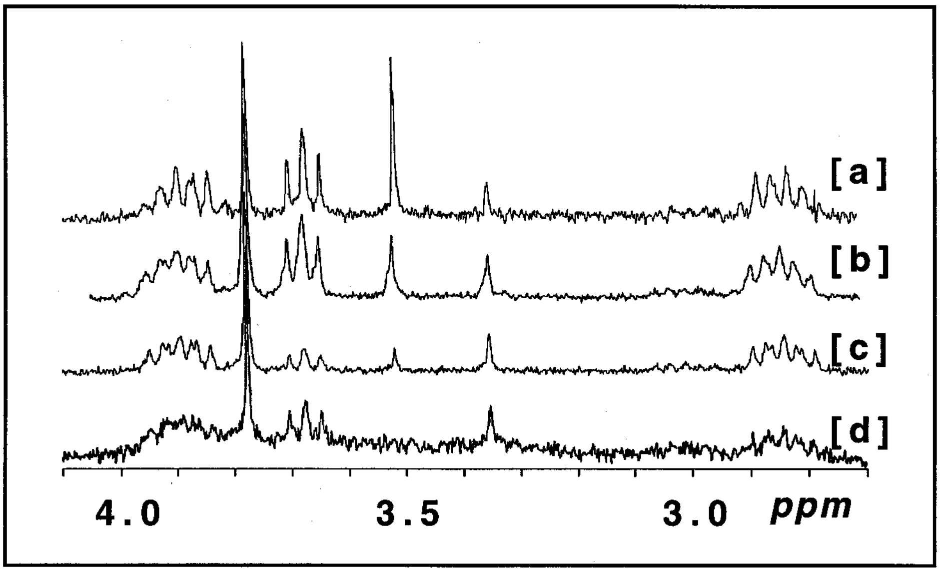


Figure 15

NMR Spectra of Photodimers from Needles of 1-*n*-Alkylthymines in $CDCl_3$.

[a] 1-*n*-Octylthymine, [b] 1-*n*-Undecylthymine

[c] 1-*n*-Tridecylthymine, [d] 1-*n*-Hexadecylthymine

Effect of the Alkyl Chain Length on the Crystal Structure

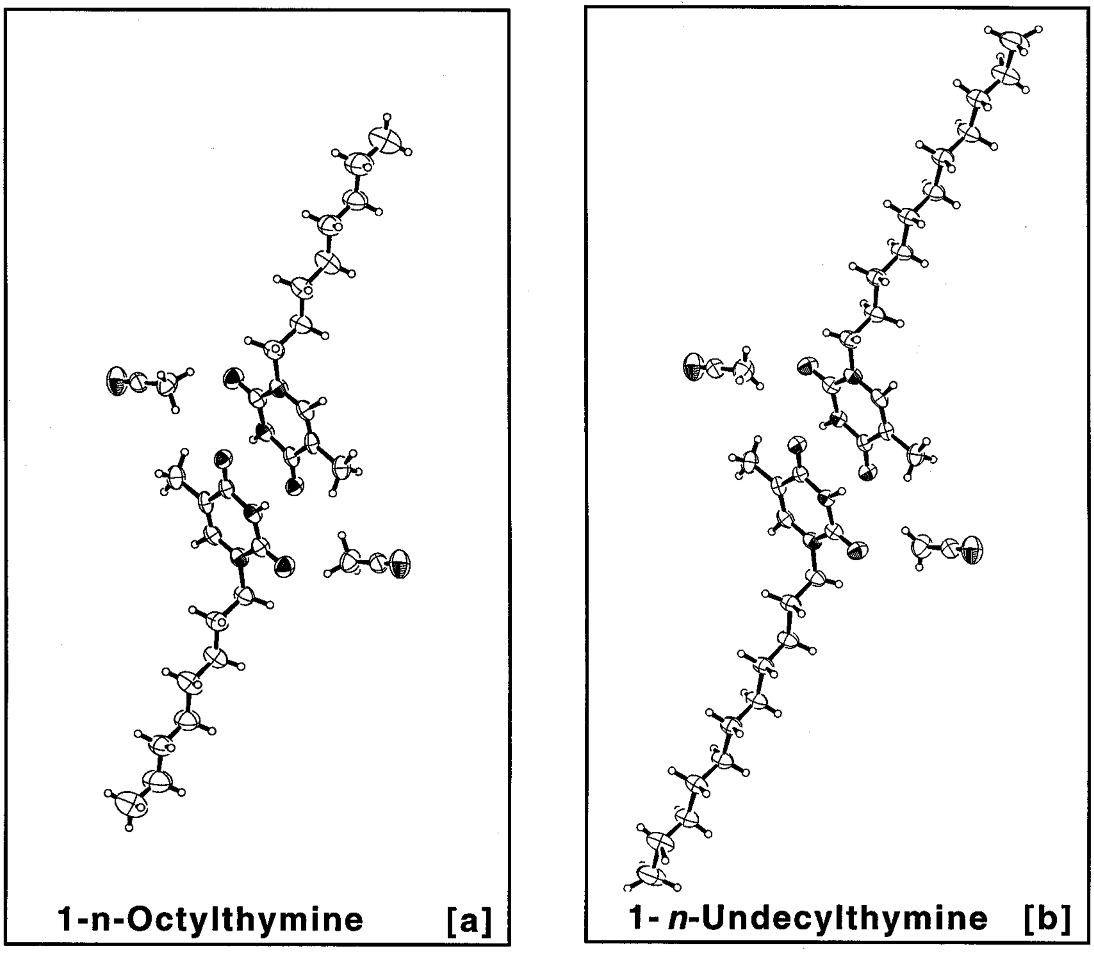
The 1-*n*-alkylthymine derivatives were prepared for *n*-alkyl groups having carbon number (Cn) of 5 to 20. When the length of alkyl chain was comparatively short (Cn=5 and 6), all crystals formed were the plates as shown in Figure 6. The compounds having carbon number of 7 and 8 gave both plates and needles. Above the carbon number of 9, crystals obtained were all needles as shown in Figures 3 and 4. If alkyl chain becomes longer than *n*-icosyl (Cn=20), the thymine derivatives having long alkyl chain would give non-crystalline solid from acetonitrile solution. Two factors, the aggregation of the alkyl chain and the hydrogen bonding between thymines, therefor, may be important factors that determine the crystal form.

The forms of needles varied much less with the length of the alkyl chain. The forms of needles for 1-*n*-alkylthymines became clear from X-ray structure analysis. Those thymine derivatives had *n*-octyl (Cn=8), *n*-nonyl (Cn=9), and *n*-undecyl (Cn=11) groups. The crystal data of those thymine derivatives were shown in Table 1. These data showed all thymine derivatives had same space group. All *a* axes and *c* axes were quite similar. In addition, β angles were about 100° almost equal.

In Figure 16, the molecular packing structure of 1-*n*-octylthymine (Cn=8) was compared with that of 1-*n*-undecylthymine (Cn=11). The both crystals include acetonitrile in the cavity, and show similar orientation of thymines. Figure 17 compares the arrangement of the *ab* plane. The all crystals had the cumulated bilayered structure with the cavity where acetonitrile was included.

It was difficult to obtain single crystals of thymine derivatives having longer alkyl chain for X-ray structure analysis. The structures of thymine derivatives having longer alkyl chain (Cn=12, 13, and 16) were predicted from the X-ray powder diffraction data (Figure 18) and the crystal structures data for Cn=8, 9, 10, and 11.

According to X-ray structure analysis (Table 1), the needles of the thymine derivatives with different length of the alkyl chain had the same assembly fashion. In addition, the each space group was $P\bar{1}$. The same inclusion fashion of acetonitrile was found for 1-n-



1-n-Octylthymine [a]

1-*n*-Undecylthymine [b]

Figure 16

Molecular Packing Structures of Needles from Acetonitrile Solution.

[a] 1-*n*-Octylthymine

[b] 1-*n*-Undecylthymine

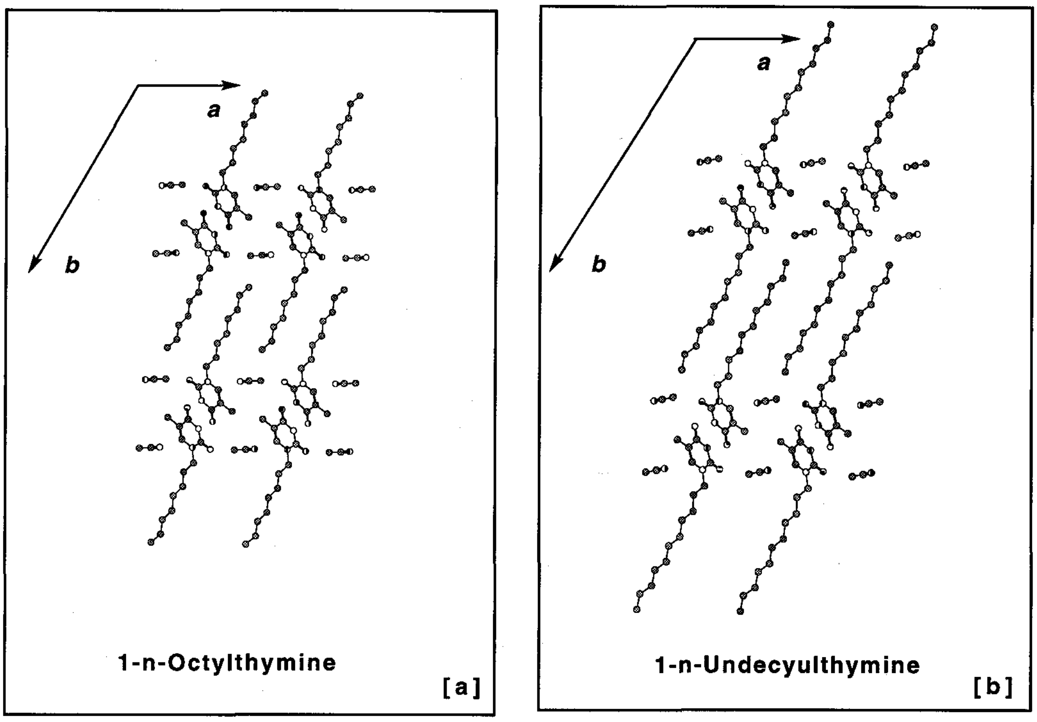


Figure 17

Molecular arrangement of *ab* Plane in Needles.

[a] 1-*n*-Octylthymine

[b] 1-*n*-Undecylthymine

alkylthymines. However, *b* axis expanded with the length of alkyl chain. The length of *b* axes observed were 18.80Å, 20.16Å, 21.30Å and 22.39Å for 1-*n*-octylthymine, 1-*n*-nonylthymine, 1-*n*-decylthymine and 1-*n*-undecylthymine (Cn=8, 9, 10, and 11). The length of *b* axis expands by about 1.2Å per a methylene unit. The length of *b* axes obtained by X-ray structure analysis and calculated values from X-ray powder diffraction (Figure 18) were plotted in Figure 19. All the data follows a straight line as shown in Figure 19. Moreover, the length of *a* and *c* axes obtained from X-ray powder diffraction had hardly changed for all thymine derivatives. The length of *a* axes were about 9.2 Å and *c* axes were about 5.0 Å (Table 1). It was seemed that the molecular arrangement for 1-*n*-hexadecylthymine was similar to 1-*n*-octylthymine or 1-*n*-undecylthymine, except for *b* axis which expanded to be about 28Å.

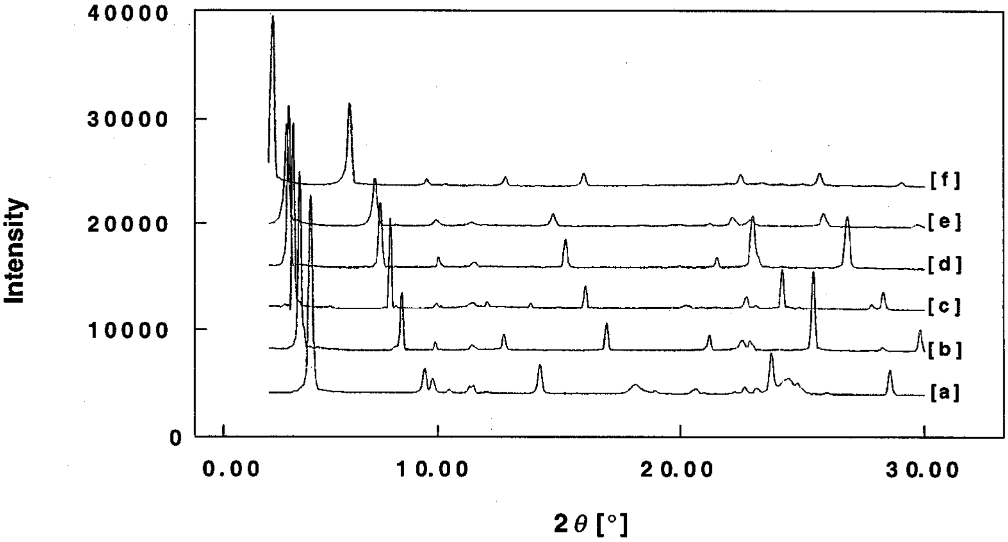


Figure 18

Powder X-ray Diffractions of 1-*n*-Alkylthymines in Needles.

[a] 1-*n*-octylthymine, [b] 1-*n*-decylthymine, [c] 1-*n*-undecylthymine

[d] 1-*n*-dodecylthymine, [e] 1-*n*-tridecylthymine, [f] 1-*n*-hexadecylthymine

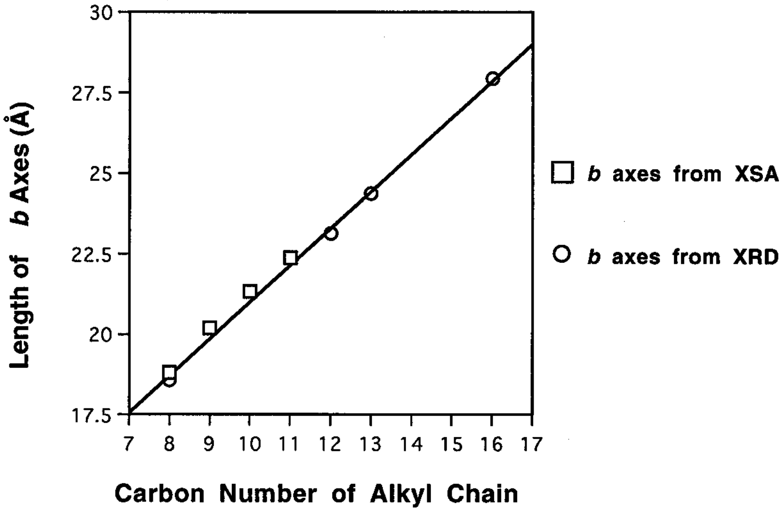


Figure 19

Relationship between Length of *b* Axes and Carbon Number of Alkyl Groups for Needles of 1-*n*-Alkylthymines.

square; Data from X-ray Structure Analysis (XSA).

circle; Data from Powder X-ray Diffraction (XRD).

Effect of the Alkyl Chain Length on the Release of Acetonitrile

The release points of acetonitrile from the crystals were obtained by differential thermal analysis (DTA) study (Figure 20). For all thymine derivatives having long alkyl chain, endothermic peaks were found around 65°C. The weight decreases were accompanied with these endothermic peaks. Acetonitrile was included in all needle crystals of 1-*n*-alkylthymine and released at around 65°C. Similar release points indicated that assembly fashions around acetonitrile were similar for all including crystals. A large endothermic peak at 123-124°C should be melting point. The thymine bases associated strongly with two hydrogen bonds at the hydrophilic layer as shown in Figure 5. It was implied that 1-*n*-dodecylthymine and 1-*n*-hexadecylthymine had the same hydrogen-bonding mode as 1-*n*-octylthymine. From the DTA data, properties of the needles were concluded to be identical for all 1-*n*-alkylthymines.

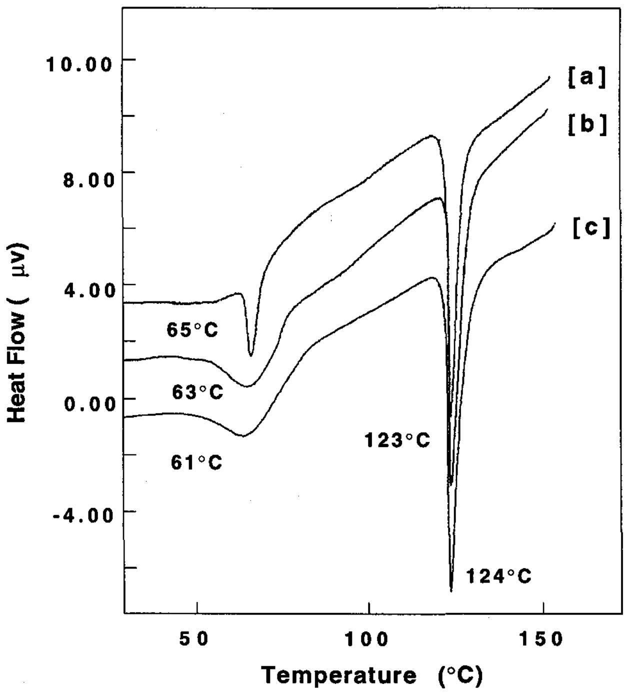


Figure 20

Differential Thermal Analysis for Needles of 1-*n*-Alkylthymines.

Scanning rate was 5K/ min.

[a] 1-*n*-Octylthymine, [b] 1-*n*-Dodecylthymine, [c] 1-*n*-Hexadecylthymine

Effect of the Alkyl Chain Length on the Isomer Ratio of Photodimers

Needles of 1-*n*-octylthymine gave both *trans-syn* and *trans-anti* photodimers. Needles of 1-*n*-hexadecylthymine, however, gave only the *trans-anti* photodimer (Figure 15). For the formation of the *trans-syn* photodimer from the needles, two thymines approach each other and cause rotation of thymines. Therefore, two molecules should shrink to give the photodimer accompanying moving of the alkyl chain in the crystal (illustration in Figure 21). The interaction of the long alkyl chain becomes strong with increase of length of chain, and the moving of such a chain becomes difficult. This is the reason for the decrease of the *trans-syn* photodimer when an alkyl chain becomes long.

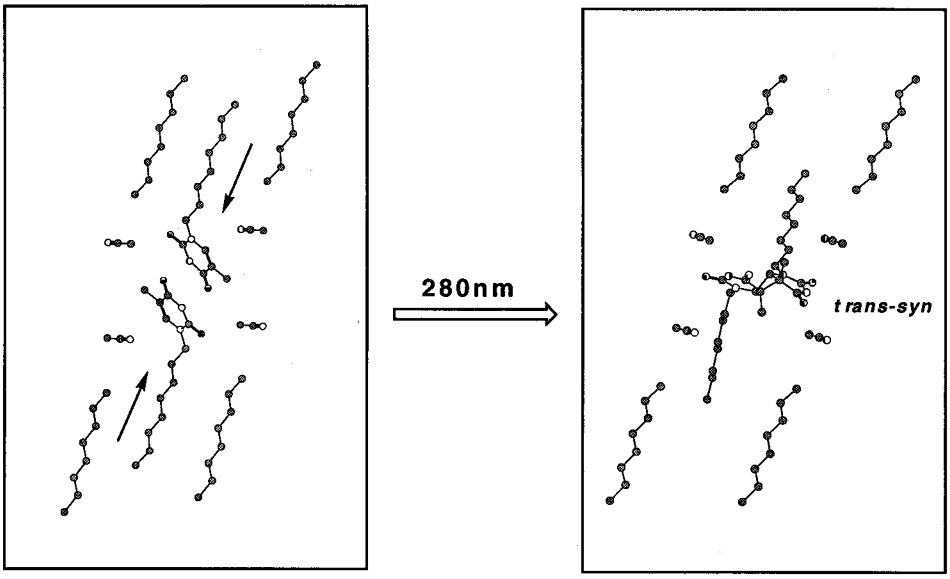


Figure 21

Illustration of Photodimerization for *cis-syn* Orientation in Needles giving *trans-syn* Photodimer.

4-4. CONCLUSION

Two kinds of single crystals were obtained when 1-*n*-alkylthymine derivatives were crystallized from acetonitrile solution. One single crystal was the needles including acetonitrile, the other one was the plates without acetonitrile. The plates were inactive for photodimerization by irradiation of UV light because the packing of the molecules was tight. On the other hand, the needles give photodimers, which contain two isomers for 1-*n*-octylthymine; *trans-anti* and *trans-syn* isomers. The crystal structure indicated that the thymines rotated disrotatory in the crystal during photodimerization reaction. For the formation of *trans-syn* photodimer, shrinking of molecule should be occurred during photodimerization. Formation of the *trans-syn* isomer decreased with increase of chain length of alkyl group, because the moving of the alkyl chain was inhibited by the strong interaction of the long alkyl chain.

4-5. CRYSTAL DATA

1-OCTYLTHYMINE FROM ACETONITRILE

Table 1A. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms.

atom	x	y	z	B(eq)
O(1)	0.6340(8)	0.3151(4)	0.760(1)	7.9(2)
O(1*)	0.3660(8)	0.6849(4)	0.240(1)	7.9(2)
O(1*)	0.3660(8)	0.6849(4)	1.240(1)	7.9(2)
O(2)	0.3521(6)	0.5267(3)	0.7520(9)	6.1(2)
O(2*)	0.6479(6)	0.4733(3)	0.2480(9)	6.1(2)
O(2*)	0.6479(6)	0.4733(3)	1.2480(9)	6.1(2)
N(1)	0.4495(10)	0.3335(4)	0.401(1)	6.0(2)
N(1*)	0.5505(10)	0.6665(4)	0.599(1)	6.0(2)
N(1*)	0.5505(10)	0.6665(4)	1.599(1)	6.0(2)
N(2)	0.489(1)	0.4195(5)	0.748(1)	5.9(2)
N(2*)	0.511(1)	0.5805(5)	0.252(1)	5.9(2)
N(2*)	0.511(1)	0.5805(5)	1.252(1)	5.9(2)
C(1)	0.531(1)	0.3539(6)	0.646(2)	5.9(3)
C(1*)	0.469(1)	0.6461(6)	0.354(2)	5.9(3)
C(1*)	0.469(1)	0.6461(6)	1.354(2)	5.9(3)
C(2)	0.375(1)	0.4687(6)	0.639(2)	5.4(3)
C(2*)	0.625(1)	0.5313(6)	0.361(2)	5.4(3)
C(2*)	0.625(1)	0.5313(6)	1.361(2)	5.4(3)
C(3)	0.296(1)	0.4412(6)	0.378(1)	5.8(3)
C(3*)	0.704(1)	0.5588(6)	0.622(1)	5.8(3)

C(3*)	0.704(1)	0.5588(6)	1.622(1)	5.8(3)
C(4)	0.335(1)	0.3774(7)	0.279(2)	6.1(3)
C(4*)	0.665(1)	0.6226(7)	0.721(2)	6.1(3)
C(4*)	0.665(1)	0.6226(7)	1.721(2)	6.1(3)
C(5)	0.170(1)	0.4905(7)	0.246(2)	7.8(4)
C(5*)	0.830(1)	0.5095(7)	0.754(2)	7.8(4)
C(5*)	0.830(1)	0.5095(7)	1.754(2)	7.8(4)
C(6)	0.481(1)	0.2590(5)	0.279(1)	7.1(3)
C(6*)	0.519(1)	0.7410(5)	0.721(1)	7.1(3)
C(6*)	0.519(1)	0.7410(5)	1.721(1)	7.1(3)
C(7)	0.381(1)	0.2084(5)	0.359(2)	8.2(3)
C(7*)	0.619(1)	0.7916(5)	0.641(2)	8.2(3)
C(7*)	0.619(1)	0.7916(5)	1.641(2)	8.2(3)

Table 2. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.094(6)	0.104(7)	0.092(4)	0.002(5)	-0.005(4)	0.013(4)
O(1*)	0.073(6)	0.084(7)	0.067(4)	0.001(5)	-0.003(4)	-0.001(4)
O(1*)	0.073(6)	0.084(7)	0.067(4)	0.001(5)	-0.003(4)	-0.001(4)
O(2)	0.073(4)	0.084(5)	0.067(3)	0.001(4)	-0.003(3)	-0.001(3)
O(2*)	0.073(4)	0.084(5)	0.067(3)	0.001(4)	-0.003(3)	-0.001(3)
O(2*)	0.073(4)	0.084(5)	0.067(3)	0.001(4)	-0.003(3)	-0.001(3)
N(1)	0.080(6)	0.084(7)	0.064(4)	-0.019(6)	0.009(4)	-0.004(4)
N(1*)	0.073(6)	0.084(7)	0.067(4)	0.001(6)	-0.003(4)	-0.001(4)
N(1*)	0.073(6)	0.084(7)	0.067(4)	0.001(6)	-0.003(4)	-0.001(4)
N(2)	0.077(7)	0.087(7)	0.058(4)	-0.019(6)	0.000(4)	-0.001(5)
N(2*)	0.073(7)	0.084(7)	0.067(4)	0.001(6)	-0.003(4)	-0.001(5)
N(2*)	0.073(7)	0.084(7)	0.067(4)	0.001(6)	-0.003(4)	-0.001(5)
C(1)	0.077(8)	0.087(10)	0.060(6)	-0.019(8)	0.003(6)	0.007(6)
C(1*)	0.073(8)	0.084(10)	0.067(6)	0.001(8)	-0.003(6)	-0.001(6)
C(1*)	0.073(8)	0.084(10)	0.067(6)	0.001(8)	-0.003(6)	-0.001(6)
C(2)	0.061(7)	0.094(9)	0.053(5)	-0.025(7)	0.009(5)	0.012(5)
C(2*)	0.073(7)	0.084(9)	0.067(5)	0.001(7)	-0.003(5)	-0.001(5)
C(2*)	0.073(7)	0.084(9)	0.067(5)	0.001(7)	-0.003(5)	-0.001(5)
C(3)	0.053(7)	0.114(10)	0.055(5)	-0.023(7)	-0.001(5)	0.021(5)
C(3*)	0.073(7)	0.084(10)	0.067(5)	0.001(7)	-0.003(5)	-0.001(5)
C(3*)	0.073(7)	0.084(10)	0.067(5)	0.001(7)	-0.003(5)	-0.001(5)
C(4)	0.076(9)	0.093(10)	0.064(6)	-0.030(8)	0.002(6)	0.000(6)

C(4*)	0.073(9)	0.084(10)	0.067(6)	0.001(8)	-0.003(6)	-0.001(6)
C(4*)	0.073(9)	0.084(10)	0.067(6)	0.001(8)	-0.003(6)	-0.001(6)
C(5)	0.080(9)	0.13(1)	0.079(7)	-0.014(8)	-0.003(6)	0.007(7)
C(5*)	0.073(9)	0.08(1)	0.067(7)	0.001(8)	-0.003(6)	-0.001(7)
C(5*)	0.073(9)	0.08(1)	0.067(7)	0.001(8)	-0.003(6)	-0.001(7)
C(6)	0.096(8)	0.085(8)	0.091(6)	-0.017(7)	0.023(5)	-0.004(5)
C(6*)	0.073(8)	0.084(8)	0.067(6)	0.001(7)	-0.003(5)	-0.001(5)
C(6*)	0.073(8)	0.084(8)	0.067(6)	0.001(7)	-0.003(5)	-0.001(5)
C(7)	0.117(9)	0.083(9)	0.116(7)	-0.025(8)	0.022(6)	-0.001(6)
C(7*)	0.073(9)	0.084(9)	0.067(7)	0.001(8)	-0.003(6)	-0.001(6)
C(7*)	0.073(9)	0.084(9)	0.067(7)	0.001(8)	-0.003(6)	-0.001(6)

1-NONYLTHYMINE FROM ACETONITRILE

Table 1A. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms.

atom	x	y	z	B(eq)
O(1)	0.6395(8)	0.8293(3)	0.776(1)	7.8(2)
O(2)	0.3515(5)	1.0241(2)	0.7502(9)	6.0(1)
N(1)	0.4513(8)	0.8450(3)	0.420(1)	6.1(2)
N(2)	0.4892(8)	0.9255(3)	0.758(1)	5.7(2)
N(3)	0.899(1)	0.1702(5)	0.264(2)	11.0(3)
C(1)	0.534(1)	0.8642(4)	0.657(1)	5.8(2)
C(2)	0.3773(9)	0.9693(5)	0.639(1)	5.5(2)
C(3)	0.2925(8)	0.9465(4)	0.391(1)	5.6(2)
C(4)	0.334(1)	0.8867(5)	0.292(2)	6.3(3)
C(5)	0.165(1)	0.9921(7)	0.248(2)	7.7(3)
C(6)	0.482(1)	0.7768(4)	0.303(2)	7.4(3)
C(7)	0.390(1)	0.7279(5)	0.402(2)	8.4(3)
C(8)	0.403(2)	0.6614(5)	0.260(2)	8.3(3)
C(9)	0.320(2)	0.6103(6)	0.360(3)	9.4(4)
C(10)	0.317(2)	0.5446(6)	0.215(2)	9.3(4)
C(11)	0.232(2)	0.4932(7)	0.307(3)	11.2(5)
C(12)	0.224(2)	0.4304(8)	0.164(3)	12.0(5)
C(13)	0.135(4)	0.384(1)	0.254(5)	17.5(9)
C(14)	0.107(4)	0.329(2)	0.118(8)	22(1)
C(15)	0.987(1)	0.1671(4)	0.442(2)	7.3(3)
C(16)	1.104(2)	0.1612(7)	0.672(3)	9.6(4)

Table 2A. Atomic coordinates and equivalent isotropic thermal parameters of hydrogen atoms.

atom	x	y	z	B(eq)
H(1)	0.540(8)	0.941(3)	0.89(1)	5(1)
H(2)	0.28(1)	0.861(5)	0.14(2)	13(2)
H(3)	0.09(1)	1.006(6)	0.34(3)	14(3)
H(4)	0.17(2)	1.022(8)	0.18(3)	16(5)
H(5)	0.09(2)	0.958(6)	0.09(3)	14(3)
H(6)	0.468(7)	0.780(3)	0.11(1)	5(1)
H(7)	0.60(1)	0.761(4)	0.34(2)	9(2)
H(8)	0.44(1)	0.713(5)	0.61(3)	15(2)
H(9)	0.29(1)	0.735(5)	0.40(2)	13(2)
H(10)	0.394(9)	0.664(4)	0.06(2)	10(2)
H(11)	0.52(1)	0.654(4)	0.29(2)	9(2)
H(12)	0.37(1)	0.590(5)	0.55(3)	12(3)
H(13)	0.23(1)	0.618(5)	0.37(2)	8(2)
H(14)	0.288(10)	0.556(4)	0.01(2)	10(2)
H(15)	0.42(1)	0.530(5)	0.22(2)	10(2)
H(16)	0.26(1)	0.486(4)	0.52(2)	11(2)
H(17)	0.15(1)	0.506(6)	0.33(3)	11(3)
H(18)	0.20(1)	0.442(4)	-0.03(2)	10(2)
H(19)	0.33(1)	0.410(5)	0.17(2)	13(3)
H(20)	0.15(1)	0.369(5)	0.47(2)	13(2)

H(21)	0.02(1)	0.391(7)	0.24(3)	11(3)
H(22)	0.05(1)	0.294(5)	0.19(2)	12(2)
H(23)	0.09(2)	0.351(7)	-0.08(3)	16(3)
H(24)	0.18(1)	0.310(7)	0.09(3)	9(2)
H(25)	1.07(1)	0.139(6)	0.82(2)	13(3)
H(26)	1.20(1)	0.151(5)	0.65(2)	14(3)
H(27)	1.09(1)	0.193(5)	0.77(2)	11(2)

Table 3A. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.109(5)	0.091(4)	0.088(4)	0.012(4)	0.000(3)	0.007(3)
O(2)	0.084(4)	0.077(4)	0.062(3)	0.007(3)	0.002(3)	0.002(3)
N(1)	0.080(5)	0.085(5)	0.071(4)	-0.015(4)	0.015(4)	-0.004(3)
N(2)	0.079(5)	0.085(5)	0.051(4)	-0.015(4)	0.005(3)	-0.004(3)
N(3)	0.142(9)	0.166(8)	0.103(6)	-0.037(7)	-0.004(6)	-0.015(5)
C(1)	0.085(7)	0.076(6)	0.061(5)	-0.027(5)	0.003(5)	0.003(4)
C(2)	0.062(6)	0.085(6)	0.061(5)	-0.010(5)	0.005(4)	0.014(5)
C(3)	0.060(6)	0.097(6)	0.057(4)	-0.018(5)	0.005(4)	0.003(4)
C(4)	0.081(7)	0.092(7)	0.074(5)	-0.032(6)	0.024(5)	-0.007(5)
C(5)	0.063(7)	0.14(1)	0.083(6)	0.004(7)	0.000(5)	-0.004(6)
C(6)	0.13(1)	0.077(6)	0.082(6)	-0.024(6)	0.040(6)	-0.023(5)
C(7)	0.122(10)	0.093(7)	0.117(7)	-0.028(7)	0.043(7)	-0.011(6)
C(8)	0.14(1)	0.088(7)	0.102(7)	-0.031(7)	0.041(6)	-0.023(5)
C(9)	0.14(1)	0.097(8)	0.128(9)	-0.030(9)	0.033(9)	-0.013(6)
C(10)	0.15(1)	0.098(8)	0.107(8)	-0.036(8)	0.024(8)	-0.018(6)
C(11)	0.20(2)	0.10(1)	0.13(1)	-0.06(1)	0.04(1)	-0.008(7)
C(12)	0.19(2)	0.12(1)	0.15(1)	-0.04(1)	0.01(1)	0.008(9)
C(13)	0.35(4)	0.12(1)	0.22(2)	-0.12(2)	0.07(2)	-0.03(1)
C(14)	0.29(5)	0.24(4)	0.31(4)	-0.04(4)	0.04(3)	0.10(3)
C(15)	0.091(7)	0.114(7)	0.075(5)	-0.032(6)	0.017(5)	-0.014(5)
C(16)	0.10(1)	0.14(1)	0.114(9)	0.002(9)	0.004(8)	-0.020(7)

1-DECYLTHYMINE FROM ACETONITRILE

Table 1. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms and hydrogen atoms

atom	x	y	z	B(eq)
O(1)	0.3457	0.1634	-0.2947	11.9395
O(2)	0.6224	-0.0490	-0.2727	15.2294
N(1)	0.5602	0.1209	0.0469	8.4076
N(2)	0.5050	0.0527	-0.3413	8.4577
H(2)	0.4552	0.0452	-0.4986	-94.7482
N(3)	0.8839	0.1429	0.7103	16.0854
C(1)	0.4795	0.1038	-0.1831	5.1918
C(2)	0.6338	0.0107	-0.2020	2.8908
C(3)	0.7013	0.0216	0.0727	11.2453
C(4)	0.6658	0.0900	0.1735	5.8054
H(4)	0.7226	0.1070	0.3249	-94.7482
C(5)	0.8388	-0.0063	0.1952	9.3709
H(5A)	0.8507	0.0054	0.3852	-118.4352
H(5B)	0.9157	0.0079	0.1178	-118.4352
H(5C)	0.8468	-0.0518	0.1688	-118.4352
C(6)	0.5075	0.1828	0.1382	2.7762
H(6A)	0.5242	0.1850	0.3343	-94.7482
H(6B)	0.4001	0.1920	0.0774	-94.7482
C(7)	0.5778	0.2308	0.0468	8.5490
H(7A)	0.6821	0.2132	0.0400	-94.7482
H(7B)	0.5299	0.2401	-0.1364	-94.7482

C(8)	0.5733	0.2898	0.2068	6.8568
H(8A)	0.4736	0.3142	0.1630	-94.7482
H(8B)	0.5868	0.2800	0.3954	-94.7482
C(9)	0.6790	0.3295	0.1799	11.2845
H(9A)	0.6935	0.3242	-0.0078	-94.7482
H(9B)	0.7732	0.3112	0.2853	-94.7482
C(10)	0.6617	0.3967	0.2465	8.8466
H(10A)	0.5942	0.4128	0.0876	-94.7482
H(10B)	0.5983	0.4002	0.3849	-94.7482
C(11)	0.7393	0.4496	0.3279	12.1039
H(11A)	0.8427	0.4283	0.3487	-94.7482
H(11B)	0.7191	0.4584	0.5116	-94.7482
C(12)	0.7575	0.5117	0.2625	8.0011
H(12A)	0.7550	0.5345	0.4371	-94.7482
H(12B)	0.6593	0.5257	0.1595	-94.7482
C(13)	0.8474	0.5479	0.1457	10.4387
H(13A)	0.9508	0.5265	0.1742	-94.7482
H(13B)	0.8132	0.5484	-0.0478	-94.7482
C(14)	0.8425	0.6116	0.2541	8.3594
H(14A)	0.8730	0.6057	0.4460	-94.7482
H(14B)	0.7353	0.6268	0.2333	-94.7482
C(15)	0.9009	0.6682	0.2216	13.8616
H(15A)	0.8663	0.7013	0.3480	-118.4352
H(15B)	0.8668	0.6817	0.0407	-118.4352
H(15C)	1.0086	0.6596	0.2542	-118.4352
C(16)	0.9695	0.1510	0.9097	13.1021
C(17)	1.0726	0.1729	1.1853	13.8852

Table 2. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.1614	0.1630	0.1264	-0.0387	-0.0194	0.0853
O(2)	0.1918	0.2418	0.1279	0.0633	0.0243	0.0705
N(1)	0.1243	0.1147	0.0736	-0.0061	0.0305	-0.0342
N(2)	0.0852	0.0941	0.1353	-0.0030	0.0034	0.0125
N(3)	0.0252	0.3032	0.1788	0.0085	0.0005	-0.0737
C(1)	0.0587	0.0700	0.0680	-0.0438	-0.0084	0.0061
C(2)	0.0043	0.0363	0.0518	0.0206	-0.0283	-0.0006
C(3)	0.1404	0.1364	0.1501	0.0192	-0.0159	0.0541
C(4)	0.0489	0.1046	0.0538	-0.0210	-0.0367	-0.0004
C(5)	0.0276	0.1341	0.1534	0.1124	-0.0052	0.0728
C(6)	0.0447	0.0026	0.0413	0.0020	0.0617	-0.0109
C(7)	0.1214	0.0979	0.1041	-0.0074	0.0089	-0.0358
C(8)	0.0719	0.0777	0.1069	-0.0254	-0.0294	0.0052
C(9)	0.1423	0.1116	0.1691	-0.0268	-0.0140	0.0157
C(10)	0.1178	0.0609	0.1417	-0.0133	0.0081	-0.0128
C(11)	0.1585	0.1494	0.1519	0.0166	0.0225	0.0092
C(12)	0.1061	0.0986	0.0992	0.0153	0.0389	0.0334
C(13)	0.1371	0.0886	0.1606	-0.0072	0.0264	-0.0080
C(14)	0.1190	0.0555	0.1280	-0.0107	0.0345	-0.0003
C(15)	0.2134	0.1210	0.1797	0.0498	0.1011	0.1116
C(16)	0.0859	0.2442	0.1249	-0.0521	0.0041	0.0391
C(17)	0.1743	0.1543	0.1964	-0.0862	0.0394	0.0572

1-UNDECYLTHYMINE FROM ACETONITRILE

Table 1A. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms.

atom	x	y	z	B(eq)
O(1)	0.6681(3)	0.3438(1)	0.7952(6)	6.85(7)
O(2)	0.3467(3)	0.5229(1)	0.7478(5)	5.47(6)
N(1)	0.4766(4)	0.3602(1)	0.4346(6)	5.40(7)
N(2)	0.5042(3)	0.4327(1)	0.7652(6)	4.80(7)
N(3)	0.1306(5)	0.3453(3)	0.765(1)	10.1(1)
C(1)	0.5584(4)	0.3763(2)	0.6731(7)	5.24(9)
C(2)	0.3809(4)	0.4735(2)	0.6429(6)	4.52(8)
C(3)	0.3013(4)	0.4531(2)	0.3966(7)	5.02(8)
C(4)	0.3527(4)	0.3981(2)	0.3057(7)	5.44(9)
C(5)	0.1653(5)	0.4936(3)	0.2495(10)	6.9(1)
C(6)	0.5169(6)	0.2985(2)	0.330(1)	6.4(1)
C(7)	0.4340(6)	0.2550(2)	0.4340(9)	6.6(1)
C(8)	0.4503(6)	0.1941(2)	0.291(1)	6.7(1)
C(9)	0.3683(6)	0.1499(2)	0.398(1)	6.9(1)
C(10)	0.3661(7)	0.0913(2)	0.241(1)	7.0(1)
C(11)	0.2816(7)	0.0483(2)	0.347(1)	7.3(1)
C(12)	0.2707(7)	-0.0090(2)	0.186(1)	7.1(1)
C(13)	0.1841(7)	-0.0507(2)	0.291(1)	7.7(1)
C(14)	0.1703(8)	-0.1076(3)	0.130(1)	8.3(2)
C(15)	0.080(1)	-0.1486(3)	0.236(2)	10.7(2)
C(16)	0.068(2)	-0.2049(4)	0.075(2)	12.7(3)
C(17)	0.0424(5)	0.3478(2)	0.5824(10)	6.5(1)

C(18)	-0.0740(9)	0.3512(4)	0.346(2)	8.9(2)

Table 2. Atomic coordinates and equivalent isotropic thermal parameters of hydrogen atoms.

atom	x	y	z	B(eq)
H(1)	0.562(5)	0.445(2)	0.93(1)	7(1)
H(2)	0.306(4)	0.376(2)	0.159(9)	6.2(9)
H(3)	0.182(5)	0.532(2)	0.222(9)	9(1)
H(4)	0.132(6)	0.471(2)	0.09(1)	11(1)
H(5)	0.092(5)	0.501(2)	0.36(1)	9(1)
H(6)	0.616(6)	0.287(2)	0.37(1)	8(1)
H(7)	0.487(5)	0.299(2)	0.13(1)	9(1)
H(8)	0.485(5)	0.238(2)	0.65(1)	13(1)
H(9)	0.324(6)	0.272(2)	0.424(10)	9(1)
H(11)	0.414(5)	0.201(2)	0.06(1)	9(1)
H(12)	0.418(4)	0.135(2)	0.607(9)	7.7(9)
H(13)	0.269(5)	0.170(2)	0.426(9)	6(1)
H(15)	0.311(6)	0.104(2)	0.05(1)	10(1)
H(16)	0.321(5)	0.035(2)	0.56(1)	11(1)
H(17)	0.182(5)	0.071(2)	0.359(10)	8(1)
H(18)	0.375(5)	-0.031(2)	0.164(9)	8(1)
H(19)	0.227(6)	0.010(2)	-0.02(1)	12(1)
H(20)	0.230(5)	-0.066(2)	0.50(1)	8(1)
H(21)	0.073(6)	-0.028(2)	0.27(1)	10(1)
H(22)	0.268(5)	-0.135(2)	0.134(10)	7(1)

H(23)	0.128(5)	-0.094(2)	-0.07(1)	12(1)
H(25)	0.462(6)	0.069(2)	0.24(1)	8(1)
H(26)	0.558(6)	0.175(2)	0.31(1)	12(1)
H(27)	0.11(1)	-0.180(5)	0.46(3)	21(3)
H(28)	-0.011(10)	-0.123(4)	0.23(2)	17(3)
H(29)	-0.02(1)	-0.226(4)	0.13(2)	21(2)
H(30)	0.024(6)	-0.188(3)	-0.14(1)	11(1)
H(31)	0.18(2)	-0.225(6)	0.16(3)	31(5)
H(32)	-0.15(1)	0.378(5)	0.39(2)	24(3)
H(33)	-0.07(1)	0.369(4)	0.24(2)	22(4)
H(34)	-0.070(9)	0.317(4)	0.29(2)	21(2)

Table 3. Anisotropic temperature factors of non-hydrogen atoms

atom	U11	U22	U33	U12	U13	U23
O(1)	0.098(2)	0.074(2)	0.080(2)	0.000(1)	0.005(2)	0.001(1)
O(2)	0.077(2)	0.072(2)	0.054(1)	-0.006(1)	0.005(1)	-0.007(1)
N(1)	0.084(2)	0.068(2)	0.059(2)	-0.025(2)	0.017(2)	-0.010(1)
N(2)	0.070(2)	0.065(2)	0.048(2)	-0.015(1)	0.008(1)	-0.002(1)
N(3)	0.106(3)	0.184(5)	0.094(3)	-0.036(3)	0.002(3)	-0.022(3)
C(1)	0.080(2)	0.068(2)	0.055(2)	-0.022(2)	0.015(2)	-0.002(2)
C(2)	0.060(2)	0.068(2)	0.047(2)	-0.019(2)	0.011(1)	0.005(2)
C(3)	0.058(2)	0.084(2)	0.053(2)	-0.025(2)	0.008(2)	0.000(2)
C(4)	0.079(2)	0.083(3)	0.053(2)	-0.037(2)	0.011(2)	-0.008(2)
C(5)	0.071(3)	0.117(4)	0.070(3)	-0.015(2)	-0.001(2)	-0.002(2)
C(6)	0.106(4)	0.074(3)	0.077(3)	-0.032(2)	0.033(3)	-0.021(2)
C(7)	0.110(4)	0.069(2)	0.086(3)	-0.030(2)	0.038(3)	-0.015(2)
C(8)	0.112(4)	0.073(3)	0.078(3)	-0.028(2)	0.031(3)	-0.018(2)
C(9)	0.115(4)	0.070(3)	0.090(3)	-0.028(2)	0.040(3)	-0.017(2)
C(10)	0.116(4)	0.070(3)	0.090(3)	-0.031(2)	0.030(3)	-0.015(2)
C(11)	0.117(4)	0.078(3)	0.089(3)	-0.028(3)	0.031(3)	-0.018(2)
C(12)	0.117(4)	0.075(3)	0.087(3)	-0.028(3)	0.030(3)	-0.014(2)
C(13)	0.127(4)	0.082(3)	0.096(3)	-0.042(3)	0.030(3)	-0.016(2)
C(14)	0.135(5)	0.081(3)	0.107(4)	-0.034(3)	0.028(4)	-0.013(3)
C(15)	0.195(8)	0.092(4)	0.135(6)	-0.060(5)	0.038(5)	-0.007(4)
C(16)	0.218(10)	0.097(5)	0.170(9)	-0.065(6)	-0.003(8)	0.000(5)
C(17)	0.085(3)	0.091(3)	0.079(3)	-0.023(2)	0.023(3)	-0.015(2)
C(18)	0.104(4)	0.131(6)	0.093(4)	-0.017(4)	-0.005(3)	-0.017(4)

1-OCTYLTHYMINE FROM DMF

Table 1A. Atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms and hydrogen atoms

atom	x	y	z	B(eq)
O(1)	-0.2444(5)	0.632(2)	0.7548(5)	5.0(2)
O(1*)	0.2444(5)	0.132(2)	1.2452(5)	5.0(2)
O(2)	-0.1162(4)	0.392(2)	1.0561(5)	4.8(1)
O(2*)	0.1162(4)	-0.108(2)	0.9439(5)	4.8(1)
O(3)	0.7454(5)	0.180(2)	1.2466(6)	5.3(2)
O(4)	0.6155(5)	0.414(2)	0.9464(4)	3.5(1)
N(1)	-0.0618(5)	0.634(1)	0.7969(6)	3.9(1)
N(1*)	0.0618(5)	0.134(1)	1.2031(6)	3.9(1)
N(2)	-0.1759(6)	0.511(1)	0.9034(6)	3.3(1)
N(2*)	0.1759(6)	0.011(1)	1.0966(6)	3.3(1)
N(3)	0.5609(5)	0.179(1)	1.1971(5)	2.9(1)
N(4)	0.6771(6)	0.297(2)	1.0976(6)	3.6(1)
C(1)	-0.1651(7)	0.597(1)	0.8147(6)	3.6(1)
C(1*)	0.1651(7)	0.097(1)	1.1853(6)	3.6(1)
C(2)	-0.0911(6)	0.466(1)	0.9782(6)	3.2(1)
C(2*)	0.0911(6)	-0.034(1)	1.0218(6)	3.2(1)
C(3)	0.0105(6)	0.515(2)	0.9589(6)	4.2(2)
C(3*)	-0.0105(6)	0.015(2)	1.0411(6)	4.2(2)
C(4)	0.0265(7)	0.586(2)	0.8769(7)	4.2(2)
C(4*)	-0.0265(7)	0.086(2)	1.1231(7)	4.2(2)

C(5)	0.1070(9)	0.476(2)	1.036(1)	5.4(3)
C(5*)	-0.1070(9)	-0.024(2)	0.964(1)	5.4(3)
C(6)	0.6683(6)	0.217(1)	1.1866(7)	3.6(1)
C(6*)	0.0361(5)	0.217(1)	1.2897(6)	3.2(1)
C(7)	0.5976(5)	0.341(1)	1.0220(6)	3.5(1)
C(7*)	-0.0105(7)	0.117(1)	1.3714(5)	3.8(2)
C(8)	0.4849(5)	0.296(1)	1.0404(6)	2.9(1)
C(9)	0.4796(5)	0.214(1)	1.1314(6)	2.6(1)
C(10)	0.3932(7)	0.342(2)	0.9621(9)	4.9(2)
C(11)	-0.0361(5)	0.717(1)	0.7103(6)	3.2(1)
C(12)	0.5421(9)	0.084(2)	1.2954(7)	5.0(2)
C(13)	0.0105(7)	0.617(1)	0.6286(5)	3.8(2)
C(14)	0.4897(8)	0.180(1)	1.3728(8)	4.5(2)

Table 2. Anisotropic temperature factors of non-hydrogen atoms.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.043(3)	0.106(5)	0.043(3)	-0.001(3)	0.010(2)	0.021(4)
O(1*)	0.041(3)	0.076(5)	0.082(3)	-0.010(3)	0.002(2)	-0.024(4)
O(2)	0.033(3)	0.071(4)	0.084(4)	0.003(2)	0.029(3)	0.030(3)
O(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(2)	0.002(3)	-0.024(3)
O(3)	0.041(3)	0.076(5)	0.082(5)	0.010(3)	0.002(3)	0.024(4)
O(4)	0.049(3)	0.056(4)	0.028(2)	-0.004(2)	0.001(2)	0.001(2)
N(1)	0.041(3)	0.041(4)	0.063(4)	-0.007(3)	0.002(2)	-0.006(3)
N(1*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(3)
N(2)	0.031(3)	0.046(4)	0.049(4)	-0.012(3)	0.014(2)	0.005(3)
N(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(3)
N(3)	0.036(2)	0.050(4)	0.029(3)	0.004(2)	0.024(2)	0.011(2)
N(4)	0.034(3)	0.058(4)	0.047(4)	0.010(3)	0.010(2)	0.005(3)
C(1)	0.045(3)	0.049(5)	0.042(3)	-0.006(3)	0.006(2)	-0.006(3)
C(1*)	0.041(3)	0.076(5)	0.082(3)	-0.010(3)	0.002(2)	-0.024(3)
C(2)	0.047(3)	0.027(4)	0.046(4)	0.006(3)	0.003(2)	-0.017(2)
C(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(2)
C(3)	0.041(3)	0.081(6)	0.036(3)	0.010(3)	0.001(3)	-0.022(3)
C(3*)	0.041(3)	0.076(6)	0.082(3)	-0.010(3)	0.002(3)	-0.024(3)
C(4)	0.033(4)	0.067(6)	0.061(4)	0.011(3)	0.007(3)	-0.009(4)
C(4*)	0.041(4)	0.076(6)	0.082(4)	-0.010(3)	0.002(3)	-0.024(4)
C(5)	0.045(5)	0.094(9)	0.065(7)	0.010(6)	-0.005(4)	0.019(6)
C(5*)	0.041(5)	0.076(9)	0.082(7)	-0.010(6)	0.002(4)	-0.024(6)

C(6)	0.035(2)	0.041(4)	0.065(4)	0.007(3)	0.023(2)	0.017(4)
C(6*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(3)	-0.024(2)
C(7)	0.024(2)	0.063(5)	0.048(4)	0.000(3)	0.019(2)	0.016(3)
C(7*)	0.041(4)	0.076(5)	0.082(3)	-0.010(4)	0.002(3)	-0.024(3)
C(8)	0.026(2)	0.024(3)	0.063(4)	-0.011(2)	0.019(3)	0.011(3)
C(9)	0.028(3)	0.027(3)	0.044(3)	-0.013(2)	0.017(2)	-0.002(3)
C(10)	0.024(3)	0.105(9)	0.057(6)	-0.013(4)	0.011(3)	0.009(5)
C(11)	0.030(3)	0.029(4)	0.061(4)	0.001(3)	0.007(3)	-0.007(2)
C(12)	0.082(6)	0.077(6)	0.039(4)	-0.001(5)	0.035(4)	0.033(4)
C(13)	0.055(4)	0.072(5)	0.018(3)	-0.018(4)	0.012(3)	-0.021(3)
C(14)	0.059(5)	0.029(4)	0.084(6)	-0.001(3)	0.016(4)	0.026(3)
O(1)	0.043(3)	0.106(5)	0.043(3)	-0.001(3)	0.010(2)	0.021(4)
O(1*)	0.041(3)	0.076(5)	0.082(3)	-0.010(3)	0.002(2)	-0.024(4)
O(2)	0.033(3)	0.071(4)	0.084(4)	0.003(2)	0.029(3)	0.030(3)
O(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(2)	0.002(3)	-0.024(3)
O(3)	0.041(3)	0.076(5)	0.082(5)	0.010(3)	0.002(3)	0.024(4)
O(4)	0.049(3)	0.056(4)	0.028(2)	-0.004(2)	0.001(2)	0.001(2)
N(1)	0.041(3)	0.041(4)	0.063(4)	-0.007(3)	0.002(2)	-0.006(3)
N(1*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(3)
N(2)	0.031(3)	0.046(4)	0.049(4)	-0.012(3)	0.014(2)	0.005(3)
N(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(3)
N(3)	0.036(2)	0.050(4)	0.029(3)	0.004(2)	0.024(2)	0.011(2)
N(4)	0.034(3)	0.058(4)	0.047(4)	0.010(3)	0.010(2)	0.005(3)
C(1)	0.045(3)	0.049(5)	0.042(3)	-0.006(3)	0.006(2)	-0.006(3)
C(1*)	0.041(3)	0.076(5)	0.082(3)	-0.010(3)	0.002(2)	-0.024(3)
C(2)	0.047(3)	0.027(4)	0.046(4)	0.006(3)	0.003(2)	-0.017(2)

C(2*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(2)	-0.024(2)
C(3)	0.041(3)	0.081(6)	0.036(3)	0.010(3)	0.001(3)	-0.022(3)
C(3*)	0.041(3)	0.076(6)	0.082(3)	-0.010(3)	0.002(3)	-0.024(3)
C(4)	0.033(4)	0.067(6)	0.061(4)	0.011(3)	0.007(3)	-0.009(4)
C(4*)	0.041(4)	0.076(6)	0.082(4)	-0.010(3)	0.002(3)	-0.024(4)
C(5)	0.045(5)	0.094(9)	0.065(7)	0.010(6)	-0.005(4)	0.019(6)
C(5*)	0.041(5)	0.076(9)	0.082(7)	-0.010(6)	0.002(4)	-0.024(6)
C(6)	0.035(2)	0.041(4)	0.065(4)	0.007(3)	0.023(2)	0.017(4)
C(6*)	0.041(3)	0.076(4)	0.082(4)	-0.010(3)	0.002(3)	-0.024(2)
C(7)	0.024(2)	0.063(5)	0.048(4)	0.000(3)	0.019(2)	0.016(3)
C(7*)	0.041(4)	0.076(5)	0.082(3)	-0.010(4)	0.002(3)	-0.024(3)
C(8)	0.026(2)	0.024(3)	0.063(4)	-0.011(2)	0.019(3)	0.011(3)
C(9)	0.028(3)	0.027(3)	0.044(3)	-0.013(2)	0.017(2)	-0.002(3)
C(10)	0.024(3)	0.105(9)	0.057(6)	-0.013(4)	0.011(3)	0.009(5)
C(11)	0.030(3)	0.029(4)	0.061(4)	0.001(3)	0.007(3)	-0.007(2)
C(12)	0.082(6)	0.077(6)	0.039(4)	-0.001(5)	0.035(4)	0.033(4)
C(13)	0.055(4)	0.072(5)	0.018(3)	-0.018(4)	0.012(3)	-0.021(3)
C(14)	0.059(5)	0.029(4)	0.084(6)	-0.001(3)	0.016(4)	0.026(3)

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CONCLUSION

This thesis deals with the studies of photodimerization for thymine compounds in solid states.

In Chapter 1, the author showed the photodimerizations in spin-coat film and in the annealed film . Reversible photodimerizations of thymine compounds having long alkyl chain were fast in spin-coat thin film where thymine bases aggregated feasibly for photodimerization. Annealing of the film caused an acceleration of the reaction because of crystallization of the thymine compound to Structure I that was just appropriate for photodimerization. Prolonged annealing, however, caused a deceleration of the photodimerization because the Structure I deformed to Structure II that is inactive for photodimerization. The highest reactivity of the photodimerization was observed for the thymine compounds having moderate chain length of alkyl group (tridecyl [Cn=13] for the ester compounds, and decyl [Cn=10] for 1-n-alkylthymines). In these compounds, the competitions between hydrogen bonding and hydrophobic interactions made the crystal unstable. Therefore, the thymines can rotate in these crystals during photodimerization.

The steric hindrance of the methyl group at 5-position is the main reason for the photo splitting of the thymine photodimer by irradiation at 240 nm. The reverse photodimerization did not occur for the photodimer of uracil that has no methyl group. The strain should be generated during the photodimerization of the thymine compound in crystal because the photodimerization accompany the rotation of the thymine bases. The reverse photodimerization in crystal, consequently, was a fast reaction releasing the strain in the crystal.

In Chapter 2, the author revealed the plate crystal of 1-octylthymine recrystallized from ethyl acetate had a very high photoreactivity and gave only one isomer of photodimer. The crystal structure suggested the formation of the *trans-syn* photodimer. The photodimer obtained, however, was identified to be the *trans-anti* isomer from the NMR spectrum. The *trans-anti* photodimer was concluded to be formed by disrotatory motion of the thymine in the crystal. The mechanism of the intermolecular photodimerization of thymines in crystal was found to be the same as the intramolecular photocycloaddition of dienes because the thymine derivative was fixed with the alkyl group in the crystal.

In Chapter 3, the author clarified reactivity for the photodimerization of 1-octylthymine in the crystal derived from ethanol solution. The spin-coated thin film showed very high photoreactivity. But, that, however, was disappeared by annealing at 100-110°C. The crystal structure of the thin film before annealing corresponded to the photoreactive crystal obtained from ethyl acetate. The crystal structure of the thin film after annealing corresponded to the inactive crystal recrystallized from ethanol. The powder X-ray diffraction and the differential thermal analysis indicated that the annealing of the thin film caused the structure transformation with keeping the plane structure by the hydrogen bonding. In the annealed films or the crystal from ethanol, thymine compounds could not rotate to give photodimers when UV light was irradiated.

In Chapter 4, the author clarified the photoreactivity of 1-alkylthymines in the crystals obtained from acetonitrile solution. Two kinds of single crystals were obtained when 1-alkylthymine derivatives were crystallized from acetonitrile solution. One single crystal was the needles including acetonitrile, the other one was the plates without acetonitrile. The plates were inactive for photodimerization by irradiation of UV light because the packing of the molecules was tight. On the other hand, the needles give photodimers, which contain two isomers for 1-octylthymine; *trans-anti* and *trans-syn* isomers. The crystal structure indicated that the thymines rotated disrotatory in the crystal during photodimerization reaction. For the formation of *trans-syn* photodimer, shrinking of molecule should be occurred during photodimerization. Formation of the *trans-syn* isomer decreased with increase of chain length of alkyl group, because the moving of the alkyl chain was inhibited by the strong interaction of the long alkyl chain.

LIST OF PUBLICATIONS

1. Photodimerization and Crystal Structure of Long Alkyl Thymine Derivatives
   N. Tohnai, T. Sugiki, E. Mochizuki, T. Wada, Y. Inaki
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   Bull. Chem. Soc. Jpn. in press. (Full Paper)
5. Photodimerization of 1-*n*-Alkylthymine Crystallized from Acetonitrile Solution
   N. Tohnai, Y. Inaki, M. Miyata, N. Yasui, E. Mochizuki, Y. Kai
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   in preparation. (Full Paper)
7. Photodimerization of 3-*n*-Alkylthymines in Several States; Active and Inactive States
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   39, **1998** 97-98

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