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# Photodimerization of 1-Alkylthymines Crystallized from Acetonitrile Solution

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Crystallization of 1-octylthymine from acetonitrile solution gave needles and plates. The needles gave the photodimer by irradiation of UV light, but the plates did not give the photodimer. Crystal structures of needles and plates were determined by X-ray analysis. There were two pairs of thymine, which gave the photodimers in the needles of 1-octylthymine. The isomer ratio of the photodimers indicated that thymine rotated disrotatory during the photodimerization reaction to give *trans-anti*, *cis-anti*, and *trans-syn* isomers. The crystal structure of the plates from acetonitrile solution was identical to the structure of plates obtained from ethanol solution, which was inactive for the photodimerization as reported in the previous paper. When the alkyl group became long, the formation of *trans-syn* photodimer decreased because strong interaction with the alkyl group inhibited moving of molecules. The photodimerization of 1-alkylthymine was concluded to occur when the rotation of the thymine is possible in the crystal.

Thymine, one of the nucleic acid bases, converts to photodimers upon irradiation with UV light near 280 nm (Fig. 1). Four isomers of the photodimer can be obtained by photodimerization in solution. 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 to the photorecording system by controlling the wavelength of irradiating UV light.[6,7]

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 determine the mechanism of photodimerization of thymines in solid state, the photodimerization reactions were studied for single crystals. The single crystal of 1-octylthymine from ethyl acetate solution 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-octylthymine in single crystal suggested that the thymine base rotated in the single crystal during photodimerization (Fig. 2).

Crystallization of 1-octylthymine from acetonitrile solution gave two kinds of crystals, needles and plates. The needles were found to give photodimers by irradiation of ultraviolet light at around 280 nm, but the plates could not give the photodimer. This paper deals with the crystal structure of a series of 1-alkylthymine crystals obtained from acetonitrile solution, with photodimerization of these crystals, and with effects of length of alkyl group on the photodimerization.

## Experimental

**Preparations of 1-Alkylthymines.** The alkylthymine derivatives were prepared according to a method reported in the literature.[12] Thymine was reacted with hexamethyldisilazane to give 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine. A mixture of 1-octyl bromide and 5-methyl-2, 4-bis(trimethylsiloxy)-pyrimidine was stirred for 10 d at 60 °C to afford 1-octylthymine. The other 1-alkylthymines, 1-decylthymine, 1-undecylthymine, 1-dodecylthymine, 1-tridecylthymine, and 1-hexadecylthymine were prepared by the same method as that of 1-octylthymine.

**Instruments.** Photodimerizations in single crystal were carried out by SUPER CURE-203S UV Light Source San-Ei Electric, where the light source was a Hg–Xe lamp (200 W) with a cut filter (Toshiba U340). $^1$H 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-octylthymine 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-nonylthymine, 1-decylthymine and 1-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, 1146, 1208, and 2150 were measured up to $2\theta$ of 51.7°, 59.7, 60.4 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, LODEM,

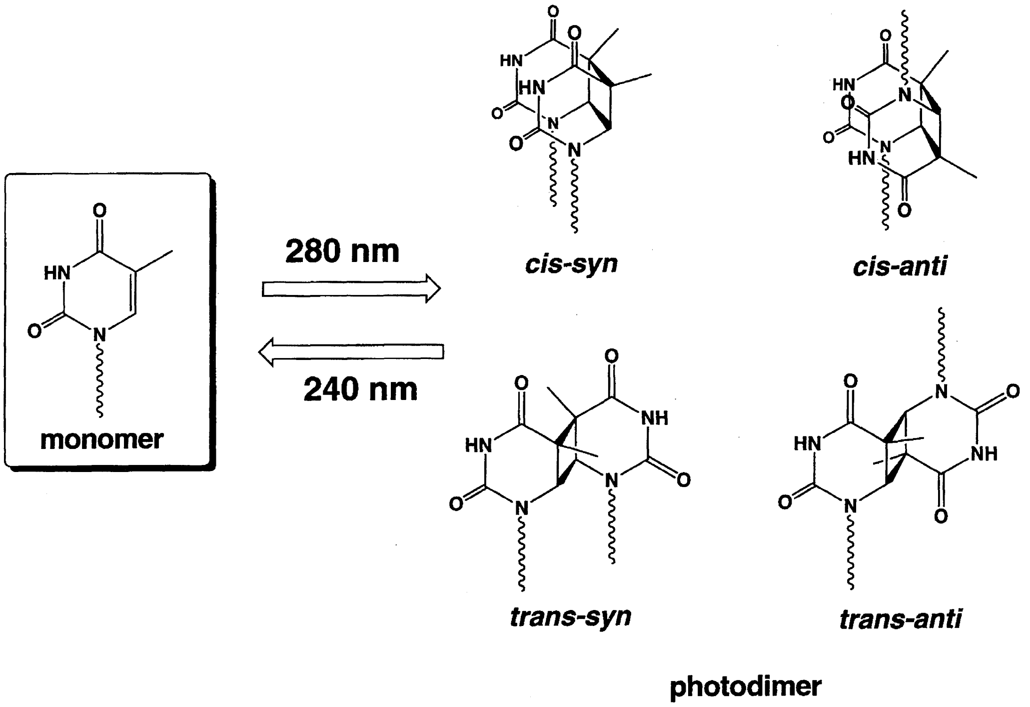


Fig. 1. Reversible photodimerization of thymine derivatives and four stereo isomers of 1-alkylthymine photodimer.

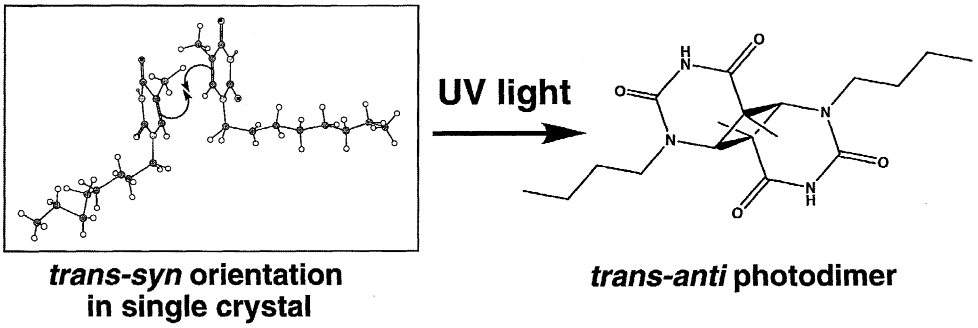


Fig. 2. Photodimerization of 1-octylthymine in crystal from ethyl acetate solution.[12]

SHELXS-97 and SHELXS-97), and refined by the full-matrix least squares. All non-hydrogen atoms were refined anisotropically. 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.

## Results and Discussion

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

The crystal structure of the needles was greatly different from those of the crystals obtained from ethyl acetate[12] and ethanol solutions.[13] Figure 3 shows a molecular packing structure of 1-octylthymine in needles for *ab* plane (**a**) and for *bc* plane (**b**). 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. The crystal had the cumulated bilayer structure with the cavity where acetonitrile was included (Fig. 3b). Thymine bases stacked along the $c$ axis but did not completely overlap. Hydrogen bondings were formed between thymines in the hydrophilic layer between N$^3$–H and C$^4$–O with the same bond length (2.848 Å N$^3$–O$^4$). The lamella structure in Fig. 3b consisted of the hydrophilic and hydrophobic layers. The hydrophilic layer was composed of thymine bases and acetonitrile, and the hydrophobic layer was composed of the long alkyl chains. Two layers were conjugated by hydrogen bonding and they contributed to the stability of the hydrophilic layer.

The plates of 1-ocytlthymine obtained by slow evaporation of acetonitrile gave the same crystal structure as the plates from ethanol solution reported in a previous paper.[13]

**Thermal Analysis of the Crystals.** Inclusion of acetonitrile in the needles of 1-octylthymine was supported by differential thermal analysis (DTA) and thermogravimetry (TGA) (Fig. 4). The DTA of the needles in Fig. 4 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

Table 1. Data of X-Ray Structure Analysis for 1-Alkylthymines Having Different Length of Alkyl Group in Needles from Acetonitrile Solution

| Compounds | 1-Octylthymine | 1-Nonylthymine | 1-Decylthymine | 1-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 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Lattice parameter | | | | |
| $a/\text{Å}$ | 9.200(5) | 9.31(5) | 9.151(7) | 9.265(6) |
| $b/\text{Å}$ | 18.80(1) | 20.26(2) | 21.30(2) | 22.39(2) |
| $c/\text{Å}$ | 5.027(1) | 5.003(6) | 5.026(2) | 4.981(8) |
| $\alpha/°$ | 94.33(5) | 92.2(3) | 94.62(5) | 90.61(8) |
| $\beta/°$ | 99.94(4) | 100.1(3) | 99.81(4) | 99.78(7) |
| $\gamma/°$ | 84.52(3) | 84.2(8) | 80.28(6) | 79.88(6) |
| $V/\text{Å}^3$ | 851.0(7) | 920(8) | 950(1) | 1002(1) |
| $Z$ value | 2 | 2 | 2 | 2 |
| Unique reflections | 1807 | 1146 | 1208 | 2150 |
| $R$, $R_w$ | 0.073, 0.068 | 0.090, 0.103 | — | 0.075, 0.116 |
| $D_{\text{calcd}}/\text{g cm}^{-3}$ | 1.090 | 1.059 | 1.074 | 1.065 |
| $F_{000}$ | 304.00 | 320.00 | 336.00 | 352.00 |
| $\mu(\text{Mo}\,K\alpha)/\text{cm}^{-1}$ | 0.73 | 0.71 | 0.71 | 0.70 |

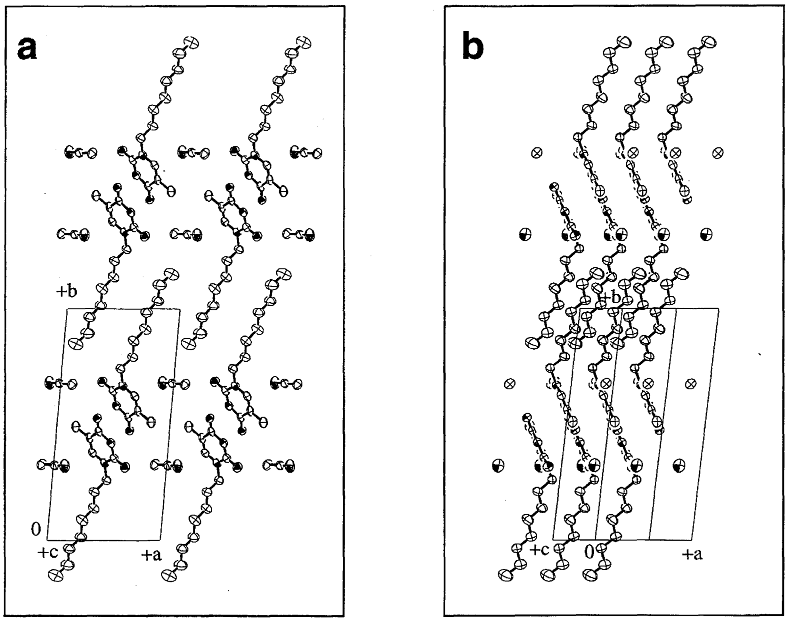


Fig. 3. Molecular arrangement of 1-octylthymine in needles from acetonitrile solution. [**a**] *ab* Plane and [**b**] *bc* Plane.

crystal at this temperature. The melting point was 123 °C, where the hydrogen bonds between thymines broke down.[13]

The X-ray powder diffraction was measured to establish the crystal structure before and after release of acetonitrile at 65 °C. The data in Fig. 5 suggest that the needles containing acetonitrile (**a**) gave a new crystal (**b**) by release of acetonitrile at 100 °C. The value of $2\theta$ (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°). Therefore, the crystal structure of the annealed crystal (**b**) was concluded to be different from both the structure of plates from ethyl acetate solution[12] and the structure of plates from ethanol solution.[13]

**Photodimerization of 1-Octylthymine.** Irradiation of UV light around 280 nm on the needles obtained from the acetonitrile solution gave the photodimer. The plates, however, didn't show photochemical reactivity as in the case of the plates obtained from the ethanol solution.[13] Conversion to photodimer from thymines in needles was 60—80% by irradiation for 12 h. The rate of photodimerization of the thymines in needles was much slower than that of the thymine in plates obtained from ethyl acetate solution. In the case of plates from ethyl acetate, conversion to photodimer was almost 100% by irradiation for 2 h.[12]

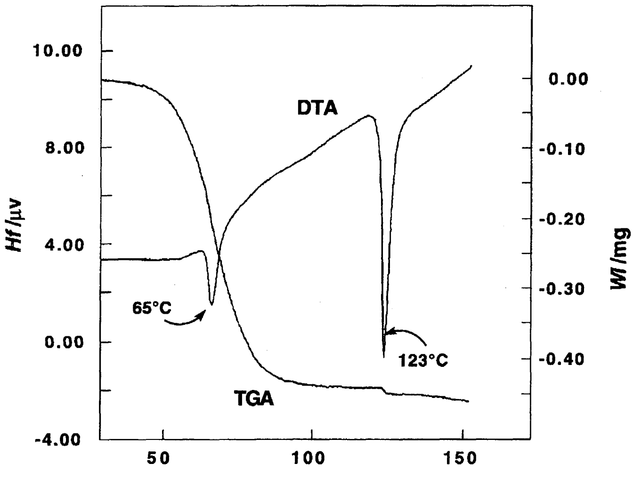


Fig. 4. DTA and TGA of 1-octylthymine in needles. (Scanning rate was 5 K min$^{-1}$. Heat flow ($H_f$) and weight loss ($W_l$) vs. temperature.

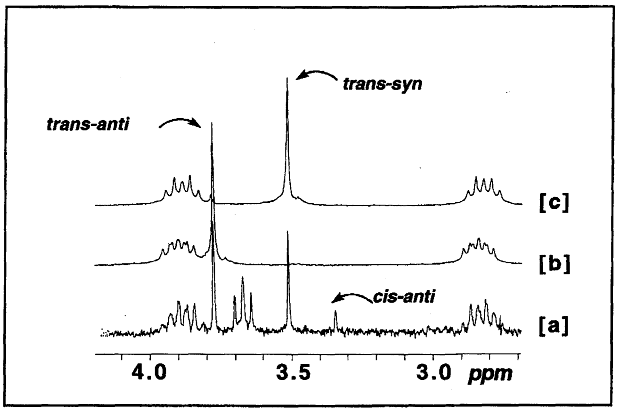


Fig. 6. $^1$H NMR spectra of photodimers in $CDCl_3$. [a] Mixture of Photodimerization products of 1-octylthymine in needles including unreacted compound (*t*, 3.69 ppm), [b] Isolated *trans-anti* isomer,[12] and [c] Isolated *trans-syn* isomer.[12]

Photodimerization of the 1-alkylthymines in solution with acetone as a sensitizer gave four kinds of isomers (Fig. 1).[14—17] The crystal from ethyl acetate, however, gave only *trans-anti* isomer by irradiation of UV light.[12] Irradiation of UV light on the needles from acetonitrile also gave photodimers that were identified by NMR spectra. Figure 6[**a**] is the NMR spectrum of the reaction mixture containing starting material ($\delta$ = 3.69 (t, N–$CH_2$–)). The NMR spectrum in Fig. 6[**a**] suggests the formation of three kinds of photodimers by photodimerization of the needle of 1-octylthymine ([**a**]). The three isomers were identified from the chemical shifts of 6-H as *trans-anti* ($\delta$ = 3.78 (s, 6-H)) and *trans-syn* ($\delta$ = 3.52 (s, 6-H)) isomers with small amounts of *cis-anti* ($\delta$ = 3.34 (s, 6-H)) isomer. The NMR spectra of the isolated photodimers[12] of *trans-anti* [**b**] and *trans-syn* [**c**] are also shown in Fig. 6.

**Mechanism of Photodimerization.** Mechanisms of the formation of three kinds of photodimers were estimated from the crystal structure of the needles. In the plates from ethyl acetate, the pair of thymine which forms the photodimer exists in *trans-syn* orientation, but gave *trans-anti* photodimer by rotation of the thymines during photodimerization reaction (Fig. 2).[12] On the other hand, there are two orientations of the thymine pairs that form a photodimer in the needles from acetonitrile solution (Fig. 7a).

One is the *trans-anti* orientation. As shown in Fig. 8, thymines in *trans-anti* orientation rotate for the reaction between $C^5$ and $C^{5'}$, and rotate again for the formation of a photodimer, giving *trans-syn* isomer. The disrotatory motion of thymines is illustrated in detail (Fig. 9). This illustration is based on the assumption that the photodimerization takes place only through a biradial intermediate. Rotation of thymines in *trans-anti* orientation gives *cis-anti* intermediate by reaction between $C^5$ and $C^{5'}$. Then the intermediate gives *trans-syn* photodimer by reaction between $C^6$ and $C^{6'}$ with internal rotation. Both inside and outside rotations give the same photodimer of *trans-syn* isomer.

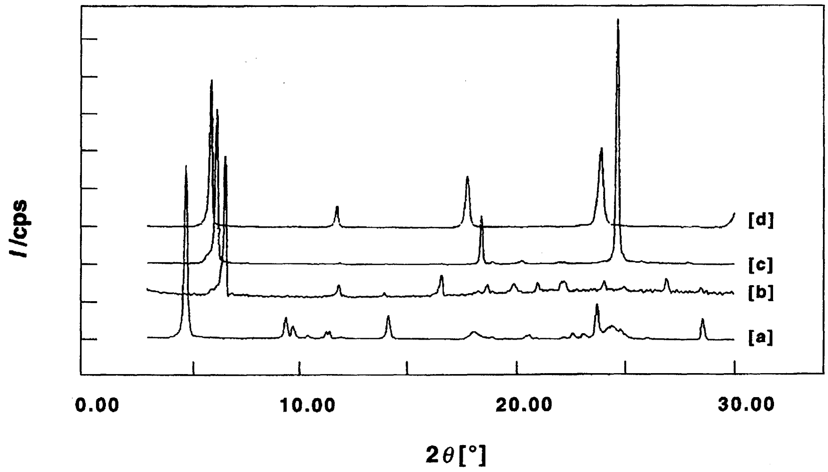
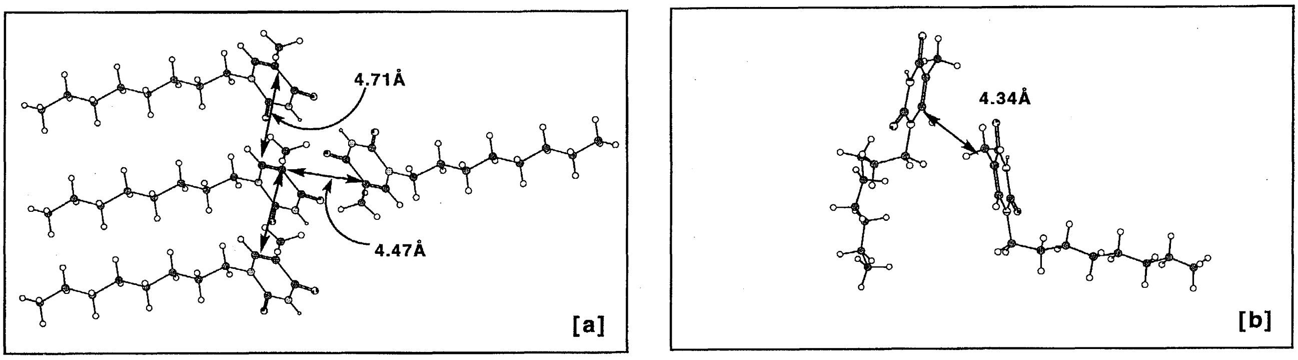


Fig. 5. Powder X-ray diffraction patterns of 1-octylthymine. [a] Needles from acetonitrile solution, [b] Annealing of the needles at 100 °C (after releasing of acetonitrile), [c] Plates from acetonitrile solution, and [d] Plates from ethyl acetate solution. (Intensity ($I$) vs. $2\theta$).



**Acetonitrile (Needle)**

**Acetonitrile (Plate)**

Fig. 7. Orientation of thymines in crystals from acetonitrile solution. [a] Needles from acetonitrile solution and [b] Plates from acetonitrile solution.

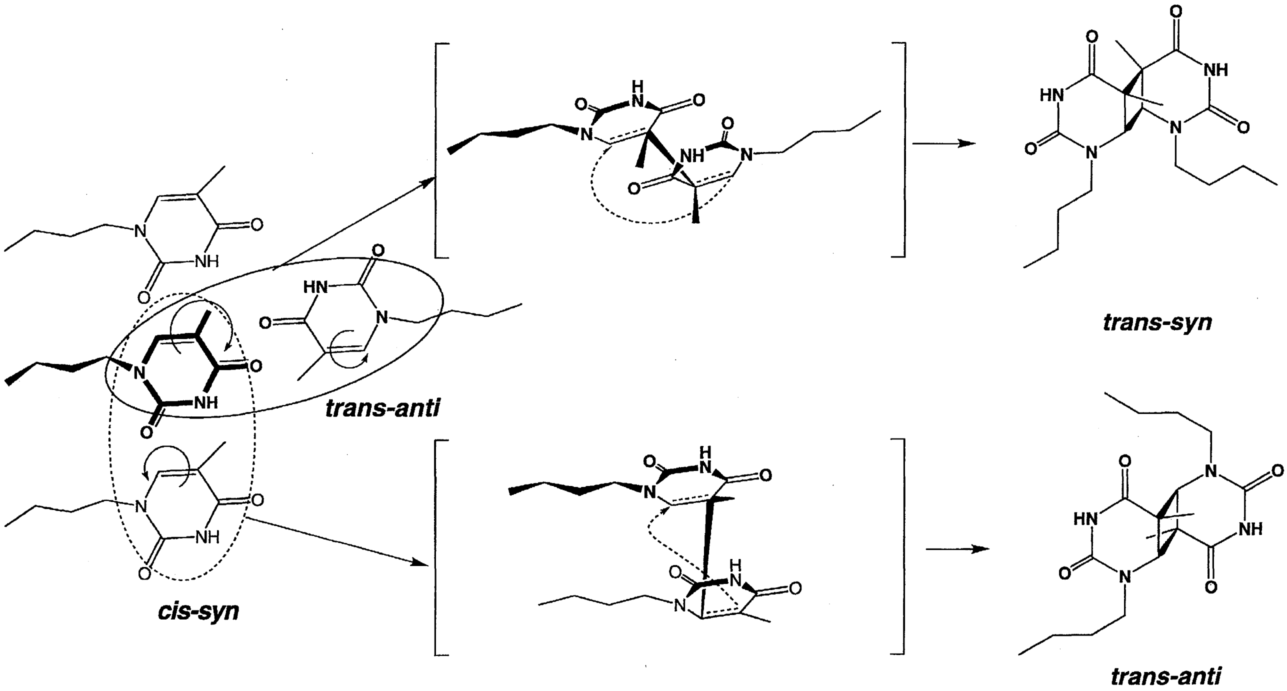


Fig. 8. Mechanisms of photodimerization for 1-octylthymine in needles. [a] Orientation of *trans-anti* giving *trans-syn* photodimer and [b] Orientation of *cis-syn* giving *trans-anti* photodimer.

The other orientation of thymine is *cis-syn*, and gives the *trans-anti* photodimer by rotation of thymines during the photodimerization reaction (Fig. 8). As illustrated in Fig. 10, the thymines in *cis-syn* orientation rotate outside to give *cis-syn* orientation of the intermediate by reaction between $C^6$ and $C^{5'}$. Then the intermediate gives the *trans-anti* photodimer by reaction between $C^5$ and $C^{6'}$ with internal rotation. When the thymines rotate inside, the *cis-anti* photodimer should be obtained through the *trans-syn* intermediate. 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 Fig. 6. In both pairs, *trans-anti* and *cis-syn* orientations, the thymines gave the photodimers by disrotatory motion in the crystals during the photodimerization reaction. If conrotatory motion occurred during the photodimerization, other isomers could be obtained.

The plates obtained from acetonitrile solution gave no photodimer under the same conditions as used for the needles. Figure 7 shows the distance between the nearest carbon atoms of thymines in crystal for needles [**a**] and the plates [**b**]. The distance between the nearest carbon ($C^6$ and $C^{5'}$) for the plates (4.34 Å Fig. 7b) was shorter than the distance for the needles (4.47 Å between $C^6$ and $C^{5'}$ for *cis-syn* orientation, and 4.71 Å between $C^6$ and $C^{6'}$ for *trans-anti* orientation, Fig. 7a). Therefore, the distance between the nearest carbon atoms in plates can not explain the low photodimerization reactivity of the plates. Difficulty of rotation during phtodimerization was concluded to be the reason for the inactivity of the plates from ethanol solution.[13] For the same reason, the plates from acetonitrile gave no photodimer, because the crystal structure of the plates from acetonitrile

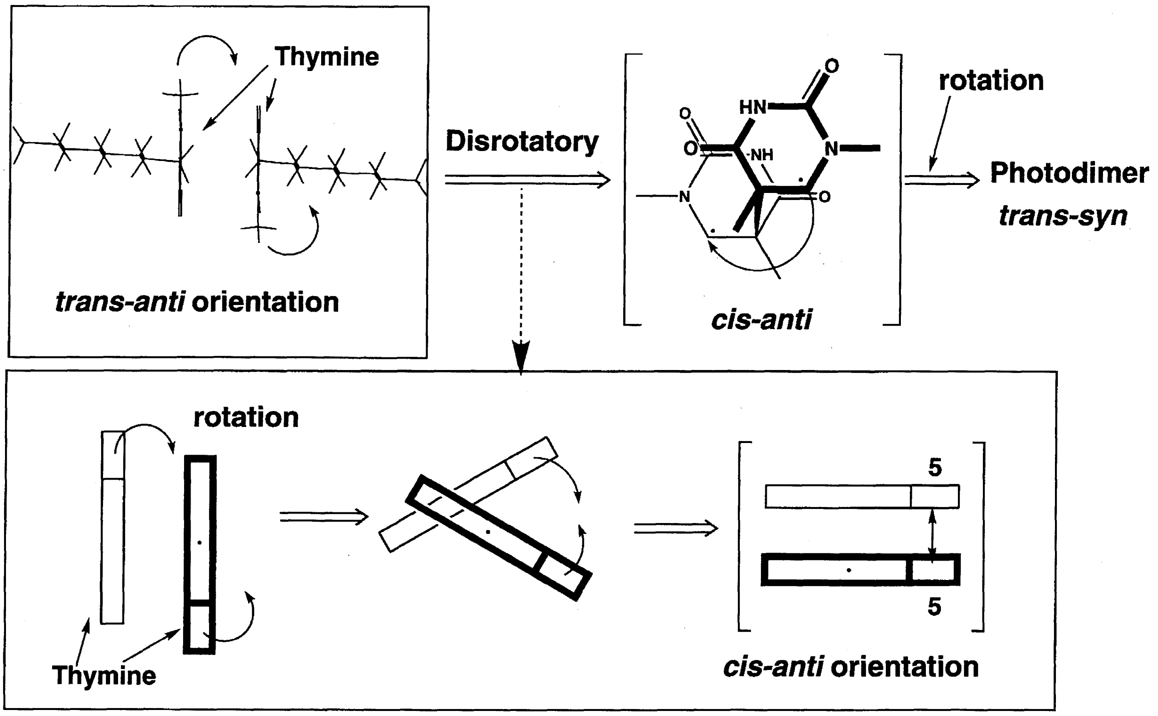


Fig. 9. Illustration of disrotatory motion from *trans-anti* orientation in crystal to *cis-anti* intermediate.

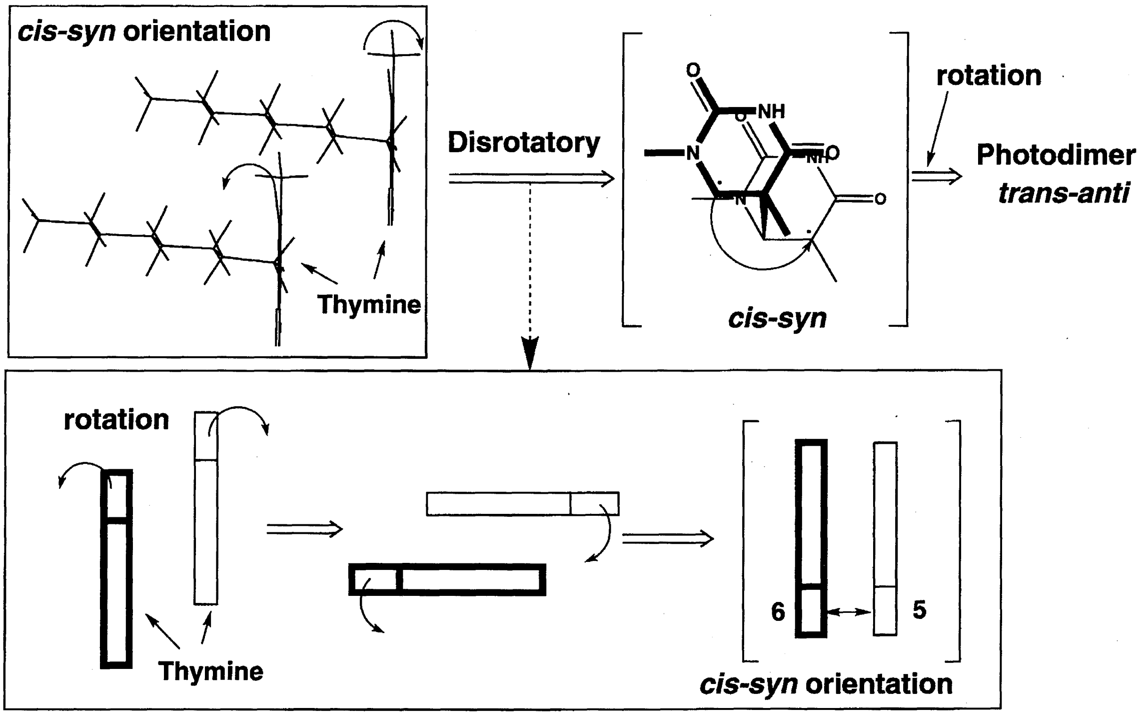


Fig. 10. Illustration of disrotatory motion from *cis-syn* orientation in crystal to *cis-syn* intermediate.

solution was identical with the structure of the plates from ethanol.

**Effect of the Alkyl Chain Length on the Crystal Structure.** The 1-alkylthymine derivatives were prepared for alkyls having carbon numbers (C$n$) of 5 to 20. When the length of alkyl chain was comparatively short (C$n$ = 5 and 6), all crystals formed were plates. 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. When the alkyl chain becomes longer than icosyl (C$n$ = 20), the thymine derivatives having a long alkyl chain gave non-crystalline solids from acetonitrile solution. Two factors, the aggregation of the alkyl chain and the hydrogen bonding between thymines, therefore, may be the important factors that determine the crystal form.

The crystal structure of needles for 1-alkylthymines became clear from X-ray structure analysis for octyl (C*n* = 8), nonyl (C*n* = 9), and undecyl (C*n* = 11) derivatives. The crystal data of these thymine derivatives are shown in Table 1. These data showed that all thymine derivatives had the same space group. All *a* axes and *c* axes were quite similar. In addition, $\beta$ angles were about 100°, almost equal. Figure 11 shows the molecular packing structure of 1-undecylthymine (C*n* = 11). The crystal includes acetonitrile in the cavity, and show similar orientation of thymines to 1-octylthymine (C*n* = 8, Fig. 3). The crystal had the cumulated bilayered structure, with the cavity where acetonitrile was included.

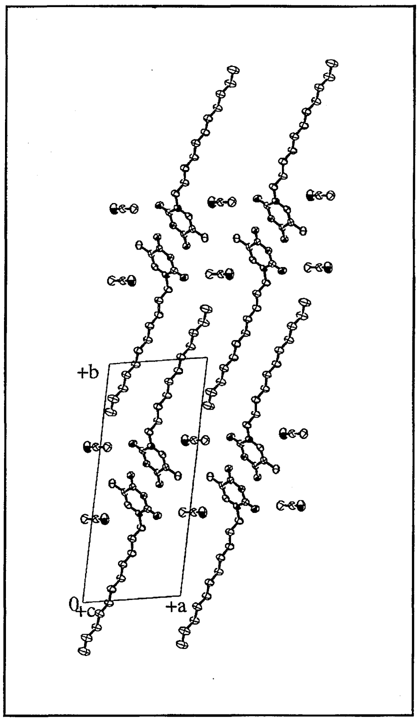


Fig. 11. Molecular packing structures and molecular arrangement of *ab* plane of 1-undecylthymine in needles from acetonitrile solution.

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

According to X-ray structure analysis (Table 1), the needles of the thymine derivatives with different lengths of the alkyl chain (C*n* = 8, 9, 10, and 11) had the same assembly fashion and the same space group ($P\bar{1}$). In addition, the same inclusion fashion of acetonitrile was found for 1-alkylthymines. All *a* axes and *c* axes were quite similar for the alkyl derivatives of C*n* = 8, 9, 10, and 11. The length of *b* axes, however, expanded with the length of alkyl chain by about 1.2 Å per methylene.

For six 1-alkylthymines, X-ray powder diffractions were measured (Fig. 12). The interplanar spacings (010) calculated from X-ray powder diffraction are plotted in Fig. 13 (solid circles). All the data follow a straight line, as shown in Fig. 13. For the alkyl derivatives of C*n* = 8, 9, 10, and 11, the length of *b* axes (open squares) agreed with the interplanar spacing (solid circles). Moreover, the spacing of (100) and (001) obtained from X-ray powder diffraction corresponding to the length of *a* and *c* axes had hardly changed at all for thymine derivatives. From these data, we conclude that the molecular arrangements for 1-dodecylthymine, 1-tridecylthymine, and 1-hexadecylthymine are similar to that for 1-octylthymine except for the *b* axis.

**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 (Fig. 14). For all thymine derivatives having long alkyl chain, endothermic peaks were found around 65 °C. The weight losses accompanied these endothermic peaks. Acetonitrile was included in all needle crystals of 1-alkylthymine and was released at around 65 °C. Similar release points

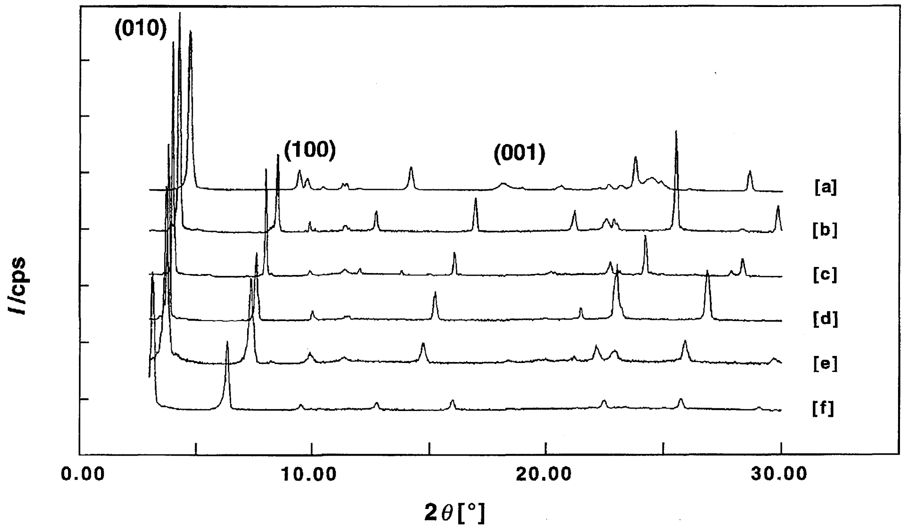


Fig. 12. Powder X-ray diffractions of 1-alkylthymines in needles. [a] 1-Octylthymine, [b] 1-Decylthymine, [c] 1-Undecylthymine, [d] 1-Dodecylthymine, [e] 1-Tridecylthymine, and [f] 1-Hexadecylthymine.

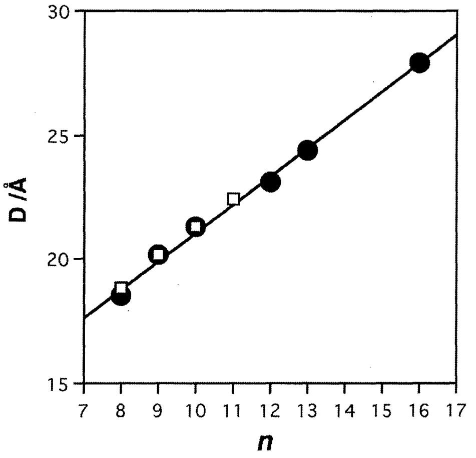


Fig. 13. Relationship between interplanar spacing and carbon number of alkyl groups for needles of 1-alkylthymines. Open squares are data from X-ray structure analysis (XSA), and solid circles are data from powder X-ray diffraction (XRD). (Interplanar spacing (*D*) vs. carbon number of alkyl groups (*n*)).

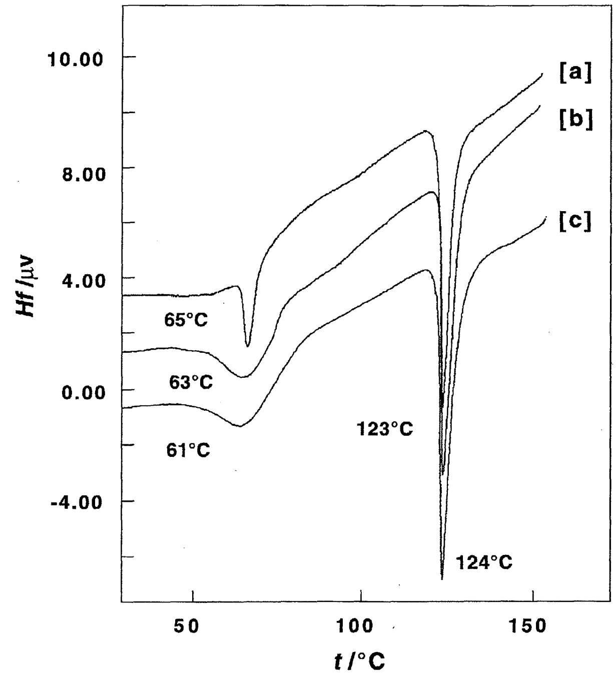


Fig. 14. DTA for needles of 1-alkylthymines. (Scanning rate was 5 K min$^{-1}$. Heat flow ($H_f$)). [a] 1-Octylthymine, [b] 1-Dodecylthymine, and [c] 1-Hexadecylthymine.

indicated that assembly fashions around acetonitrile were similar for all including crystals. A large endothermic peak at 123—124 °C should be the melting point. The thymine bases associated strongly with two hydrogen bonds at the hydrophilic layer, as shown in Fig. 3. It was implied that 1-dodecylthymine and 1-hexadecylthymine had the same hydrogen-bonding mode as 1-octylthymine. From the DTA data, properties of the needles were concluded to be identical for all 1-alkylthymines.

**Effect of the Alkyl Chain Length on the Isomer Ratio of Photodimers.** When the length of the alkyl group in the 1-alkylthymines changes, the result of the photodimerization changes. The structures of the photodimers were determined by NMR spectra for the reaction mixture from the needles of 1-alkylthymine having different lengths of the alkyl group. The NMR spectra show that the ratio of the isomer varies according to the length of the alkyl group (Table 2). The *trans-syn* isomer decreased with increase of alkyl chain length (1-nonylthymine, 1-undecylthymine), and disappeared for 1-hexadecylthymine.

Table 2. Isomer Ratio of Photodimers Obtained from Needles of 1-Alkylthymines[a]

| | *cis-syn* | *trans-syn* | *cis-anti* | *trans-anti* |
|---|---|---|---|---|
| 1-Octylthymine | — | 0.80 | 0.20 | 1.00 |
| 1-Undecylthymine | — | 0.36 | 0.24 | 1.00 |
| 1-Tridecylthymine | — | 0.11 | 0.21 | 1.00 |
| 1-Hexadecylthymine | — | — | 0.25 | 1.00 |

a) Ratios were calculated from NMR spectra.

Needles of 1-octylthymine gave *trans-syn*, *trans-anti*, and *cis-anti* photodimers. Needles of 1-hexadecylthymine, however, gave *trans-anti* and *cis-anti* photodimers. This result indicated that the reactivity of thymines in *trans-anti* orientation giving *trans-syn* photodimer decreased with increase of the length of alkyl chain. The distance between the nearest carbon atoms ($C^5$ and $C^{5'}$) for thymines in *trans-anti* orientation changed only slightly by increase of length of alkyl chain (C*n* = 8 [4.47 Å], 9 [4.56 Å], and 11 [4.52 Å]). The distance between the nearest carbon atoms, therefore, is not the reason for decreasing reactivity of thymines in *trans-anti* orientation. For the formation of the *trans-syn* photodimer from the *trans-anti* orientation in needles, two thymines approach each other and cause rotation of thymines. Therefore, two molecules should shrink to give the photodimer as the alkyl chain moves in the crystal. The interaction of the long alkyl chain becomes stronger with increase of length of chain, then the moving of such a chain becomes more difficult. This may be the reason for the decrease of the *trans-syn* photodimer when an alkyl chain becomes longer.

## Conclusion

Two kinds of single crystals were obtained when 1-alkylthymine derivatives were crystallized from acetonitrile solution. One single crystal type was the needles including acetonitrile, the other type was the plates without acetonitrile. The plates were inactive for photodimerization by irradiation of UV light because the rotation of the thymines is restricted in crystal. On the other hand, the needles give photodimers, which contain three isomers for 1-octylthymine: *trans-anti*, *cis-anti*, and *trans-syn* isomers. The crystal structure and the isomers of the photodimer indicated that the thymines rotated disrotatory in the crystal during photodimerization reaction. 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.

## References

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