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Structures and Photodimerizations of 1-Alkylthymine Crystals Obtained from *N*,*N*-Dimethylformamide

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Single crystals of 1-alkylthymine (carbon numbers of the alkyl chain were 8, 11, 12, 13, 14, and 16) were obtained from *N*,*N*-dimethylformamide (DMF) solution as plates, and the crystal structures were determined by X-ray crystal analysis. The terminal methyl group of the alkyl chain was found to approach to the double bond of the thymine base in the crystal. The thymine bases in these crystals did not give the photodimer by UV irradiation, while the crystals obtained from ethyl acetate and acetonitrile gave the photodimer as reported previously. The terminal methyl group of the alkyl chain was concluded to inhibit the rotation of the thymine bases in crystal, which made the crystal from DMF inactive for the photodimerization.

The photodimerization of thymine derivatives in solution is known to give four kinds of isomers as the photodimers by UV irradiation at 280 nm.[1] In the case of the photoreaction of DNA, the isomer of the cyclobutane type photodimer obtained was only *cis-syn* photodimer.[2] The stereoselective photodimerization of thymine bases in DNA occurred under the control of polymer chain and the hydrogen bonding with adenine bases. Therefore, the stereoselective photodimerization can be expected for the thymine base in single crystal under the control of crystal lattice.

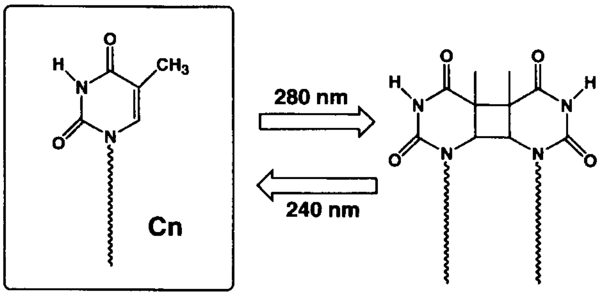


Fig. 1. Reversible photodimerization of 1-alkylthymine.

The photodimerization of thymine compounds is reversible (Fig. 1) and is applicable to photoresists[3—7] and reversible photo-recording systems.[8—12] In order to apply the thymine compounds to photosensitive materials, it is necessary to study the photodimerization reactions in solid state. For a highly efficient reversible photodimerization system of the thymine compounds, the stereoselective photodimerization is an important factor, because the splitting reaction of the photodimer depends on the kinds of stereo isomer of the photodimer. The studies of the crystal structure and the photodimerization of the thymine derivatives will make the mechanism of the photodimerization clear for the solid state reaction.

We have recently reported that 1-octylthymine in single crystal obtained from ethyl acetate solution undergoes photodimerization when irradiated at 280 nm to form *trans-anti* photodimer (Fig. 2).[13] The X-ray structure analysis of 1-octylthymine crystal obtained from ethyl acetate solution (**Form I**) showed the thymine rings to be lying in *trans-syn* arrangement to each other. The arrangement of the thymine rings is such that the photodimer resulting from irradiation of the crystal would be expected to attain *trans-syn* geometry. The isomer of the photodimer obtained from the crystal was not the *trans-syn* but the *trans-anti* photodimer. The *trans-anti* photodimer of the 1-octylthymine was concluded to be formed by disrotatory motion in the crystal during the photodimerization reaction (Fig. 2).

The plates of 1-octylthymine were obtained from ethanol solution (**Form II**), but the crystal did not undergo photodimerization by UV irradiation at 280 nm.[14] The X-ray structure analysis of the plates of 1-octylthymine showed that the crystal structure of the **Form II** resembled that of the **Form I** obtained from ethyl acetate solution except for the packing of the long alkyl chains.

The third crystal of **Form III** of 1-octylthymine was obtained from acetonitrile solution as needles.[15] The third crystal underwent photodimerization efficiently to form *trans-anti* and *trans-syn* photodimers. The thymine rings in the **Form III** were able to rotate during the photodimerization reaction to form two kinds of photodimers. In addition to 1-octylthymine, the crystal structure and the photodimerization of other 1-alkylthymines having long alkyl chains were studied for the needles obtained from acetonitrile. All these crystals have similar crystal structure and activity for the

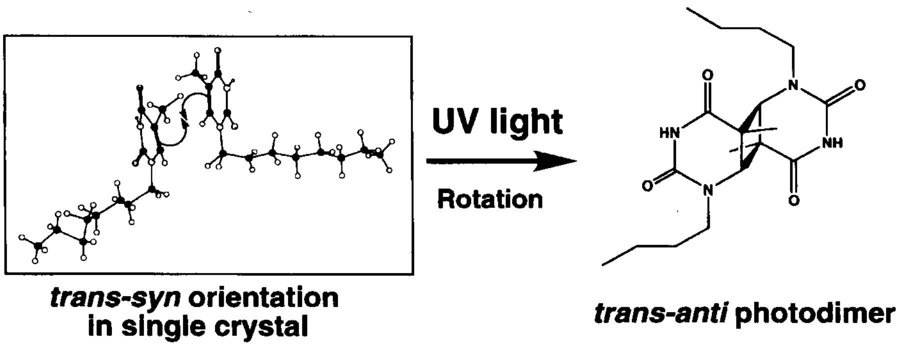


Fig. 2. Photodimerization of 1-octylthymine in single crystal.[13]

photodimerization. Polymorphism and photodimerization of 1-octylthymine are summarized for three crystal forms in Table 1.

Intensive studies concerning topochemical reactions have been reported on the photodimerization of cinnamic acid and its derivatives. Schmidt and his coworkers proposed a geometrical criterion for the photodimerization in the crystalline state: that the reacting double bonds should be situated within about 4.2 Å of each other and aligned parallel to each other.[16] In the case of the photoactive single crystal of 1-octylthymine obtained from acetonitrile solution (**Form III**), however, the distance between the reacting double bonds of the thymine bases was 4.47 Å.[15] It is difficult to apply Schmidt's rule to the photodimerization of the 1-octylthymine crystal. Therefore, it is necessary to determine the factor of the crystal structure of 1-alkylthymine for the photodimerization reaction in crystal state.

This paper deals with the structure of the 1-alkylthymine crystals (**Form IV**) obtained from *N*,*N*-dimethylformamide (DMF) solution, where the carbon numbers of the alkyl chain were 8, 11, 12, 13, 14, and 16. These crystals did not undergo photodimerization by UV irradiation at 280 nm. Then, the reason of inactivity for the photodimerization of the crystal from DMF was studied by comparing the crystal structure of 1-octylthymine with three forms (**Forms I**, **II**, and **III**) reported previously.

Experimental

Materials. Preparations of the 1-alkylthymines are reported in our previous papers.[13—15] Solvents used for recrystallization were purified by a conventional method.

Instruments. Photodimerizations of the thymine bases in the single crystals (crystal size was around 0.5×0.2×0.05 mm) were carried out by SUPER CURE-203S UV, where the light source was a Hg-Xe lamp (200 W) (San-Ei Electric) with a cut filter (Toshiba U340).[15] The photodimerization was followed by measuring UV spectra (Nihon Bunko UV/vis 600) in chloroform solution.

A Seiko I&E DSC6200 series performed differential scanning calorimetric (DSC) measurements. X-Ray powder diffraction patterns were measured by a Rigaku X-ray diffractometer RINT 2000 with Cu $K\alpha$ radiation.

Crystal Structure Analysis. Data of X-ray diffraction for 1-alkylthymine were collected by a Rigaku RAXIS-CS imaging plate two-dimensional area detector using graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71070 Å). Using TEXSAN software package of the Molecular Structure Corporation we performed all the crystallographic calculations. The crystal structures were solved by the direct methods (shelxs 97) and refined by the full-matrix least squares. The positions of hydrogen atoms attached to nitrogen atoms were obtained from the difference Fourier syntheses. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The crystal data of six thymine derivatives are shown in Table 2.

Results and Discussion

Structure of 1-Alkylthymine Crystals Obtained from DMF. Six single crystals of 1-alkylthymine were obtained from DMF for 1-octylthymine (**C8**), 1-undecylthymine (**C11**), 1-dodecylthymine (**C12**), 1-tridecylthymine (**C13**), 1-tetradecylthymine (**C14**), and 1-hexadecylthymine (**C16**); the crystal data for these crystals are tabulated in Table 2. The single crystals for the longer alkyl chain (**C14** and **C16**) were obtained from benzene as well as DMF. Unfortunately, single crystals suitable for X-ray crystal analysis were not obtained for 1-nonylthymine (**C9**), 1-decylthymine (**C10**),

Table 1. Polymorphism and Photodimerization of 1-Octylthymine

Crystal structure	Solvent	Shape	Photoreaction	Isomers of photodimer	Ref.
Form I	Ethyl acetate, Chloroform	Plate	○	*trans-anti*	13
Form II	Ethanol, Methanol, Acetonitrile Acetone	Plate	×	—	14
Form III	Acetonitrile	Needle	○	*trans-anti*, *trans-syn* (1 : 1)	15

Table 2. The Crystal Data of Six 1-Alkylthymine Derivatives

Alkyl	Octyl (**C8**)	Undecyl (**C11**)	Dodecyl (**C12**)	Tridecyl (**C13**)	Tetradecyl (**C14**)	Hexadecyl (**C16**)
Solvent	DMF	DMF	DMF	DMF	Benzene	Benzene/*p*-Xylene
Formula	$C_{13}H_{22}N_2O_2$	$C_{16}H_{28}N_2O_2$	$C_{17}H_{30}N_2O_2$	$C_{18}H_{32}N_2O_2$	$C_{19}H_{34}N_2O_2$	$C_{21}H_{38}N_2O_2$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a/Å	12.405(4)	12.416(3)	12.416(3)	12.43(2)	12.424(7)	12.46(2)
b/Å	8.791(4)	8.884(5)	8.862(4)	8.921(3)	8.947(2)	8.972(7)
c/Å	16.87(1)	15.350(3)	18.17(2)	16.775(6)	18.234(6)	20.014(8)
α/°						
β/°	130.61(4)	96.51(2)	114.28(6)	90.88(6)	106.15(5)	100.27(7)
γ/°						
V/Å^3	1397(1)	1682.3(8)	1822(2)	1860(2)	1951(1)	2202(3)
Z	4	4	4	4	4	4
D_{calc}/g cm^{-3}	1.13	1.11	1.07	1.10	1.11	1.06
No. of used reflns	1880	1859	1541	2427	3260	1824
R	0.083	0.073	0.091	0.087	0.057	0.091
Temp/°C	25	−50	25	−50	−50	−50

and 1-pentadecylthymine (**C15**).

The crystal data in Table 2 show the dependence on the chain length of the alkyl chains for the plates obtained from DMF. When the carbon number of the alkyl chain is odd, the values of *c* axis is shorter, and the β value is smaller than the values for the compounds having even numbered carbon atoms of the alkyl chain.

Molecular packing along *a* axis is shown in Fig. 3 for **C11** and **C12**. In this figure, the structure of **C11** having odd-numbered alkyl chain is similar to the structure of **C12** having even-numbered alkyl chain. Molecular packing along *b* axis in Fig. 4, however, shows clearly the difference between even-numbered and odd-numbered alkyl chains. The β value of **C11** is nearly a right angle (96.51°), and the β value of **C12** is large (114.28°). The difference of these values reflects

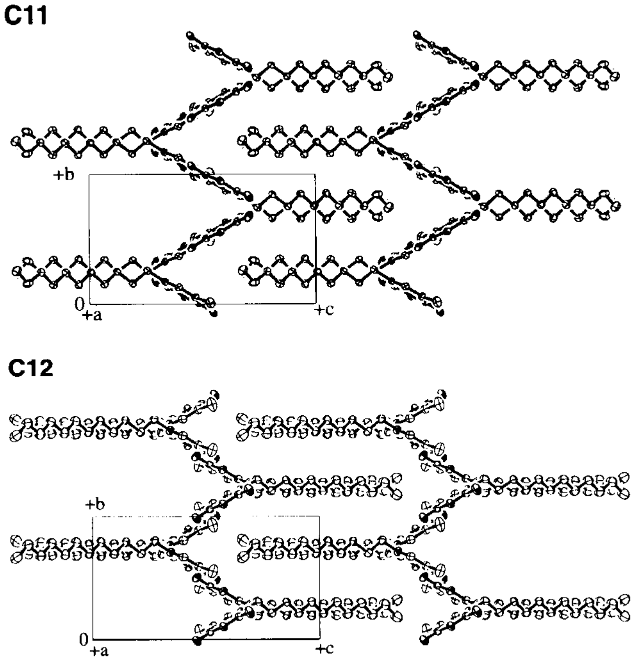


Fig. 3. Molecular packing of 1-undecylthymine (**C11**) and 1-dodecylthymine (**C12**) along *a* axis.

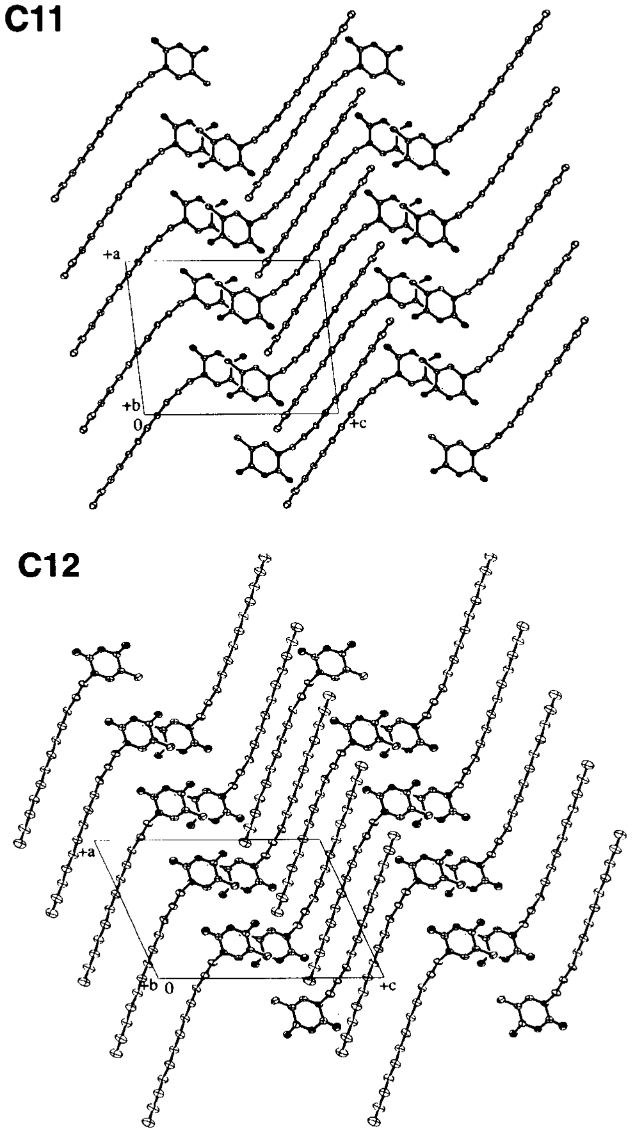


Fig. 4. Molecular packing of 1-undecylthymine (**C11**) and 1-dodecylthymine (**C12**) along *b* axis.

the angle between thymine bases and the alkyl chains, which extend along *ac* plane.

The nearest neighboring molecules are picked up from the crystal structures in Fig. 4 for **C11** and **C12** to give Fig. 5. The molecular packing of 1-undecylthymine (**C11**) along *b* axis (Fig. 4 (**C11**)) showed that the alkyl chains were curved and arranged face to face or back to back. The view of the pairs from *b* axis for the face to face pair is shown in a rectangle of Fig. 5 (**C11**). In this figure, the thymine rings of molecules (**d**) and (**c**) are not parallel, the alkyl chains are face to face, and the terminal methyl group of the molecule (**d**) approaches to the double bond of the thymine base in the molecule (**c**) (3.64 Å). The terminal methyl group of the molecule (**c**), on the other hand, approaches to the thymine base of the molecule (**b**) (3.64 Å). Then the molecules of **C11** connected like a helix. In the case of **C12**, however, the thymine rings arrange parallel for the molecules where the alkyl chains are face to face as shown in a rectangle of Fig. 5 (**C12**). This figure indicates that the terminal methyl group of the molecule (**b**) is closely located to the double bond of the thymine base in the molecule (**a**) with the distance of 3.62 Å, and the terminal methyl group of the molecule (**a**) is closely located to the thymine base of the molecule (**b**). Then two molecules in the crystal of **C12** form a pair instead of a helix.

The carbon number dependence of the crystal structure in Fig. 5 was caused by the direction of the methyl group. The direction of the terminal methyl group in the odd-numbered alkyl chain (**C11**) is opposite to the direction of the thymine bases (**b** and **d** in Fig. 5 (**C11**)). Then the methyl group approaches to the upper thymine base (**a** and **c** in Fig. 5 (**C11**)). When the carbon number of the alkyl chain is even (**C12**), the direction of the terminal methyl group is the same as the direction of the thymine bases (**b** and **d** in Fig. 5 (**C12**)) forming the pairs (**a**–**b** and **c**–**d**). The difference of the interaction between the methyl group and the thymine base caused the difference of *c* axis and the value of β. The interaction between the terminal methyl group and the thymine base observed in these crystals should be the van der Waals interaction.

Photodimerization of 1-Octylthymine. UV light was irradiated on the single crystal obtained from DMF for 1-octylthymine using an optical fiber with cut-filter (above 280 nm). The photodimerization of the thymine bases was followed by UV spectra at 270 nm in chloroform solution. Decrease of UV absorption at 270 nm, however, was not detected after irradiation for 2 d. The photodimerization occurred for the crystals of 1-octylthymine in **Form I**[13] and **Form III**,[15] while **Form II**[14] was inactive for the photodimerization. Irradiation of UV light on the crystal of **Form I** gave the photodimer quantitatively within 2 h, which was detected by UV, IR, and NMR spectra. The crystal after photodimerization, however, was found to be amorphous from powder X-ray diffraction.[13] The single crystal of **Form III** obtained

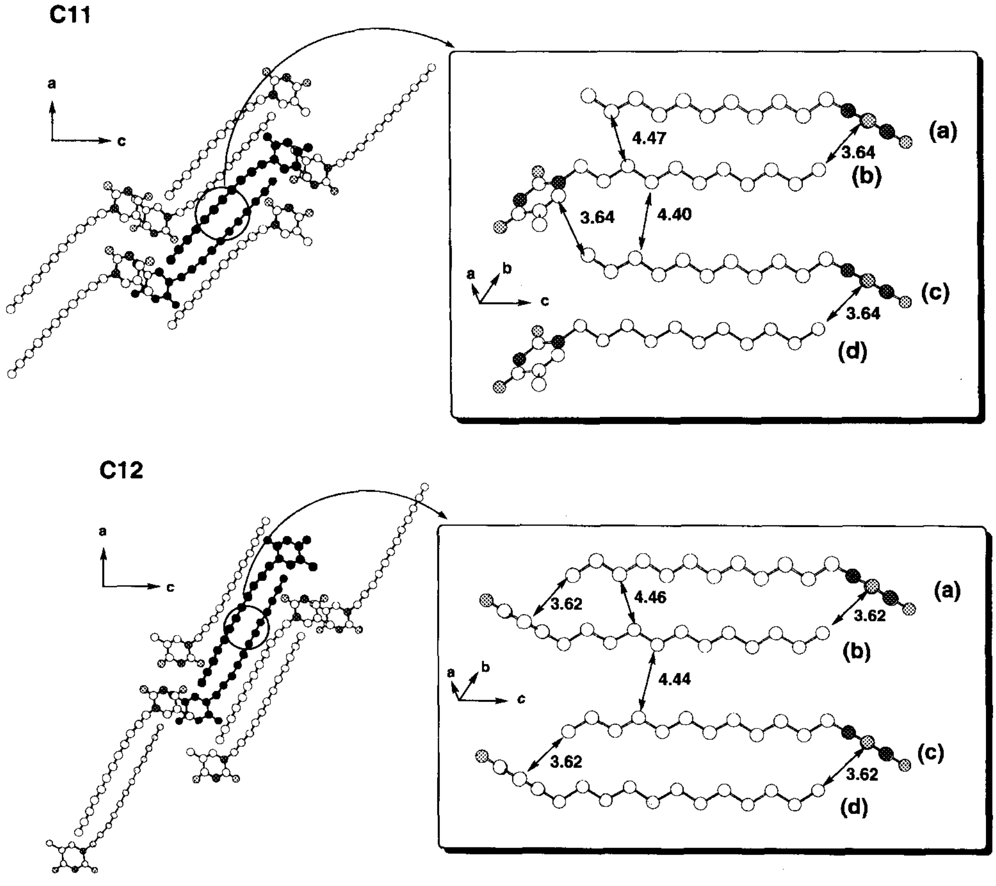


Fig. 5. Neighboring molecules for 1-undecylthymine (**C11**) and 1-dodecylthymine (**C12**).

from acetonitrile also gave the photodimer by irradiation of UV light, although the conversion was lower (60—80% after irradiation for 12 h) than the case of **Form I**.[15] These results indicated that the crystal structure influenced the photoactivity of 1-octylthymine in crystalline state.

Crystal Structure and Photodimerization of 1-Octylthymine. In order to find the relationship between the crystal structure and the photoactivity for the photodimerization, the crystal structures of 1-octylthymine were compared for **Forms I, II, III,** and **IV**. From the crystal structure of 1-octylthymine, we will study the factors determining the activity of the crystals for the photodimerization. The possible factors for the crystal structure are summarized in Table 3.

An important feature of the thymine compounds is the hydrogen bonding between thymine bases. The hydrogen bondings of the thymine bases do not directly influence the photoactivity, but are important for the stability of the crystal structure. The crystallization of 1-octylthymine from solution may begin from the hydrogen bonding of the thymine bases, followed by aggregation of the long alkyl chains. Figure 6 shows the hydrogen-bonded pairs for four crystal forms of 1-octylthymine. In **Form I** and **Form II**, the long alkyl chains extended to the same direction from the plane of the hydrogen bonded thymine bases. On the other hand, in the case of **Form III** and **Form IV**, the long alkyl chains extended in the opposite direction from the plane of the hydrogen bonded thymine bases. The direction of the long alkyl chain may determine the aggregation of the long alkyl chains and the crystal structure. The interaction of the solvent with the molecules may cause the direction of the long alkyl chain during crystallization in solution.

An important factor of the crystal structure for the photoactivity is the distance between the C5–C6 double bonds of the thymine bases, as proposed by Schmidt and his coworkers.[16] Two facing thymine bases in crystals are shown in Fig. 7 for four crystal forms of 1-octylthymine, and the distances between the adjacent double bonds of thymine bases are tabulated in Table 3. The distances between the thymine bases in **Form IV** are 4.36 and 4.56 Å, which are longer than the distance of the photoactive **Form I** (3.40 Å) but shorter than the distance of the photoactive **Form III** (4.47 and 4.71 Å). Therefore, the distance between the double bonds of the thymine bases is not the main factor for the photodimerization of thymine bases in crystal.

As mentioned above, the characteristic of the crystal structure for **Form IV** is the presence of the terminal methyl group in the vicinity of the double bond in thymine base. The nearest neighboring terminal methyl groups and thymine bases are picked out from the crystal structure of 1-octylthymine for **Forms I, II, III,** and **IV** in Fig. 8, and the distances are tabulated in Table 3. The distance between the methyl group and the thymine base (C5) are long for the photoactive **Form I** (4.26 Å) and **Form III** (7.34 Å), but are short for the inactive **Form II** (3.86 Å) and **Form IV** (3.64 Å). The terminal methyl group of the alkyl chain should be important for the photodimerization of the thymine bases, although the methyl group did not participate directly in the photodimerization.

The DSC curves of 1-octylthymine indicate the stability of the crystals (Fig. 9). The inactive crystals of **Form II** and **Form IV** gave only one peak at high temperature around

Table 3. Data of 1-Octylthymine Crystals Related to the Photodimerization

	Form I[13]	Form II[14]	Form III[15]	Form IV
Thymine–Thymine (Å)[a)]	3.40	4.34	4.47, 4.71	4.36, 4.56
Thymine–Methyl (Å)[b)]				
[Thymine] 5C	4.26	3.86	7.34	3.64
6C	4.55	3.86	6.90	3.60
5Me	5.14	3.96	7.80	3.86
DSC/°C	108.9, 119.9	120.1	59.3, 120.1	122.6

a) The distance between the adjacent double bonds of thymine bases (see Fig. 7). b) The distance between the thymine bases and the terminal methyl group of alkyl chain (see Fig. 8).

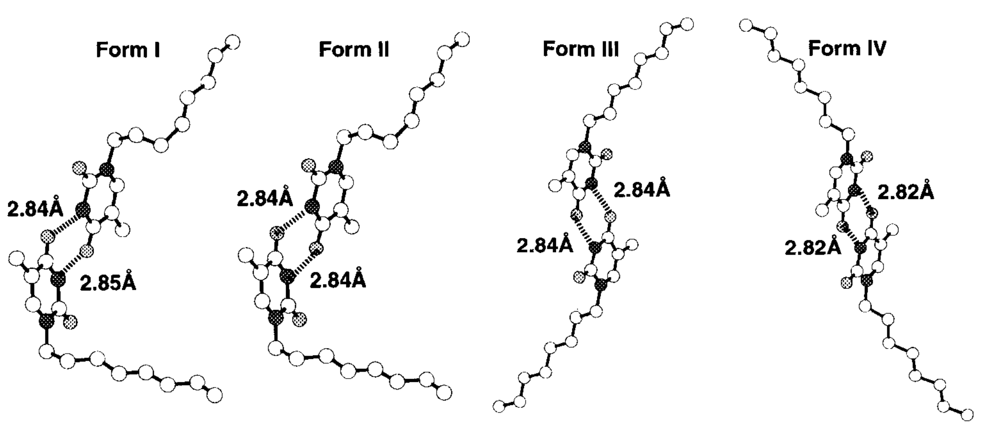


Fig. 6. Hydrogen bonded pairs of 1-octylthymine for **Form I**, **Form II**, **Form III**, and **Form IV**.

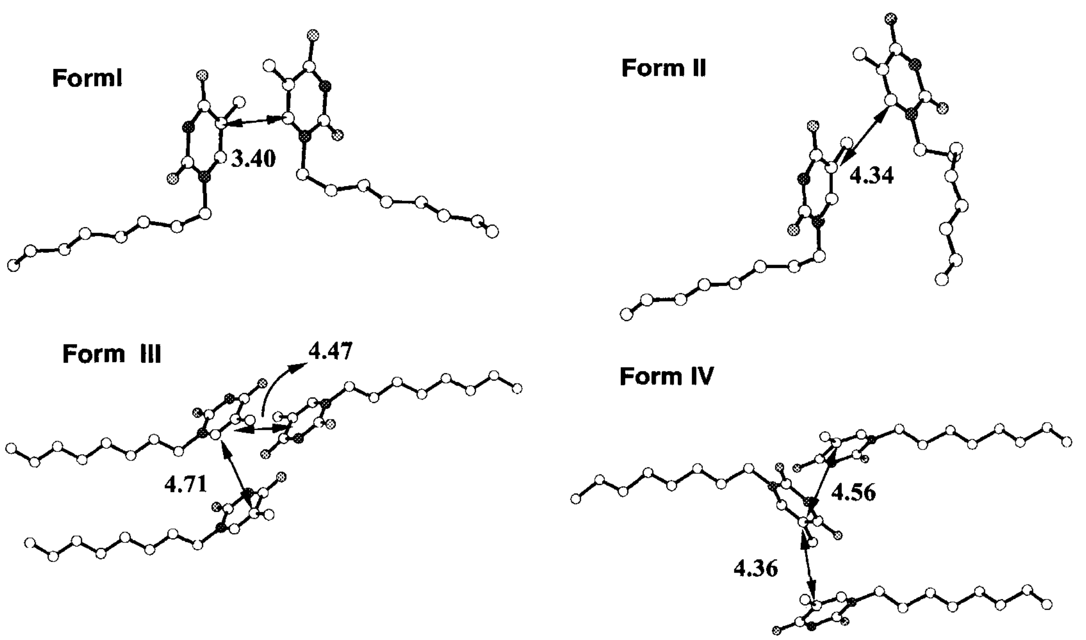
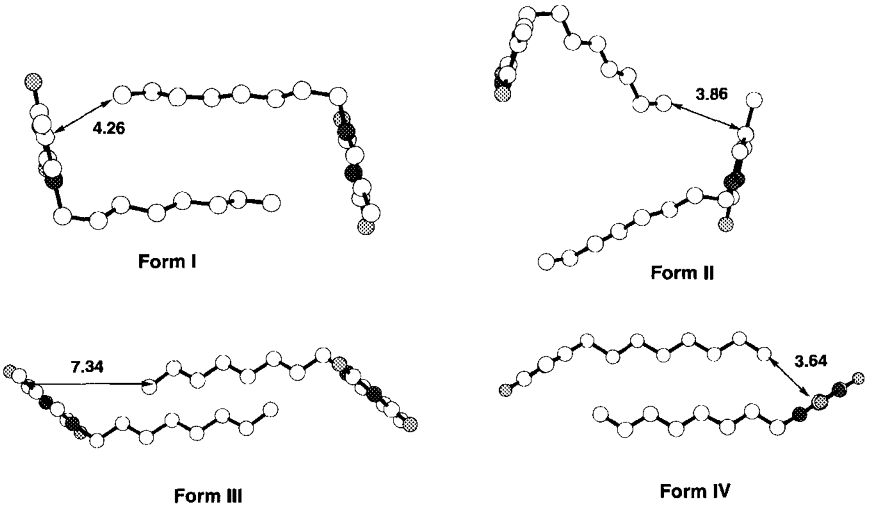


Fig. 7. Facing thymine bases in **Form I**, **Form II**, **Form III**, and **Form IV**.



Form I Form II

Form III Form IV

Fig. 8. The nearest neighboring molecules of 1-octylthymine for **Form I**, **Form II**, **Form III**, and **Form IV**.

120 °C. The photoactive crystals of **Form I** and **Form III**, however, had one more peak in DSC. **Form III** including acetonitrile molecules released acetonitrile at 59.3 °C, followed by melting at 120.1 °C. **Form III** underwent photodimerization, but became inactive after annealing at 100 °C.[15]**Form I** was also active for the photodimerization, but became inactive after annealing at 100 °C.[13] Then, the unstable crystals suggested by the DSC curves were active for the photodimerization.

The alignment of the active double bonds is one more important factor for the photodimerization, as proposed by Schmidt and his coworkers.[16] From the molecular arrangement of the thymine bases in crystal and the structure of the photodimer, the thymine bases were concluded to rotate in opposite directions (disrotation) in the crystal during photodimerization reaction.[13] Conrotatory motion and disrotatory motion were proposed for thermal and photo cyclization of polyene compounds by Woodward and Hoffmann.[17] The photodimerization of the thymine bases is an intermolecular reaction, but the interaction of the alkyl chain may make the photodimerization in crystal to become an intramolecular reaction. Therefore, the alignment of the thymine bases in crystal is not the important factor for the photodimerization, but determines the structure of the photodimer after the disrotatory motion during the photodimerization reaction.

In photoactive **Form I**, the distance between the double bonds of the thymine bases is short (3.40 Å), and the terminal methyl group of the alkyl chain is not near the thymine base (4.26 Å). The DSC data of **Form I** indicate that the crystal is unstable to change to the stable crystal. Consequently, the thymine bases in **Form I** can rotate in crystal to give the photodimer. In photoactive **Form III** from acetonitrile, the distance between the photoactive double bonds of the thymine base was 4.36 Å, which was longer than 4.2 Å of

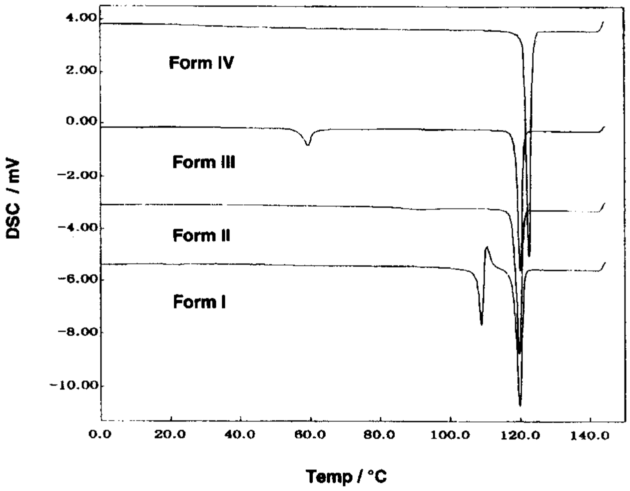


Fig. 9. DSC of 1-octylthymine for **Form I**, **Form II**, **Form III**, and **Form IV**.

Schmidt's rule. However, the distance between the methyl group and the thymine base (C5) are long enough (7.34 Å) for the disrotatory motion of the thymine bases in crystal. The DSC data also support the instability of the crystal in **Form III**. Therefore, the crystal of **Form III** is active for photodimerization to give the photodimer.

When the terminal methyl group of the long alkyl chain is closely located to the double bond of thymine bases, the terminal methyl group of the alkyl chain should block the rotation of the thymine bases during photodimerization. The DSC data indicated that the crystals of **Forms II** and **IV** were stable and could not transform to another crystal form. Therefore, the blocking of the disrotatory motion of the thymine base by the terminal methyl group of the alkyl chain was concluded to be the reason of the inactivity for the photodimerization of **Form II** and **Form IV**. The distance between the terminal methyl group and the C5–C6 double bond of thymine bases is a measure of the blocking effect of the disrotatory motion of the thymine base by the methyl group.

Conclusion

Single crystals of 1-alkylthymine having long alkyl chain were obtained from *N*,*N*-dimethylformamide solution, and the crystal structure (**Form IV**) was determined by X-ray crystal analysis. The most remarkable feature of the crystal structure for **Form IV** was the short distance between the terminal methyl group of the long alkyl chain and the double bond of the thymine bases. For 1-alkylthymine having even-numbered alkyl chain, two molecules formed a pair by the interaction of alkyl chains and the interaction of the terminal methyl group with the thymine bases. For 1-alkylthymine having odd-numbered alkyl chain, on the other hand, molecules connected like a helix.

Irradiation of UV light on the crystal of 1-alkylthymine obtained from DMF did not give the photodimer. Factors of the crystal structure affecting the photoactivity of 1-alkylthymine were determined by comparing the crystal structures of 1-octylthymine for **Forms I**, **II**, **III**, and **IV**. The distance between the active double bonds of thymine bases could not explain the photoinactivity of 1-octylthymine crystals. The photoinactivity was found to relate closely to the distance between the terminal methyl group of alkyl chain and the double bond of the thymine base. The disrotatory motion of the thymine base is necessary for the photodimerization of 1-octylthymine in crystal, but the closely situated terminal methyl group inhibits the rotation of the thymine base. Therefore, it is concluded that the important factor of the crystal structure for inactivity of the photodimerization of the thymine base is the inhibition of the disrotatory motion by the terminal methyl group of the alkyl chain.

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