diated on a merry-go-round apparatus at 25 °C. Direct irradiations were carried out through a K_2CO_3 (1.3%)–K_2CrO_4 (0.13%) filter solution (mainly 313 nm). Benzophenone-sensitized irradiations were done through a phenanthrene solution (5 g/L) in methanol (>350 nm) or through a glass filter (Riko U-360, mainly 366 nm). The reaction mixtures were analyzed by HPLC, using naphthalene or *m*-terphenyl as the internal standard. A small amount of isomeric olefin impurities involved in the starting material was carefully checked by HPLC: the purities of the *tt*- and *t*-isomers were >99.99% and those of the other isomers were >99.4%. When necessary, corrections were made in the calculation of the quantum yields. In all cases the reaction was stopped at a small conversion (<4%). Two parallel runs for quantum yield measurements agreed within experimental error (±5%). The trans → cis isomerization of *t*-S was used for actinometry ($\Phi^{\text{direct}} = \Phi^{\text{sens}} = 0.50$[39]).

Intramolecular End-to-End Reactions of Photoactive Terminal Groups Linked by Polymethylene Chains

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Abstract: Intramolecular end-to-end reactions of a pair of photoactive terminal groups, dibenz[*b,f*]azepine (DBA) chromophores, linked by a series of polymethylene chains ($DBA–CO(CH_2)_nCO–DBA$, $n = 2–30$) were studied by two different approaches. One approach is to measure the intramolecular deactivation rate constants of the excited triplet state of terminal DBA groups by the nanosecond laser photolysis and the other is to measure the intramolecular photocyclization rates of these bichromophoric compounds by the quantitative product analysis with GPC. The excited triplet state of the DBA group is the intermediate of the reaction. The intramolecular deactivation rate constant, k^{intra}, of each compound showed a pronounced chain length dependence, while the intermolecular deactivation rate constant, k^{inter}, was independent of its chain length within the range $n = 2–30$. The first peak of k^{intra} appeared at the chain length $n = 4$, and the second peak appeared at $n = 18$. On the other hand, intramolecular cyclization products were obtained above $n = 14$, and the quantum yield of the reaction showed the maximum at $n = 26$ ($\Phi_d^{\text{intra}} = 0.34$). This chain length is slightly longer than that for k^{intra} at the second peak. This chain length is interpreted in terms of the ring-closure probability that becomes maximum for a pair of terminal bonds being oriented in directions opposite to each other (anti configuration).

Photoirradiation of bichromophoric compounds undergoes either intra- or intermolecular reactions. The intramolecular reaction gives macrocyclic ring-closure products,[1] while the intermolecular reaction leads to photopolymerization.[2] When intramolecular reactions are compared with the corresponding bimolecular reactions, the rates of the latter are dependent on the concentration of reactants, while those of the former are not, since the effective concentration for the reaction is kept constant by the function of a molecular chain linking two reactants. Therefore, the high reaction yield of intramolecular ring-closure product can be maintained even in highly diluted conditions.

A lot of intramolecular ring-closure reactions have been studied up to now. Intramolecular ring-closure reactions can roughly be classified into two types by the reactivity of the terminal reactants: activation-controlled reaction and diffusion-controlled one. The former occurs only after many collisions of both terminal reactants. In this case, conformational distribution of a molecular chain linking a pair of terminal reactants is kept in equilibrium during the reaction. Therefore, the reaction rate is directly proportional to the ring-closure probability of a molecular chain. On the other hand, the latter occurs immediately when two reactants happen to collide, since the activation energy of the terminal reactants is sufficiently low. Therefore, the reaction rate is proportional to the frequency of collision of terminal reactants.

In the present work, intra- and intermolecular photochemical reactivities are examined by using a series of polymethylene chains having the dibenz[*b,f*]azepine (DBA) group as a pair of terminal groups as shown in Figure 1. Compounds shown in Figure 1 are denoted by DC-*n* ($n = 2–30$), each numeral representing the number of methylene units for each polymethylene chain. This reaction system belongs to the activation-controlled one in the classification of the terminal reactivity as mentioned above, since the terminal reactant, DBA, shows a smaller rate constant (3.0×10^7 M^{-1} s^{-1} for 5-valeryl-DBA in dichloromethane at 25 °C)[3] compared with the diffusion rate constant in fluid solutions ($\approx 10^{10}$ M^{-1} s^{-1}). Therefore, the intramolecular reaction rate obtained for a series of bichromophoric compounds in this system will reflect the ring-closure probability of a polymethylene chain.

In the examination on the function of a molecular chain in an intramolecular ring-closure reaction, it is very important to take into consideration the direction of a molecular chain at the terminal position where a pair of terminal groups approach to react with each other. Boens and his co-workers carried out the intramolecular cycloaddition of polymethylene–bis(2–anthroates).[4] They examined chain length dependence of syn head-to-head and syn head-to-tail cyclomer formations and showed that the differences of the terminal structures, i.e., head-to-head or head-to-tail, bring different chain length dependence of the cyclization quantum yields: the head-to-tail cyclomer needs longer chain length, compared with the head-to-head one. As for the present reaction system, when a pair of terminal groups form a cyclobutane ring, there are two types of configurations: syn- and anti-type cyclo-

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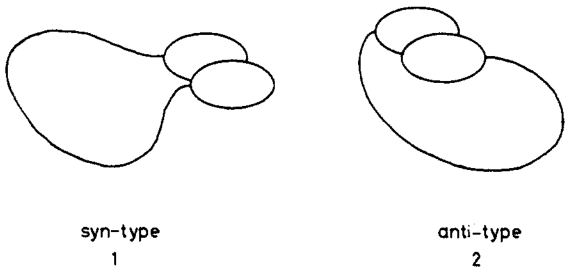

Figure 1. A pair of terminal bond directions of intramolecular cyclization product: (1) syn-type and (2) anti-type.

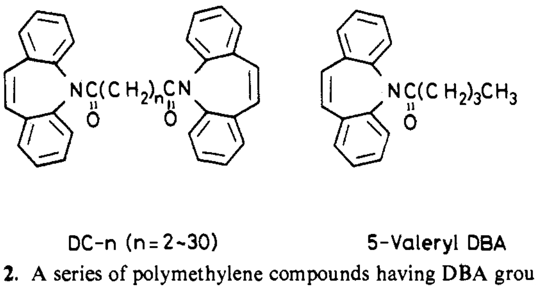

Figure 2. A series of polymethylene compounds having DBA groups as the terminal groups, DC-n (n = 2–30). Monomeric compound, 5-valeryl-DBA, is also shown.

butane rings as the products of photochemical ring-closure reaction as shown in Figure 2. To form a *syn*-cyclobutane ring, a pair of terminal chains has to be oriented in the same direction. To form an *anti*-cyclobutane ring, the terminal chains are directed oppositely to each other. Therefore, if two kinds of products in the intramolecular reaction can be distinguished clearly, further information with respect to the behavior of a molecular chain will be obtained.

The present reaction system has two features. First, the reaction intermediate is the excited triplet state[3] and the probing DBA chromophore has a long lifetime (17 μs) compared with other chromophores such as anthracene,[5] maleimide,[6] and thymine.[7] Accordingly, the ring-closure reaction of long polymethylene chains can be observed in the DBA system. Second, sensitized photochemical reaction of a pair of terminal DBA groups produces the *anti*-cyclobutane ring as the unique reaction product.[3,8] This means that two terminal DBA groups must approach each other from the opposite side for the cyclodimerization reaction. Hence, the terminal direction of molecular chains is reflected in the ring-closure reaction.

We investigated the extent of intra- and intermolecular interactions of a pair of terminal DBA groups by laser photolysis and also the reactivities in intra- and intermolecular cycloaddition reactions by the quantitative analysis of the reaction products.

Experimental Section

Materials. Bichromophoric Compounds. A series of polymethylene compounds having a pair of dibenz[b,f]azepine (DBA) groups as the chain terminals were synthesized according to the procedure of Kricka et al.,[9] i.e., by the acylation reaction of the corresponding alkanedicarboxylic acid chloride with $5H$-DBA. For example, 5,5′-tetracosanedioylbis(dibenz[b,f]azepine) (DC-22) was prepared as follows. Docosanedicarboxylic acid chloride (1.2 g) in dry benzene was added dropwise to the stirred benzene solution of $5H$-DBA (1.0 g, Aldrich) at room temperature. The reaction mixture was refluxed for 5 h and then cooled and washed with water. The solution of the reaction mixture was dried with calcium chloride, and evaporation of the solvent afforded yellow oily product. The product was purified by column chromatography on neutral alumina eluted with a mixture of dichloromethane and methanol (500:3). A series of other bichromophoric compounds were prepared by the same procedure as DC-22. All obtained compounds were identified by IR, UV, and NMR spectra. The spectra for the obtained bichromophoric compounds showed the same characteristic spectra. The data were as follows: IR (KBr) 3100, 2900, 1660, 1600, 1490, 1300, 1250, 1160, 800, and 770 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} = 287 nm; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.0–2.4 (m, methylene H), 6.9 (s, ethylenic H), 7.3–7.6 (m, aromatic H). The reaction yields of all obtained compounds were about 70%. The purity of the compounds was confirmed by TLC (one spot, on neutral alumina).

Alkanedicarboxylic Acid Chlorides. Each alkanedicarboxylic acid chloride was prepared from the corresponding alkanedicarboxylic acid by the reaction with thionyl chloride; e.g., docosanedicarboxylic acid chloride was obtained as follows. Docosanedicarboxylic acid dissolved in thionyl chloride was heated at 50 °C for 1 h with stirring. When the evolution of hydrogen chloride stopped, the excess thionyl chloride was removed by distillation and docosanedicarboxylic acid chloride was obtained. A series of other alkanedicarboxylic acid chlorides were obtained by the same procedure as docosanedicarboxylic acid chloride, except for succinic acid chloride and glutaric acid chloride. For succinic acid chloride and glutaric acid chloride, zinc chloride was added as the catalyst in order to inhibit intramolecular dehydration reaction.

Alkanedicarboxylic Acids. Commercial alkanedicarboxylic acids (Aldrich, Tokyo Kasei) were used for acids lower than hexadecanedicarboxylic acid. A series of higher alkanedicarboxylic acids than hexadecanedicarboxylic acid were prepared by the method of Hünig et al;[10a] e.g., docosanedicarboxylic acid was obtained by the following procedure. First of all, 1-morpholino-1-cyclohexene was prepared by the condensation of cyclohexanone with morpholine in toluene with p-toluenesulfonic acid as the catalyst.[10b] The reactions of the compounds in three steps gave docosanedicarboxylic acid. The first step was the synthesis of decanedioyldicyclohexanone. Decanedicarboxylic acid chloride in dry chloroform was added dropwise to the stirred chloroform solution of 1-molpholino-1-cyclohexene and anhydrous triethylamine at 35 °C. The reaction mixture was stirred for 5 h at 35 °C and then 20% hydrochloric acid was added and the mixture was refluxed for 5 h. The mixture was cooled to room temperature, and the chloroform layer was separated and washed with water. After the chloroform was removed by distillation, oily decanedioylcyclohexanone was obtained. The second step is the synthesis of disodium diketoeicosanedioate. Decanedioyldicyclohexanone in ethanol was added to the ethanol solution of sodium hydroxide at room temperature. The mixture was refluxed for 1 h. Colorless disodium diketoeicosanedioate was separated during stirring. The insoluble product was filtered off to obtain disodium diketoeicosanedioate. The final step is the synthesis of docosanedicarboxylic acid. Hydrazine hydrate was added to the triethanolamine solution of diketoeicosanedioate at 130 °C, and the mixture was refluxed for 4 h. Next, potassium hydroxide in triethanolamine was added to the mixture. The reaction mixture was heated at 200 °C for 9 h with stirring. After the reaction mixture was cooled to 100 °C, the mixture was washed out with hot water and acidified to a pH between 2 and 3 with 12 N hydrochloric acid. The reaction mixture was cooled to room temperature, and then the docosanedicarboxylic acid was precipitated and filtered off. The filter cake was washed with water and ethanol and recrystallized from 2-butanone to obtain docosanedicarboxylic acid. A series of other alkanedicarboxylic acids were prepared by the same procedure as that used for docosanedicarboxylic acid.

Benzophenone used as the triplet sensitizer was purified by recrystallization from ligroin several times and dried in vacuo.

Dichloromethane used as a solvent was purified as follows. Dichloromethane was washed with sulfuric acid and water and then washed with 10% sodium hydroxide aqueous solution and with water until it became neutral. Dried dichloromethane with calcium chloride was distilled twice over calcium hydride.

Laser Photolysis. An NEC SLG 2009 ruby laser was used for laser photolysis.[11] The concentrations of the deaerated sample solutions were in the range 5.0 × 10^{-4} to 2.0 × 10^{-3} mol/L with respect to the chromophore units. The concentration of benzophenone used as the triplet sensitizer was 2.5 × 10^{-3} mol/L for all sample solutions. Samples were excited by the second-harmonic pulse (347 nm, 16 ns, 3.02 × 10^{-8} einstein/pulse). The laser power was attenuated by a suitable combination filter so that optical density of $T_n \leftarrow T_1$ absorption was less than 0.2.

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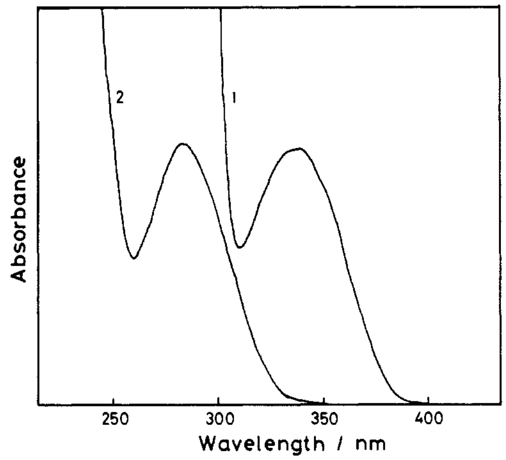

Figure 3. UV absorption spectra of benzophenone (1) and bichromophoric compounds (2) (n = 2–30) in dichloromethane. The spectra of all bichromophoric compounds are identical with the spectrum of 5-valeryl-DBA.

Under such conditions, the T–T annihilation process becomes negligibly small.

Photoirradiation. Photoirradiation was carried out for 0.5 h in the thermostat kept at 25 °C. A Toshiba 300 W high-pressure mercury lamp was used as the excitation source. A mercury line of 365 nm was selected through a combination of filters: a Toshiba UVD-2 and a Corning C.S. 0-52. The concentration of bichromophoric compounds in the deaerated solution was adjusted to be 2.0×10^{-3} mol/L with respect to the chromophore concentration. The concentration of benzophenone was 2.5×10^{-3} mol/L. All sample solutions were filled in a 1-cm quartz cell and deaerated by several freeze–pump–thaw cycles at ca. 10^{-6} Torr.

The number of photons at 365 nm was measured to be 1.89×10^{-9} einstein·cm^{-2}·s^{-1} by potassium ferrioxalate actinometry.[12]

Product Analysis. Inter- and intramolecular reaction products were analyzed by a Toyo Soda HLC 802 UR gel permeation chromatograph with double G2000HS columns eluted by THF. UV, IR, and NMR spectra of the reaction products were measured by a Shimadzu UV-200S double beam spectrophotometer, by a JASCO IR-G infrared spectrophotometer, and by a JOEL FX-90Q NMR spectrometer with TMS as an internal standard, respectively. The spectroscopic data for the obtained reaction products were as follows. IR spectra for the intra- and intermolecular products obtained in this study showed the same characteristic spectra: IR (KBr) 1660 (s, C=O), 1450 cm^{-1} (m, CH). All intermolecular reaction products showed the same characteristic ^{1}H and ^{13}C spectra whose chemical shifts were almost independent of their chain lengths: ^{1}H NMR (CD_2Cl_2) δ 1.2–2.5 (m, methylene H), 4.0 (s, methine H), 6.9 (s, ethylenic, H), 7.1–7.9 (m, aromatic H); ^{13}C NMR (CD_2Cl_2) δ 11.1–34.7 (methylene C), 48.6 (methine C), 128.1–141.8 (aromatic and ethylenic C), 173.2 (carbonyl C). For the cyclomers longer than n = 22, the NMR spectra were independent of chain lengths and gave the same characteristic patterns. The data were as follows: ^{1}H NMR (CD_2Cl_2) δ 1.5–2.6 (m, methylene H), 4.0 (s, methine H), 6.9–7.5 (m, aromatic H); ^{13}C NMR (CD_2Cl_2) δ 24.0–35.2 (methylene C), 48.7 (methine C), 128.1–142.8 (aromatic C), 173.3 (carbonyl C). On the other hand, the intramolecular cyclomers from n = 14 to 20 showed different patterns for methine signals of the cyclobutane ring; the signals affected by macrocyclic polymethylene chains[13] were split for these cyclomers. The data were as follows: δ 3.6–4.6 (q, ^{1}H NMR), δ 45.8–50.7 (^{13}C NMR) for DC-14; δ 3.7–4.3 (q, ^{1}H NMR), δ 47.3–49.9 (^{13}C NMR) for DC-16; δ 3.9–4.1 (d, ^{1}H NMR), δ 48.2–49.3 (^{13}C NMR) for DC-18; δ 3.9–4.0 (d, ^{1}H NMR), δ 48.6 (^{13}C NMR) for DC-20. It was found from their chemical shifts of methine proton signals that all cyclobutane rings of the photoproducts take anti configuration, by reference to the chemical shift of the methine proton signal of 5-acetyl-DBA dimer and 5-valeryl-DBA dimer (4.0 ppm),[3] which was identified as the anti-configuration dimer by X-ray crystallographic analysis.[8] A detailed study of the NMR spectra of the cyclomers will be published elsewhere.

Results and Discussion

Intra- and Intermolecular End-to-End Interactions Measured by Nanosecond Laser Photolysis. Absorption spectra of a series of DC compounds were measured in dichloromethane. Figure 3 shows the spectra of DC compounds together with that of a triplet sensitizer, benzophenone (BP). The spectra were independent of the chain length n and identical with that of the monomeric compound 5-valeryl-DBA. This indicates that the pair of terminal DBA groups of these bichromophoric compounds does not have any specific interaction in the ground state.

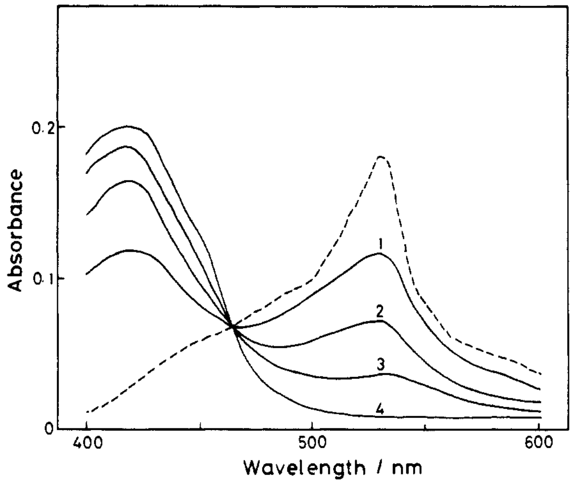

Figure 4. Benzophenone (BP)-sensitized $T_n \leftarrow T_1$ absorption spectra of bichromophoric compounds in dichloromethane at room temperature: (1) 100 ns after excitation, (2) 200 ns after excitation, (3) 300 ns after excitation, and (4) 600 ns after excitation. All absorption spectra are identical with that of the monomeric compound, 5-valeryl-DBA ([DBA] = 2.5×10^{-3} mol/L, [BP] = 2.0×10^{-3} mol/L). The $T_n \leftarrow T_1$ absorption spectrum of benzophenone is also shown for reference (- - -).

Intra- and intermolecular end-to-end interactions in the excited triplet state were examined by the nanosecond laser photolysis through the analysis of the deactivation processes of the excited triplet state. Figure 4 shows the time course of the benzophenone-sensitized $T_n \leftarrow T_1$ absorption spectra of a series of bichromophoric compounds in dichloromethane at room temperature, with the $T_n \leftarrow T_1$ absorption spectrum of benzophenone as the reference. The spectra of all DC compounds were identical and independent of the chain length n. Figure 4 shows that the $T_n \leftarrow T_1$ absorption of DC compounds at 420 nm increases with a decrease in the $T_n \leftarrow T_1$ absorption of benzophenone at 520 nm by T–T energy transfer, and that the benzophenone triplet is completely quenched by DC compounds at 600 ns after excitation. Since there is almost no overlap of $T_n \leftarrow T_1$ absorption of the DC compounds (400 nm) with that of benzophenone (520 nm), the decay curves at 400 and 520 nm can be unambiguously analyzed. For the analysis of the deactivation processes of the excited triplet state in the bichromophoric systems, the following sensitization scheme can be considered

$$\mathrm{BP} \xrightarrow{h\nu} {}^1\mathrm{BP}^* \rightarrow {}^3\mathrm{BP}^* \tag{1}$$

$$^3\mathrm{BP}^* \rightarrow \mathrm{BP} \qquad k_n^{\mathrm{s}} \tag{2}$$

$$^3\mathrm{BP}^* + \mathrm{DBA{-}DBA} \rightarrow \mathrm{BP} + {}^3\mathrm{DBA^*{-}DBA} \qquad k_t \tag{3}$$

where DBA—DBA represents a bichromophoric molecule in the ground state and ^{3}DBA*—DBA a triplet excited state of the DBA chromophore. In the above kinetic scheme, k_n^{s} is the sum of the rate constants for all unimolecular decay processes of the triplet benzophenone except for the interaction with other DBA chromophores, and k_t is the rate constant for the triplet–triplet (T–T) energy transfer from a benzophenone to a terminal DBA group. The excited triplet deactivation processes are given in eq 4–8. In

$$^3\mathrm{DBA^*{-}DBA} \rightarrow \mathrm{DBA{-}DBA} \qquad k_n \tag{4}$$

$$^3\mathrm{DBA^*{-}DBA} \rightarrow \mathrm{DBA{-}DBA} \qquad k_n^{\mathrm{intra}} \tag{5}$$

$$^3\mathrm{DBA^*{-}DBA} \rightarrow \mathrm{cyclomer} \qquad k_d^{\mathrm{intra}} \tag{6}$$

$$^3\mathrm{DBA^*{-}DBA} + \mathrm{DBA{-}DBA} \rightarrow 2\mathrm{DBA{-}DBA} \qquad k_n^{\mathrm{inter}} \tag{7}$$

$$^3\mathrm{DBA^*{-}DBA} + \mathrm{DBA{-}DBA} \rightarrow \mathrm{oligomer} \qquad k_d^{\mathrm{inter}} \tag{8}$$

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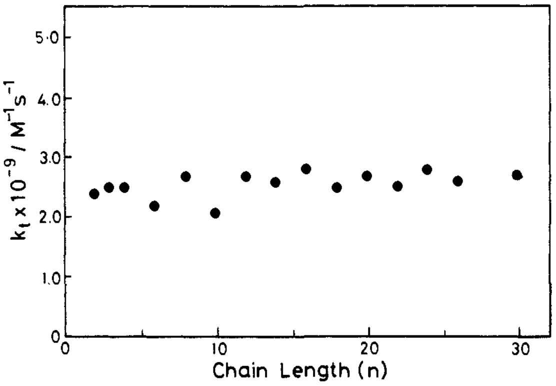

Figure 5. Chain length dependence of the rate constant of T–T energy transfer, k_t, from benzophenone to a terminal DBA group in dichloromethane at room temperature.

the above kinetic scheme, k_n is the sum of the rate constants for all unimolecular decay processes of the triplet state of DBA, k_n^{inter} the rate constant of the deactivation by intermolecular quenching, k_d^{inter} the rate constant of the intermolecular cycloaddition reaction, k_n^{intra} the rate constant of the triplet deactivation by intramolecular quenching, and k_d^{intra} the rate constant of the intramolecular cycloaddition reaction. The decay processes are roughly divided into two routes. One is the decay path in which excited triplet DBA groups are self-quenched and give no product, that is, self-quenching processes (eq 4, 5, and 7). The other is the decay path in which terminal DBA groups react and give the photoproducts (eq 6 and 8). Each decay path consists of an intermolecular and an intramolecular path. As described in the Experimental Section, the experimental condition in the laser photolysis was chosen in such a way that the T–T annihilation process is negligible.

The lifetime of benzophenone triplet (τ^D) excited by a low-intensity laser pulse was measured in the presence of several concentrations of the DC molecules which are the triplet energy acceptor of benzophenone. In this case, the Stern–Volmer equation for the lifetime of benzophenone triplet is expressed as follows

$$\tau_0^D/\tau^D = 1 + \tau_0^D k_t[\mathrm{DBA}] \qquad (9)$$

where τ_0^D is the lifetime of benzophenone triplet in the absence of an acceptor ($\tau_0^D = 3.6 \times 10^{-6}$ s), and [DBA] is the concentration of the DBA chromophore. The plot of τ_0^D/τ^D against several concentrations of the terminal DBA group for all DC compounds showed a straight line, and from the slope of the straight line the energy transfer rate constant k_t was obtained for each DC compound. Figure 5 shows the chain length dependence of the k_t values. In this figure, it is apparent that the rate constant of T–T energy transfer from benzophenone to the terminal DBA group is almost independent of the chain length within experimental error, and close to the diffusion-controlled rate constant. In the present reaction system, the molecular weight region of the bichromophoric compounds is 440 to 860. In such a molecular weight region, the diffusion rate is presumably not subjected to the influence of the molecular size.[14] Therefore, in the following discussion on the chain length dependence of the end-to-end cycloaddition reaction, the energy transfer efficiency is considered to be independent of chain length.

Next, the lifetime of the triplet state of the terminal DBA group, τ^A, in the bichromophoric system is represented by the following equation

$$1/\tau^A = k_n + k^{intra} + k^{inter}[\mathrm{DBA}] \qquad (10)$$

where k^{intra} is the sum of the rate constants of k_n^{intra} and k_d^{intra} ($k^{intra} = k_n^{intra} + k_d^{intra}$), k^{inter} the sum of k_n^{inter} and k_d^{inter} ($k^{inter} = k_n^{inter} + k_d^{inter}$), and [DBA] the concentration of the terminal DBA group. The lifetime of the excited triplet state of the terminal DBA group was measured for several concentrations by laser photolysis. The plot of $1/\tau^A$ against the concentration of the terminal DBA group gave a straight line for each DC compound.

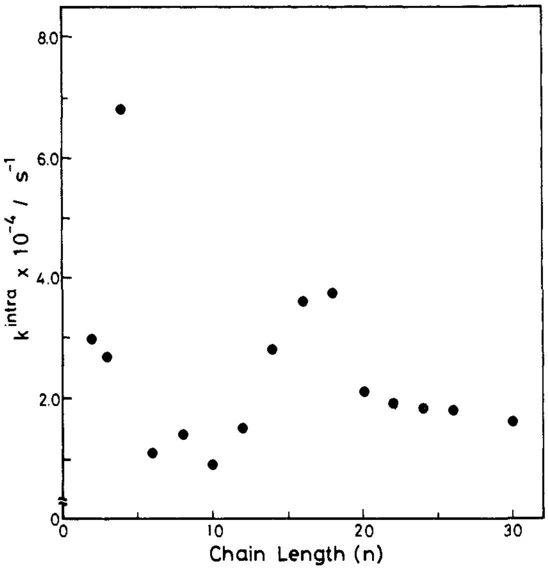

Figure 6. Chain length dependence of the rate constant of intramolecular interaction, k^{intra}, for the bichromophoric compounds at room temperature.

The intercept in the plot of $1/\tau^A$ against the terminal group concentration gave the $k_n + k^{intra}$ value in eq 10. The k^{intra} value for each bichromophoric compound was determined from the $k_n + k^{intra}$ value by the following procedure. Since the k_n value is considered to be inherent to the DBA group, the k_n value is presumed to be equal to the k_n^A value obtained for the monomeric compound, 5-valeryl-DBA: $k_n = k_n^A = 5.9 \times 10^{-4}$ s^{-1}.[3] Then, k^{intra} is obtained by subtracting the k_n value from $k_n + k^{intra}$. Figure 6 shows a plot of the k^{intra} value against chain length. It is clear that the k^{intra} value is strongly dependent on the chain length. This is a kind of genuine concentration quenching (self-quenching) of triplet states.[15] The interaction between the excited triplet of the DBA group and the ground state of the DBA group which leads to the photoproduct may dissipate the excited triplet state of DBA. The highest peak appears at the chain length $n = 4$. This means that a pair of terminal DBA groups attached to a polymethylene chain give rise to the strongest interaction at this chain length. In other words, a pair of terminal DBA groups take the most favorable position to interact with each other at this chain length. This differs from the $n = 3$ rule proposed by Hirayama,[16] who investigated intramolecular excimer formation in a bichromophoric system of α,ω-diphenylalkanes. In the present system, intramolecular interaction of a pair of terminal DBA groups separated by four methylene groups is much stronger than that by three methylene groups. This difference is considered to be due to the difference in terminal structure between the DBA system and the excimer formation system. That is, the molecular structure of the terminal DBA makes it difficult by the steric hindrance to take a sandwich parallel arrangement of two chromophores, since the terminal DBA has amide linkage whose geometry is not presumably planar and since two phenyl planes in a DBA ring are folded to be 144.4°.[8] As the result of this, a pair of bulky DBA chromophores demand a somewhat longer chain to interact intramolecularly with each other in a configuration deviated from the sandwich configuration.

In the range of the chain length $n = 6$–12, the k^{intra} values are very small compared with those for other chain lengths. This means that the polymethylene chains in this region can hardly take a favorable or stable ring conformation. These results are consistent with other types of intramolecular end-to-end reactions

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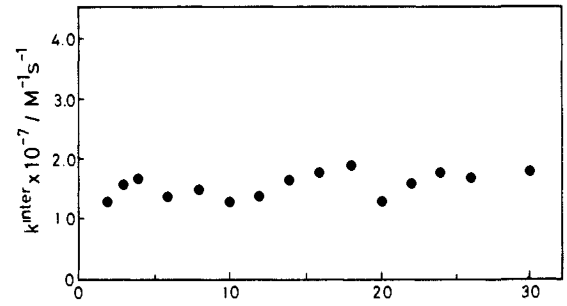

Figure 7. Chain length dependence of the rate constant of intermolecular interaction, k^{inter}, for the bichromophoric compounds in dichloromethane at room temperature.

reported by many investigators. In the region of chain lengths longer than $n = 14$, the k^{intra} value increases with increasing chain length, and the k^{intra} value reaches the maximum at the chain length $n = 18$. This fact indicates that a strong interaction occurs between a pair of terminal DBA groups with this extent of separation, too. At this chain length, the polymethylene chain takes a favorable conformation for terminal DBA groups to interact with each other. Theoretical approach to the intramolecular ring-closure reaction of a polymethylene chain in the region of these chain lengths was carried out by Sisido[17] and Winnik.[18] Sisido calculated statistically the ring-closure probability of a polymethylene chain employing the *g*–*t* rotational isomer model under the condition that the radius of the active sphere r_0 is 2.3–2.7 Å and conformations having any nonbonded C–C pairs closer than 2.77 Å (contact distance) are excluded, and he compared these results with the experimental results of lactone formation reaction from ω-oxy acids reported by Stoll and Rouvé.[19] He demonstrated that the observed values can be explained by statistical treatment and that the relative ease of cyclization is mainly determined by the conformational energy of activation; the ring-closure probability increases again with decreasing conformational energies in the longer chain region than $n \geq 14$. Our experimental results obtained by laser photolysis in the DBA system agree with this theoretical result, although the structure of the terminals is neglected in the theoretical model. The present experimental finding indicates that the ring-closure probability of a polymethylene chain also reaches a maximum at the chain length $n = 18$. This maximum of k^{intra} is called "the second peak". Winnik et al. carried out the theoretical approach to another cyclization reaction of polymethylene chains by a Monte-Carlo treatment:[18] they made the computer simulation of intramolecular hydrogen abstraction in *p*-benzophenonecarboxylate ester with hydrocarbon chains. With the theoretical treatment they could simulate the experimental results in which the site selectivity increases above the chain length $n \geq 9$.[20] They also demonstrated that the bulk of the benzophenone group, photoactive chromophore, should exert a major effect on the observed chemistry and pointed out that the steric factor of the photoactive group should be taken into consideration on the occasion of the theoretical treatment.

Next, the rate constant k^{inter} can be determined from the slope of the straight line. Figure 7 shows the chain length dependence of the k^{inter} value. In Figure 7, it is clear that the deactivation rate constant by intermolecular end-to-end interaction (the sum of intermolecular quenching and cycloaddition reaction) is independent of chain length. The absence of the influence of chain length on the rate constant k^{inter} is partly due to an activation-controlled process[21] and partly due to the rather small molecular weight.

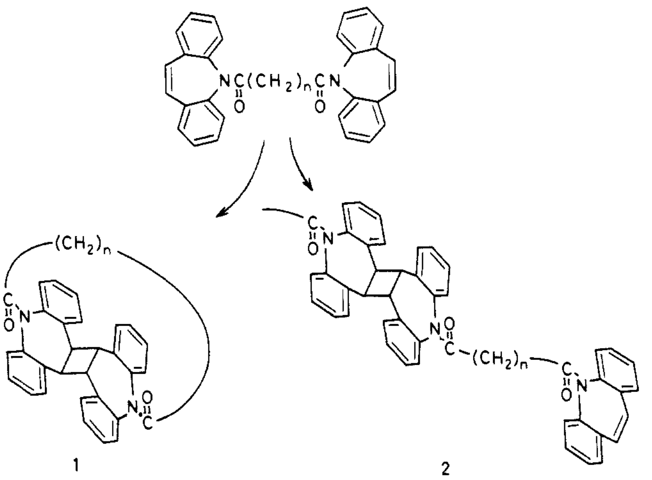

Figure 8. Structures of intramolecular ring-closure reaction product (1) and intermolecular reaction product (2).

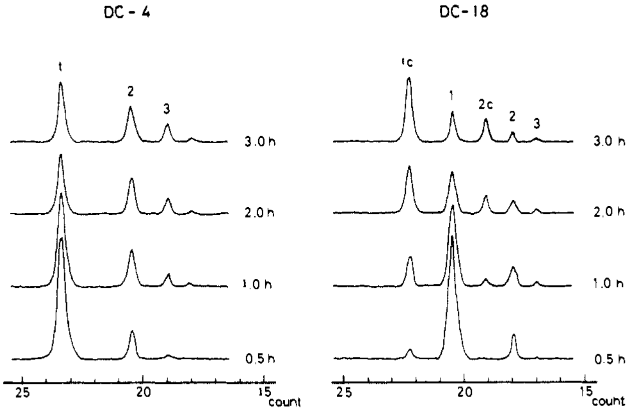

Figure 9. Typical GPC diagrams of photoirradiation products for bichromophoric compounds, DC-4 and DC-18: (1) monomer, (1c) cyclic monomer, (2) linear dimer, (2c) cyclic dimer, (3) linear trimer.

In this section, the interaction of two terminal DBA groups was investigated by the laser photolysis. For the shorter chains having $n \simeq 4$, it is reasonably assumed that a pair of chain ends are directed to the same direction (Figure 2, (1)). However, for the longer chain compounds it is possible to take two kinds of terminal structures: syn and anti configuration as shown in Figure 2. This problem is discussed in the next section through the result of intramolecular cycloaddition reaction.

Intra- and Intermolecular End-to-End Cycloaddition Reactions. A series of bichromophoric compounds, DC-*n* ($n = 2$–30), when they are excited by T–T energy transfer from benzophenone, have two kinds of reaction paths as described in the previous section. One is the way to the intermolecular reaction, which is a propagating step for photopolymerization.[2] The other is the way to the intramolecular ring-closure reaction. Figure 8 shows the product structures of these reactions schematically. Photochemical intra- and intermolecular end-to-end cycloaddition reactions have been carried out. The reaction products were analyzed and fractionated by GPC and identified by IR and NMR spectroscopy. Figure 9 shows some typical GPC diagrams of reaction products obtained after various irradiation times. In Figure 9, the residual monomers of DC-4 and DC-18 are detected at the 23.4 count and the 20.4 count, respectively. As for DC-4, the amount of unreacted monomer decreased gradually with increasing irradiation time, and at the same time, the formation of intermolecular dimers and trimers was detected at the 20.5 count and the 19.0 count, respectively. However, the intramolecular ring-closure product was never produced by irradiation of this compound, since the terminal DBA groups cannot take syn configuration intramolecularly owing to their steric hindrance as described before. On the other hand, for DC-18, the amount of unreacted monomer decreased gradually with increasing irradiation time, and the intermolecular dimer

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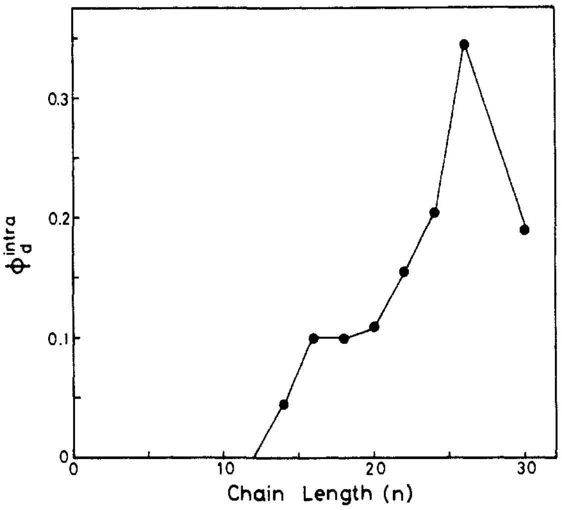

Figure 10. Chain length dependence of the quantum yield of intramolecular ring-closure reaction, Φ_d^{intra}, for bichromophoric compounds in dichloromethane at 25 °C.

and trimer were observed at the 17.9 count and the 17.0 count, respectively. Furthermore, a new signal, which was not observed for DC-4, was detected at the 22.2 count. This product was identified as an intramolecular ring-closure product. This product grew up gradually with increasing irradiation time. In addition, another new signal, which was not observed for DC-4, was observed at the 19.1 count. This product was identified as an intramolecular ring-closure product of the intermolecular dimer of DC-18. This product is formed by two consecutive reactions, that is, intermolecular addition of DC-18 followed by an intramolecular ring-closure reaction. Indeed, this signal became larger with increasing irradiation time, while the signal of intermolecular dimer decreased, which was formed within 0.5 h of irradiation. This indicates that the major part of the intermolecular linear dimer is transformed to a macroring as a result of intramolecular cycloaddition.

GPC analysis showed that the intramolecular ring-closure product was produced for the samples of chain length $n \geq 14$, but not for the samples of chain length $n = 2$–12. That is, for bichromophoric compounds having a shorter methylene chain, a pair of terminal DBA groups cannot undergo the intramolecular cycloaddition reaction. These experimental results can be explained in terms of the reactivity of a pair of terminal DBA groups. The DBA group forms only an *anti*-cyclobutane ring,[3,8] and for bichromophoric compounds having a shorter methylene chain than DC-14, a pair of terminal DBA groups cannot take a favorable orientation to form an *anti*-cyclobutane ring intramolecularly.

The quantum yields of both intra- and intermolecular cycloaddition reactions were determined by the quantitative analysis of the reaction products with GPC. In the benzophenone-sensitized system, the quantum yields of the formation of the intramolecular ring-closure product (Φ_d^{intra}) and intermolecular dimer (Φ_d^{inter}) are defined, as follows.

Φ_d^{intra} = the number of intramolecular ring-closure products/the number of photons absorbed by benzophenone

Φ_d^{inter} = the number of intermolecular dimer/the number of photons absorbed by benzophenone

As described in the previous section, the rate constant of T–T energy transfer from benzophenone to DC compounds, k_t, is almost independent of the chain length and is substantially constant. Benzophenone is selectively excited by the 365-nm mercury line as shown in Figure 3. Therefore, the efficiency of triplet energy transfer from benzophenone to the terminal DBA group of DC compounds is close to unity in the present experimental condition, and the values Φ_d^{intra} and Φ_d^{inter} are nearly equal to the quantum

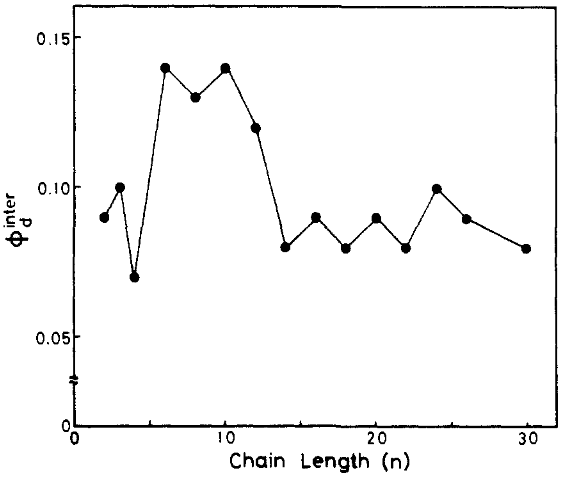

Figure 11. Chain length dependence of the quantum yield of intermolecular dimerization, Φ_d^{inter}, for bichromophoric compounds in dichloromethane at 25 °C.

yield defined by the ratio of the number of product molecules to the number of initial molecules in the excited triplet state through the sensitization.

The effect of chain length on the intramolecular ring-closure reaction was examined. Figure 10 shows the plot of the quantum yield of intramolecular ring-closure reaction against the chain length. The quantum yield increased gradually with increasing chain length and reached a maximum at $n = 26$. The chain length that gives the maximum quantum yield of intramolecular ring-closure reaction is different from that of the intramolecular end-to-end interaction, k^{intra}. In other words, the chain length for the maximum quantum yield of the intramolecular ring-closure reaction shifts to chains longer than that for the maximum intramolecular deactivation constant. The examination of the structure of the intramolecular ring-closure products shows that the terminal DBA groups form an *anti*-cyclobutane ring. This suggests that a pair of terminal DBA groups take the most favorable orientation for the *anti*-cyclobutane formation with the separation by polymethylene chain having $n = 26$. Therefore, the ring-closure probability for a pair of terminal bonds to be put in an opposite direction becomes maximum at $n = 26$.

These findings are also different from those obtained with other intramolecular end-to-end reactions such as thermal reaction,[22] electron transfer,[23] and excimer formation.[24] In the present DBA systems, a pair of terminal groups can react only in a definite orientation and gives an anti configuration product. Laser photolysis gives us information on overall end-to-end interaction of bichromophoric compounds. On the other hand, the reaction yield of this system reflects the ring-closure probability with a certain orientation of chain ends.

The quantum yield of the formation of the intramolecular ring-closure product, Φ_d^{intra}, is expressed by the following equation

$$\Phi_d^{intra} = (k_d^{intra}/(k_n + k^{intra} + k^{inter}[DBA]))\Phi(\text{triplet}) \qquad (11)$$

where Φ(triplet) is the quantum yield of DBA triplet formation and is almost unity irrespective of the chain lengths, $k_n \simeq 6 \times 10^4\ s^{-1}$, $k^{intra} = k_n^{intra} + k_d^{intra}$, and $k^{inter} = k_n^{inter} + k_d^{inter}$. The k^{inter} values are almost independent of the chain lengths (Figure 7); $k^{inter}[DBA] = (3\text{–}4) \times 10^4\ s^{-1}$, while the k^{intra} values depend on the chain length n as shown in Figure 6. The k_d^{intra} values can be estimated by eq 11, and the maximum k_d^{intra} value for DC-26 is $(4\text{–}5) \times 10^4\ s^{-1}$.

Next, the plot of the quantum yield of intermolecular cycloaddition reaction, Φ_d^{inter}, against chain length is as shown in Figure 11. In this figure, the Φ_d^{inter} values depend on chain length (n),

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although the values are small compared to the Φ_d^{intra} values. The Φ_d^{inter} values for the samples from $n = 5$ to 12 are larger than those for the samples $n \leq 4$ and $n \geq 14$. The Φ_d^{inter} is expressed by the following equation.

$$\Phi_d^{inter} = (k_d^{inter}[DBA]/(k_n + k^{intra} + k^{inter}[DBA]))\Phi(triplet) \qquad (12)$$

For the samples from $n = 5$ to 12, the k^{intra} values [$k^{intra} = (1-1.5) \times 10^4\ s^{-1}$] are smaller than those for other compounds [$k^{intra} = (2-7) \times 10^4\ s^{-1}$] as shown in Figure 6. Hence, the triplet lifetimes for the samples $5 \leq n \leq 12$ are longer than those for other compounds. Because of the longer lifetime, these samples $5 \leq n \leq 12$ have more chance to react with other DBA molecules intermolecularly than the other samples, and the Φ_d^{inter} values are higher in this region of chain lengths. The k_d^{inter} values estimated by eq 12 are almost constant: $(5-7) \times 10^6\ M^{-1}\ s^{-1}$ irrespective of the chain length. The chain length dependence of Φ_d^{inter} is a reflection of the triplet lifetime of these bichromophoric compounds.

In the present work, the highest ring-closure probability was estimated to be $n = 18$ by laser photolysis. This experimental fact was explained without taking into consideration the direction of the terminal bonds. On the other hand, the maximum quantum yield for the ring-closure reaction appears at a longer chain length, $n = 26$, because the terminal bonds must point in opposite directions to each other in order to take anti configuration. The chain length that yields the maximum quantum yield for the intrachain reaction shifts to chains longer than "the second peak" reported for other polymethylene systems. In the present reaction system, the steric factor of a pair of terminal groups must be considered in the examination of intramolecular reaction probability. It is concluded that the reaction yield of the intramolecular ring-closure reaction is determined by the equilibrium ring-closure probability of a molecular chain with a certain direction of terminal bonds.

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Binding Sites of Pyrene and Related Compounds and Chiral Excimer Formation in the Cavities of Cyclodextrins and Branched Cyclodextrins

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Abstract: Circular dichroism (CD) and circularly polarized fluorescence (CPF) spectra reveal the formation of the intermolecular dimer of pyrene having left-handed chirality and intramolecular dimers of 1,3-dinaphthylpropanes having right-handed chiralities in the γ-cyclodextrin cavity. These guest molecules are estimated to be bound to the relatively hydrophobic primary hydroxyl group side of the γ-cyclodextrin cavity, while the more hydrophilic secondary hydroxyl group side is the binding site of the chiral pyrene dimer in the 6-*O*-α-maltosyl-γ-cyclodextrin cavity because the narrower side of the cavity is capped by the maltosyl group. The pyrene dimer in the branched γ-cyclodextrin exhibits right-handed chirality.

One of the recent topics of cyclodextrin chemistry is utilization of cyclodextrins for chiral recognition,[1-4] enantioselective reactions,[5,6] asymmetric syntheses,[7-10] and separation of stereoisomers, diastereomers, and enantiomers.[11,12] Such research subjects are very interesting from the viewpoint of enzyme models and are important for developing the use of the cyclodextrins into new enzyme-mimetic reactions. In a previous paper, we reported the asymmetric formation of the pyrene excimer (or dimer) in cyclooctaamylose (γ-cyclodextrin, γ-CDx) cavity.[13] The present paper reports the formation of the chiral dimers of the achiral arenes as well as the binding sites of these arenes in the cyclodextrin cavities in greater detail.

It is known that a pyrene molecule binds to a cycloheptaamylose (β-cyclodextrin, β-CDx) molecule to form a 1:1 complex that exhibits only the pyrene monomer fluorescence,[14-21] while γ-CDx, with a larger cavity size, organizes the pyrene molecules in its cavity resulting in the observation of excimerlike fluorescence.[22-24] The stoichiometry of the pyrene–γ-CDx complex has not been clarified as yet.[25,26] Most of the studies concerning the pyrene–cyclodextrin complexes do not deal with the structures of the inclusion complexes in water. In order to understand the mechanism for formation of the chiral pyrene excimer in γ-CDx cavity, we have to know, at least, the binding site of the pyrene molecules in the cavity. In the present study, we first evaluated the binding

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