

Topochemical "Double" Photocyclodimerization of the 1,4-Dicinnamoylbenzene Crystal

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Abstract: The 1,4-dicinnamoylbenzene crystal (**1**) dimerizes on photoirradiation into 21,22,23,24-tetraphenyl-1,4,11,14-tetraoxo-2(3),12(13)-diethano[4.4]paracyclophane (**3**) in an extremely high yield through the intermediate dimer **2** by "double" cyclodimerization with a small amount of the oligomers **4**. The paracyclophane **3** has a tricyclic structure with two δ -type cyclobutane rings for which the configuration was determined on the basis of the crystal structure of **1**, the simulation of the ^1H NMR spectrum of **3**, and the HPLC analysis of **3** with chiral affinity gel. In the crystal of **1** the reacting molecular pair is arranged in a skewed position, and the distances between the intermolecular photoadductive carbons are 3.973 and 4.086 Å for one cyclobutane ring and 3.903 and 3.955 Å for the other. The two observed topochemical processes, which lead to the formation of **3** and **4**, can be reasonably interpreted from the molecular arrangement in the starting crystal **1**. The morphology changes from the crystalline state to the nearly amorphous state during the reaction. The final conversion decreases greatly with decreasing the irradiation temperature below about room temperature. This behavior is interpreted to result from crystal-lattice controlled photocycloaddition at an early stage, followed by nontopochemical miscellaneous reactions. An induction mechanism to form **3** is suggested in order to rationalize the extraordinary high yield of **3**. Another new type of cyclophane, 21,22,23,24-tetraphenyl-2(3),12(13)-diethano[4.4]paracyclophane (**5**), was derived successfully by reducing **3** with triethylsilane.

The hypothesis of the crystal lattice controlled reaction of cinnamic acid crystals¹ was visualized by Schmidt and co-workers, who correlated the crystal structure of several olefin derivatives with their photoreactivity and the configuration of the products.² In these olefinic crystals the potentially reactive double bonds are oriented parallel to each other and separated by approximately 4 Å, which is favorable for a [2 + 2] cycloaddition reaction with a minimum of atomic and molecular motions. In general, the environment of olefinic double bonds in these crystals conforms to one of three principal types: (a) the α -type crystal, in which the double bonds of neighboring molecules make contact at a distance of ≈ 3.7 Å across a center of symmetry to give a centrosymmetric dimer ($\bar{1}$ dimer); (b) the β -type, characterized by a lattice having one axial length of 4.0 ± 0.1 Å between translationally related molecules to give a dimer of mirror symmetry (*m* dimer); and (c) the photochemically inactive γ -type crystal in which no double bonds of neighboring molecules are within 4.2 Å.

On the basis of crystallographic and mechanistic results,^{3,4} it was established that in a typical topochemical photodimerization reaction, transformation into the product crystal is performed under a thermally diffusionless process with retention of space group of the starting crystal. At present it is common knowledge that the photoreactivity and the stereochemistry of photoproduct are predictable from crystallographic information of starting olefin substrates.

[2 + 2] photocyclodimerization of olefinic crystals has been widely applied to the topochemical cycloaddition polymerization of a great number of diolefinic crystals by the so-called "four-center type photopolymerization reaction".⁴ Preparative study on the four-center type of photopolymerization demonstrated that the crystalline state photodimerization of olefins such as stilbazol and cinnamic, α -cyanocinnamic, or 5-phenyl-2,4-pentadienoic acid derivatives could be extended with a high probability to the crystalline state photopolymerization of rigid linear monomers having two dimerizable olefinic units which are mutually conjugated through the 1,4-arylene group in a single molecule. This empirical rule suggests that in the crystallization processes of photoreactive olefins and photopolymerizable rigid conjugated diolefins, a common intermolecular affinity plays a very important role in producing the photoreactive molecular arrangement in

resulting crystals. Such an affinity was rationalized for the crystal structure of several mono- and diolefins.³ However, no successful photocyclopolymerization reaction has been reported on bis-(benzalacetophenone) type conjugated diolefin crystals though several photodimerization reactions of benzalacetophenone derivatives are known to occur as a topochemical reaction.⁵

We have investigated the photochemical reactivity of several diolefin crystals in which two benzalacetophenone groups are conjugated. From these studies it was found that, on photoirradiation, the crystal of 1,4-dicinnamoylbenzene (1,4-DCB) (**1**)⁶ gave a tricyclic dimer, 21,22,23,24-tetraphenyl-1,4,11,14-tetraoxo-2(3),12(13)-diethano[4.4]paracyclophane (**3**) in a high yield through an intermediate dimer **2** by a "double" photocycloaddition with a small amount of oligomeric products **4**. From crystallographic results it was concluded that in the photoreaction of a crystal of **1** two topochemical processes proceeded competitively in a single crystal. That is, the intramolecular ring-closure and the intermolecular oligomerization of the intermediate dimer **2** proceeded to form either the tricyclic dimer **3** or the oligomers **4**.

Here we report on the photochemical behavior of 1,4-DCB (**1**) in the crystalline state, and we discuss the results obtained on the basis of the topochemical principles.⁷

Experimental Section

Preparation and Photoreaction of Bis-Enone Derivatives. Five derivatives, 1,4-DCB (**1**),⁸ 1,3-dicinnamoylbenzene (1,3-DCB),⁹ bis(4-cinnamoylphenyl)methane (BCPM), 4,4'-dicinnamoylstilbene (DCS),

(1) Bernstein, H. I.; Quimby, W. C. *J. Am. Chem. Soc.* **1943**, *65*, 1845.

(2) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1969. For a review see: Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

(3) Nakanishi, H.; Hasegawa, M.; Sasada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 173.

(4) Hasegawa, M. *Adv. Polym. Soc.* **1982**, *42*, 1; *Chem. Rev.* **1983**, *83*, 507.

(5) For example, see: Ravinovich, D.; Schmidt, G. M. J. *J. Chem. Soc. (B)*, **1970**, 6.

(6) For the IUPAC nomenclature 1,1'-(1,4-phenylene)bis(3-phenyl-2-propen-1-one).

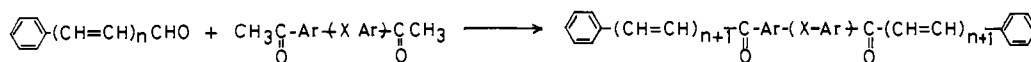
(7) For previous reports on this week see: Hasegawa, M.; Nohara, M.; Saigo, K.; Mori, T.; Nakanishi, H. *Tetrahedron Lett.* **1984**, *25*, 561. Hasegawa, M.; Saigo, K.; Mori, T. *Rad. Chem. Polym. Symp.* **1984**, *266*, 255.

(8) Tsukerman, S. V.; Nikitchenko, V. M.; Maslennikova, V. P.; Bondarenko, V. E.; Lavrushin, V. F. *Khim. Geterotsikl. Soedin.* **1968**, 1093 [*Chem. Abstr.* **1969**, *70*, 87653g].

(9) Nikitchenko, V. M.; Staroverov, V. M.; Lavrushin, V. F. *Ukr. Khim. Zh.* **1975**, *41*, 519 [*Chem. Abstr.* **1975**, *83*, 4250h].

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Table I. Preparation of Bis-Enone Derivatives^a

Ar-(X-Ar)-	reaction condition of aldol condensation	yield (crude, %)	mp, °C (recryst solv)	ref for prep
1,4-phenylene (1,4-DCB), <i>n</i> = 0	rt, 2 h/alkaline, dioxane-H ₂ O-EtOH	≈ 100	211-212 (benzene)	8
1,3-phenylene (1,3-DCB), <i>n</i> = 0	rt, 5 h/alkaline, dioxane-H ₂ O-EtOH	20	149-150 (benzene)	9
4,4'-methylenediphenyl (BCPM), <i>n</i> = 0	rt, 13 h/acidic, no solvent	90	160-161 (ethanol)	new compound
4,4'-ethylenediphenyl (DCS), <i>n</i> = 0	rt, 54 h/acidic, THF-H ₂ O-EtOH	73	235-237 (benzene)	new compound
1,4-phenylene (1,4-BPPB), <i>n</i> = 1	rt, 2 h/alkaline, dioxane-H ₂ O-EtOH	87	205-207 (benzene)	new compound

^a 1,4-DCB (1): lit.⁸ mp 214 °C; ¹H NMR (Me₂SO-*d*₆) δ 8.31 (s, 4 H), 8.00 (d, 2 H, *J* = 16 Hz), 7.39 (m, 4 H), 7.81 (d, 2 H, *J* = 16 Hz), 7.49 (m, 6 H); IR (KBr) 1650, 1570, 760, 700 cm⁻¹; UV (CH₂Cl₂) λ_{max} 322 nm (ε 4.5 × 10⁴); X-ray diffraction peaks 2θ—9.2, 13.9, 15.4, 18.6, 20.0, 24.3, 27.8, 32.8°. 1,3-DCB: ¹H NMR (Me₂SO-*d*₆) δ 8.74 (s, 1 H), 8.44 (m, 2 H), 8.04 (d, 2 H, *J* = 16 Hz), 7.95 (m, 4 H), 7.83 (d, 2 H, *J* = 16 Hz), 7.80 (t, 1 H, *J* = 8 Hz), 7.49 (m, 6 H); IR (KBr) 1660, 1570, 755 cm⁻¹. BCPM: ¹H NMR (CDCl₃) δ 7.2-8.1 (m, 22 H), 4.1 (s, 2 H); IR (KBr) 1655, 1570, 755 cm⁻¹; MS *m/e* 428 (M⁺). DCS: ¹H NMR (Me₂SO-*d*₆) δ 8.23 (d, 4 H, *J* = 9 Hz), 8.01 (d, 2 H, *J* = 16 Hz), 7.93 (m, 4 H), 7.88 (d, 4 H, *J* = 9 Hz), 7.78 (d, 2 H, *J* = 16 Hz), 7.62 (s, 2 H), 7.48 (m, 6 H); IR (KBr) 1650, 1570, 1560, 770 cm⁻¹. Anal. Calcd for C₃₂H₂₄O₂: C, 87.25; H, 5.49. Found: C, 87.50; H, 5.19. 1,4-BPPB: IR (KBr) 1642, 1572, 1000, 815 cm⁻¹; MS *m/e* 390 (M⁺). Anal. Calcd for C₂₈H₂₂O₂: C, 86.13; H, 5.68. Found: C, 86.41; H, 5.47. rt = room temperature.

and 1,4-bis(5-phenyl-2,4-pentadienyl)benzene (1,4-BPPB) were prepared by aldol condensation of the corresponding diacetyl derivatives with benzaldehyde or cinnamaldehyde in acidic or in alkaline medium as shown in Table I. An appropriate ratio of the solvent mixture was necessary in order to maintain a homogeneous, clear solution except for the case of BCPM where an excess amount of benzaldehyde made the solution clear during the condensation.

To examine the photoreactivity the finely dispersed sample crystals in heptane or in H₂O were irradiated by a 100W high-pressure mercury lamp (EIKOSHA EHB-WU- or -WF-100) with rigorous stirring for a few to several tens of hours at room temperature. Of the photochemically inactive crystals, in addition to the photoirradiation at elevated temperatures, the crystal modification into the photoreactive crystals was attempted by recrystallization from various solvents.

As a result, only the 1,4-DCB crystal (1) showed an obvious reactivity; as a typical photoreaction the finely powdered crystals of 1 (2.04 g) were irradiated in heptane (400 mL) under an argon current at 20–25 °C for 9 h. The starting crystal was made nearly amorphous as determined by X-ray powder diffraction analysis (RIGAKU Rotaflex RU-200). The products were collected by filtration and dried (1.85 g). The separation of the products by silica gel column chromatography (CH₂Cl₂, WAKO Gel C-200) gave colorless powder (1.174 g, 58% based on initial weight of 1) as a major product (3), the starting material (1) (7%), and a mixture of oligomers (4). 3: mp 348–352 °C dec, reprecipitated from THF-hexane; X-ray diffraction peaks 2θ 9.6, 12.5, 14.5, 16.6, 17.8, 19.4, 20.4, 22.0, 23.2, 23.9, 25.3, 27.0, 27.8, and 29.3°.

All the photoproduct samples as-prepared, irradiated at any temperatures between 50 and –10 °C, were nearly amorphous (2θ: two fairly sharp peaks at 10.2 and 15.3°). The yield of 4 was determined from the difference between the total conversion and the yield of 3.

For the study of time vs. conversion curve and of the temperature dependence of product ratios, a specified amount (2.0 g) of the crystal 1, which was finely powdered and dispersed by constant stirring in a specified amount of heptane or H₂O/ethanol, was irradiated at various temperatures. Continuous change of crystallinity was monitored by DSC-TG curves (RIGAKU CN 8085 EL) and ¹H NMR spectra (HITACHI R-40, 90 MHz) along with the photoreaction. A spectroirradiator, composed of a 2000 W xenon lamp and a grating monochromator (JASCO CRM-FM), was used for the study of wavelength dependence.

Structure Determination of Tricyclic Dimer 3 and Oligomers 4. 3: ¹H NMR (Me₂SO-*d*₆) δ 7.74 (pseudo-d, 4 H, *J* = 8 Hz), 7.38 (m, 20 H), 7.27 (m, 4 H), 4.24 (pseudo-d, 4 H, *J* = 9 Hz), 4.11 (pseudo-d, 4 H, *J* = 9 Hz); IR (KBr) 1675, 915, 750, 700 cm⁻¹; UV (CH₂Cl₂) λ_{max}²⁶⁷ (ε 2.55 × 10⁴), 232 (ε 1.92 × 10⁴) nm; MS *m/e* 676 (M⁺). Anal. Calcd for C₄₈H₃₆O₄: C, 85.18; H, 5.36. Found: C, 85.29; H, 5.42.

In order to determine the configuration of 3 the ¹H NMR spectrum (JEOL GX-400, 400 MHz) was compared with the simulated ¹H NMR curve. The simulation work was performed by using the modified LAOCOON III program¹⁰ of the coupling constants of cyclobutane protons.

Moreover, HPLC analysis of 3 was carried out by chiral affinity gel (MeOH, DAICEL Chiralpak OP) in order to confirm a racemic modification of 3.

Quantitative determination of 1 and 3 was carried out by GPC analysis with *p*-terphenyl as an internal standard (THF, TOYOSODA TSK-GEL Type 63000 HXL and 62500 HXL). On the determination of the photoproducts by GPC curves, 2 was included in 3. The oligomers 4 were separated from 1, 2, and 3 by column chromatography, followed by reprecipitation from a THF solution with hexane. The oligomers 4 thus isolated were submitted to ¹H NMR, IR, and UV spectroscopies. 4: ¹H NMR (Me₂SO-*d*₆) δ 7.85, 7.67, 7.45, 7.24, 7.12, 5.05, 4.90, 4.53, 4.17, 3.80; IR (KBr) 1670, 1225, 755, 700 cm⁻¹; UV (CH₂Cl₂) λ_{max} 265, 310 nm.

The number average molecular weight of 4 was approximately estimated from GPC curves with the monodispersed polystyrene samples (1.07 × 10⁵, 4.39 × 10⁴, 1.67 × 10⁴, 6.2 × 10³, and 2.8 × 10³) and the polystyrene oligomer mixtures (monomer–pentamer) as standards. The oligomer having the number average molecular weight below ca. 2300 by GPC was correlated to the molecular weight by VPO measurement (CORONA 117). In GPC curves the oligomer peaks were seen at 1040, 1420, 1820, and 2270 of the molecular weight that were estimated from the styrene oligomers. These peaks were attributed to the trimer–hexamer of 1 (mol wt 1014, 1352, 1690, and 2028), respectively, by the VPO measurement.

Crystal Structure Determination of 1,4-DCB (1). The crystallographic analysis of 1 was carried out on the crystal, 0.35 × 0.35 × 0.04 mm, by a Nicolet automated four-circle diffractometer (graphite-monochromated Cu Kα radiation λ = 1.5418 Å). Crystal data: *M*_r = 338.4 triclinic; *P*1; *a* = 5.798 (1) Å, *b* = 7.923 (1) Å, *c* = 19.307 (6) Å; α = 89.12 (2)°, β = 82.12 (2)°, γ = 88.67 (1)°; *V* = 878.2 (4) Å³; *D*_m = 1.28, *D*_x = 1.280 Mg m⁻³; *z* = 2, *R* = 0.050 for 2014 diffractometer-measured intensities. Further details on crystallographic results were described in an earlier paper.¹¹

Preparation of 21,22,23,24-Tetraphenyl-2(3),12(13)-diethano[4.4]-paracyclophane (5). The dimer 3 (1.694 g, 2.5 mmol) was treated with triethylsilane (3.5 mL, 22 mmol) in trifluoroacetic acid (7.44 mL, 100 mmol) with stirring at room temperature for 153 h. Additional amounts of trifluoroacetic acid (3.5 mL) and carbon tetrachloride (10 mL) were added by a few installments during the reaction. Then the solution was neutralized with aqueous saturated NaHCO₃ solution (550 mL) and extracted with ether twice. After the ethereal extracts were combined and dried with MgSO₄, the solvent was removed under reduced pressure to yield the residue (1.587 g). The pure product 5 (0.449 g, 37%) was obtained from the crude product (1.236 g) through the column chromatographic separation (benzene, WAKO Gel C-200). 5: mp 254–255 °C (crystallized from benzene); ¹H NMR (CDCl₃) δ 7.2–7.4 (m, 20 H), 6.57 (s, 8 H), 2.8–3.4 (m, 8 H), 2.3–2.8 (m, 8 H); IR (KBr) 1595, 750, 700 cm⁻¹; UV (dioxane) λ_{max} 264 (ε 3.1 × 10³), 270 (ε 2.6 × 10³) nm; MS *m/e* 620 (M⁺). Anal. Calcd for C₄₈H₄₄: C, 92.86; H, 7.14. Found: C, 93.33; H, 6.70.

(10) LAOCOON III program [Montaudou, G.; Cacamese, S.; Librando, V. *Org. Magn. Reson.* 1974, 6, 534] modified by Associate Prof. T. Hirano, Faculty of Engineering, The University of Tokyo.

(11) Nakanishi, H.; Hasegawa, M.; Mori, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 1984, C40, 509.

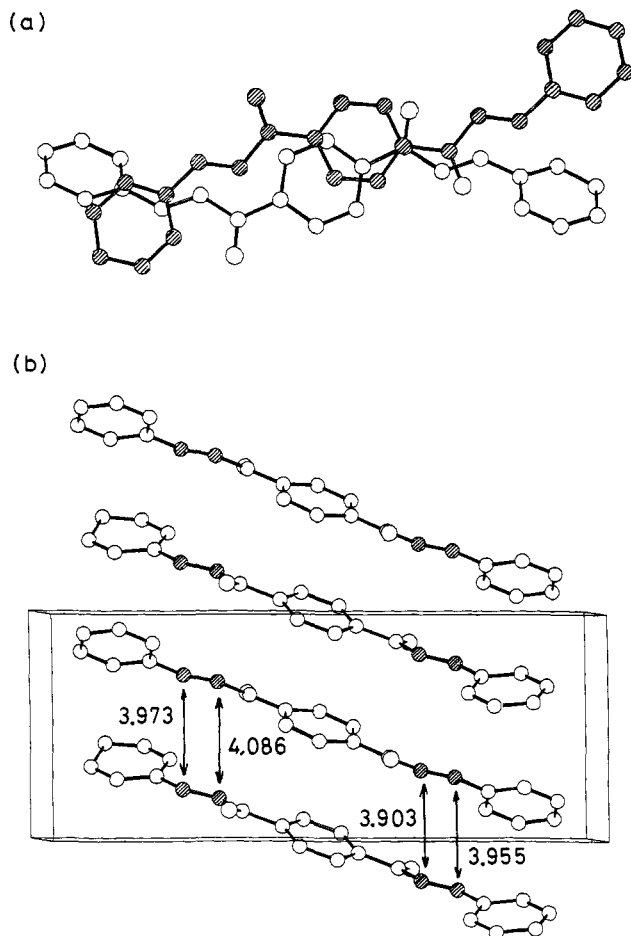


Figure 1. The crystal structures of **1** projected onto (a) the plane of central benzene and (b) the (100) plane.

Results and Discussion.

Photochemical Behavior of 1,4-DCB (**1**) in the Crystalline State.

In the present study we found that 1,4-DCB (**1**) was highly reactive with an extremely high stereoselectivity on photoirradiation in the crystalline state. The fine crystals of **1** were converted into greater than 85% of photoproducts containing 68% of the tricyclic dimer **3** in a laboratory dish with agitation under sunlight for 43 days (during the winter time in Tokyo). Although a great number of studies have been made on the photocyclodimerization of benzalacetophenone derivative crystals and on the photocycloaddition polymerization of diolefinic crystals⁴ ("four-center-type photopolymerization"), no report has been made on the photo-reactive bis(benzalacetophenone) type diolefin crystals. Indeed, we have reported that the 1,4-bis(3-oxo-3-phenyl-1-propenyl)-benzene crystal is photostable.¹² Therefore, the present result may be the first example of a photoreactive bis(benzalacetophenone) type crystal.

The structure of **3** was confirmed by UV (λ_{\max} of **1** 322 nm, λ_{\max} of **3** 267 nm) and IR spectra and by a quantitative assignment of ¹H NMR spectrum (see Experimental Section).

Only a few reports have appeared on such double [2 + 2] cycloadditions of diolefinic compounds in the crystalline state, including brief descriptions of the reactions of bis(3,4-dichlorostyryl) ketone¹³ and of carbonyldiacrylic acid¹⁴ and its methyl ester.¹⁵

The reaction of crystal **1** appears to be unique in two aspects: (1) the reacting two olefinic bonds in **1** are mutually conjugated

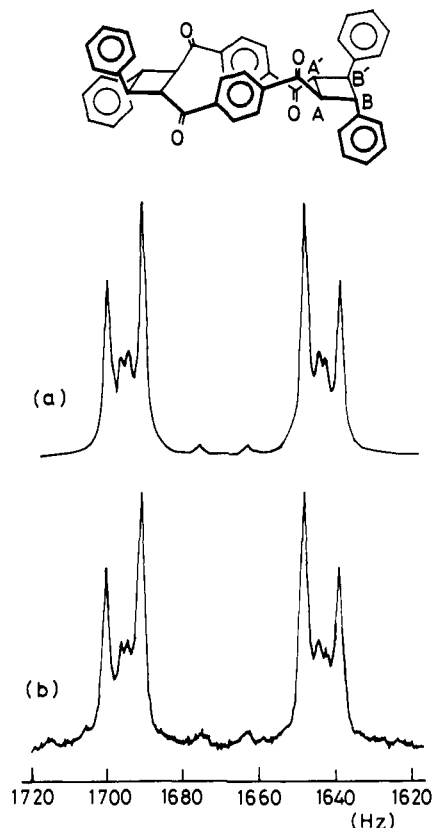


Figure 2. (a) Calculated and (b) experimental ¹H NMR spectra of cyclobutane protons of **3** at 400 MHz. Coupling constants: $J_{AA'} = 9.609$ Hz, $J_{AB} = 9.227$ Hz, $J_{AB'} = 0.011$ Hz, and $J_{BB'} = 9.609$ Hz.

through the terephthaloyl group and (2) a linear high polymer is not obtained but instead the tricyclic dimer **3** is formed as a major photoproduct. Hence, the photoreaction of **1** can be considered to be a useful synthetic route for tricyclic paracyclophane.

During the photoreaction the morphology changes from the crystalline in **1** to the nearly amorphous in the final photoproduct.

Crystal Structure of 1. The crystal structures of **1** projected onto (a) the plane of central benzene and (b) the (100) plane are shown in Figure 1.

It can be seen that the reacting molecular pair is arranged in a skewed position, and the distances between the intermolecular photoadditive carbons are 3.973 and 4.086 Å for one cyclobutane ring and 3.903 and 3.955 Å for the other. The two observed topochemical processes, which form either **3** or the oligomers **4**, can then be reasonably interpreted from the molecular arrangement in the starting crystal **1**. In general the symmetries resulting from the parallel orientation lead to photocyclodimerization reaction of the double bonds. Therefore, the dimerization of **1**, which is regarded as having a pseudo-two-fold axis symmetry, is an unusual photochemical reaction because a non-parallel arrangement is present without any symmetry in the reacting carbon-carbon double bonds. Such an arrangement for a reacting system is rare and has only been reported recently for a few crystals such as 7-methoxycoumarin.¹⁶ In a recent paper,¹⁷ we reported the crystal structure of photodimerizable 4-formylcinnamic acid in which the shortest distance between photoadditive double bonds is extraordinary large (4.825 Å) for photoreactive crystals of cinnamic derivatives. Therefore, reconsideration on topochemical principles concerning the effects of distance and relative arrangement between the intermolecular double bonds may be desirable.

Configuration of 3. Unsuccessful preparation of single crystals of **3** for X-ray crystallographic analysis led us to study the coupling

(12) Suzuki, F.; Suzuki, Y.; Nakanishi, H.; Hasegawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 2319.

(13) Green, B. S.; Schmidt, G. M. *J. Tetrahedron Lett.* **1970**, 4249.

(14) Midorikawa, H. *Bull. Chem. Soc. Jpn.* **1953**, *26*, 302.

(15) Stobbe, H.; Farber, E. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 1548.

(16) Ramasubbu, N.; Row, T. N. G.; Venkatesan, K.; Ramamurthy, V.; Rao, C. N. R. *J. Chem. Soc., Chem. Commun.* **1982**, 178.

(17) Nakanishi, H.; Hasegawa, M.; Mori, T. *Acta Crystallogr.*, in press.

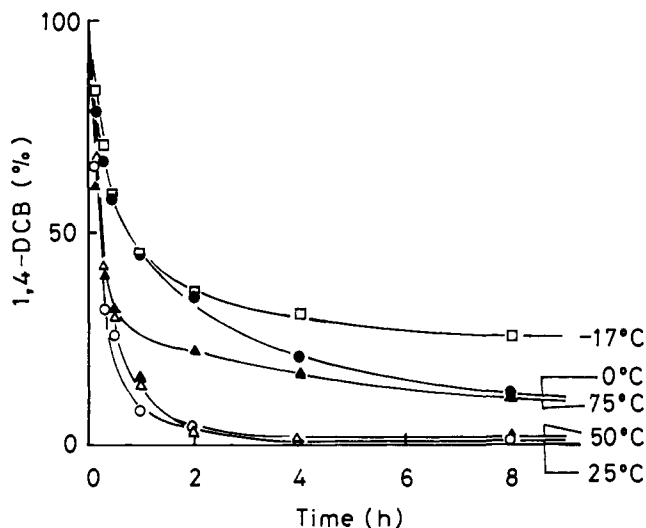


Figure 3. Photochemical conversion of 1 along with the irradiation time at various temperatures.

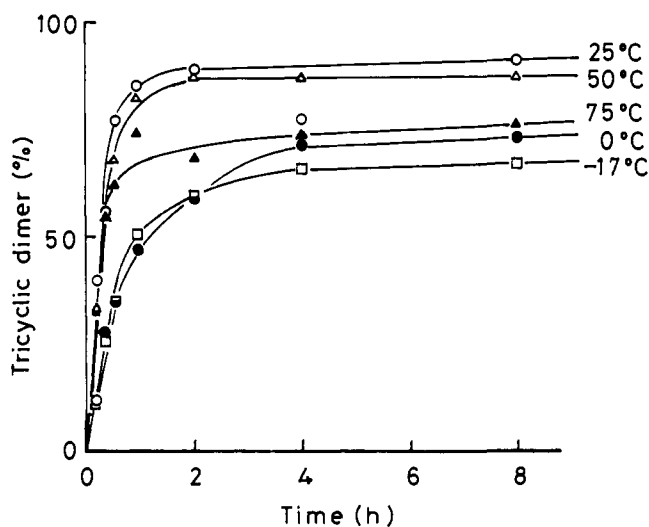


Figure 4. Yields of 3 along with the irradiation time at various temperatures.

constants of the cyclobutane protons in 3 with a modified LAOCOON III program.¹⁰ The derived ¹H NMR spectrum based on calculation is shown in Figure 2 together with the experimental spectrum.

These two spectra are almost identical and display high values for $J_{AA'}$, J_{AB} , and $J_{BB'}$, indicating that the configuration of the cyclobutane ring in 3 is $1\alpha, 2\beta, 3\alpha, 4\beta$, which is in accord with the configuration predicted from the molecular arrangement in the crystal of 1. The HPLC analysis showed two peaks with a 45:55 area ratio, the former of which corresponded to the dextrorotatory isomer at 365 nm and the later to the levorotatory one, indicating that 3 is a racemic modification. By these results the δ -type cyclobutane structure of 3 is concluded. The formation of a δ -type cyclobutane ring is extremely rare in the crystalline state photoreaction of olefin derivatives, and only one example has been previously reported on 1,1'-(trimethylene)bisthymine.¹⁸ However, the photodimerization of 1 is the first report in which δ -type cyclobutane derivatives are produced topochemically in a preparative scale. The photoproduct derived from 1, the new tricyclic [4.4]paracyclophane 3, has δ -type cyclobutane rings and no alternating axis of symmetry, showing that it is chiral, and the oligomers 4 have a zigzag shaped rigid chain structure of alternative ($1S^*, 2S^*, 3R^*, 4R^*$) and ($1R^*, 2R^*, 3S^*, 4S^*$) structures.

(18) Leonard, J. K.; McCredie, R. S.; Logue, M. W.; Cundall, R. C. *J. Am. Chem. Soc.* 1973, 95, 2320. Frank, J. K.; Paul, I. C. *J. Am. Chem. Soc.* 1973, 95, 2323.

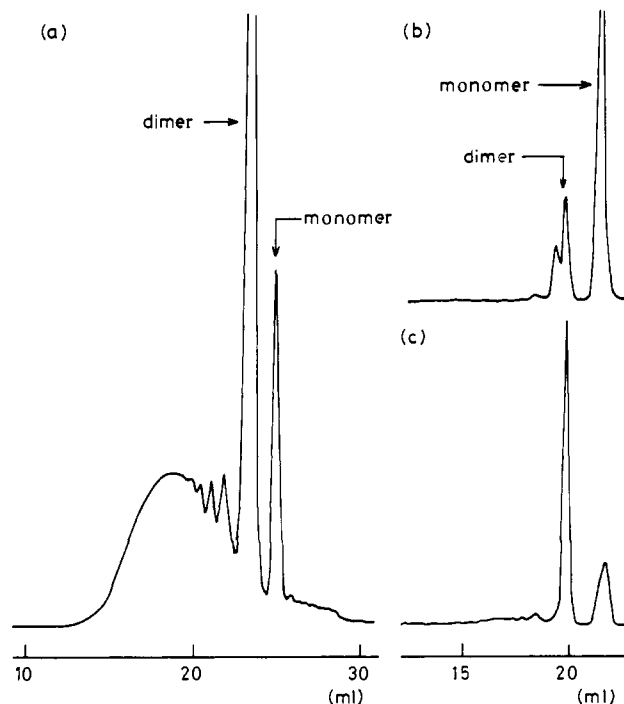
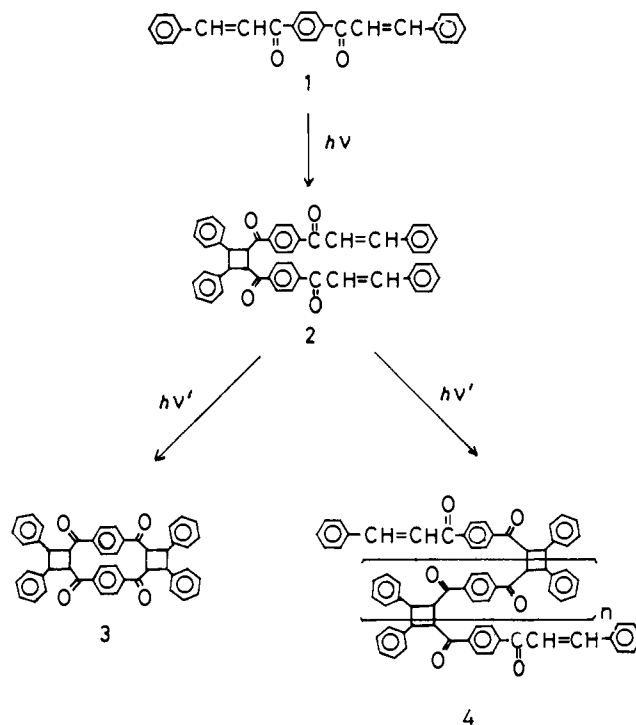


Figure 5. GPC curves of photoproducts obtained from the crystalline state reaction of 1: (a) irradiated at room temperature for 9 h, (b) irradiated at 50 °C for 10 min, and (c) irradiated at 50 °C for 8 h.

Scheme I



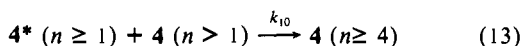
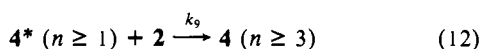
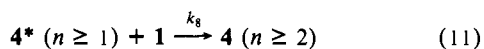
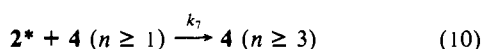
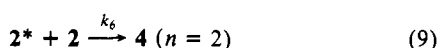
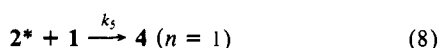
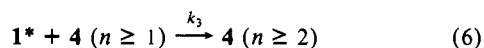
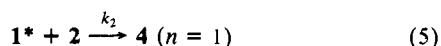
Reaction Kinetics. The conversions of 1 and the yields of 3 along with the irradiation at various temperatures are shown in Figures 3 and 4.

As can be seen in Figures 3 and 4, the photoreaction was apparently the fastest at around 25 °C and still proceeded even at -17 °C, which is much below the crystal melting point of 1 (211–212 °C). The resulting dimer 3 consisted of only a single configuration for all the experimental conditions attempted. These behaviors are consistent with those expected for a typical topochemical photocyclodimerization reaction,¹⁹ indicating that the

(19) Hasegawa, M.; Shiba, S. *J. Phys. Chem. Lett.* 1982, 86, 1490.

reaction of the crystal **1** is strictly crystal-lattice controlled. However, in contrast with a quantitative photopolymerization of the diolefins having a centrosymmetry of crystal, in the reaction of the crystal **1** the formation of the cyclic dimer **3** would disturb the topochemical polymer chain growth seriously.

The reaction schemes of topochemical photoreaction of 1,4-DCB (**1**) are illustrated in eq 1-13 where two kinds of cyclodimerization reactions through two different sets of photoadductive intermolecular double bonds are represented in one scheme.



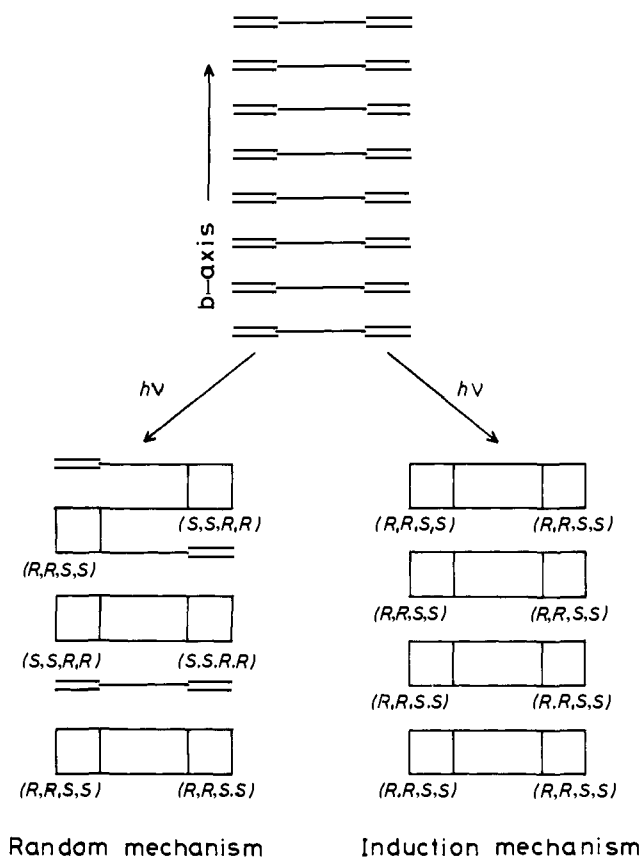
The electronic transition of the intermediate dimer **2** and the oligomers **4** ($n \geq 1$) (λ_{\max} 265, 310 nm) is shifted to a higher energy level than that of **1** (λ_{\max} 322 nm). In the above reaction schemes, **1***, **2***, and **4*** ($n \geq 1$) represent the species **1**, **2**, and **4** ($n \geq 1$), respectively, in the excited state. Equations 4 and 7 represent a dimerization reaction and a ring-closure reaction to afford **3**, and eq 5, 6, and 8-13 represent chain growth reactions. On photoirradiation at the long wavelength edge of 1,4-DCB (**1**) ($h\nu$), only reactions 4, 5, and 6 proceed, and consequently **3** should not be formed at all without any specified reason.

A typical example of the GPC curve of the final photoproducts after irradiation of **1** at room temperature for 9 h is shown in Figure 5a.

In Figure 5a almost all of the oligomers were present from the trimer to the molecular weight of 20000, as calculated with polystyrene standards. The degree of polymerization increased prominently at the later stage of photoirradiation, showing that the reaction occurred by essentially a stepwise mechanism. At the early stage of irradiation, two peaks were observed in the GPC curve at around the molecular weight of twofold of 1,4-DCB (**1**), and the major peak of these corresponded to the tricyclic dimer **3**, as shown in Figure 5b. On further irradiation two peaks of the dimer were gradually transformed into the single sharp peak of **3** as seen in Figure 5c. The minor peak can doubtlessly be attributed to an intermediate dimer **2**, which was produced by eq 4.

In the photoreaction of the bis(3,4-dichlorostyryl) ketone crystal, a monophotonic mechanism in which two cyclobutane rings are formed by a single photon has been proposed because such an intermediate dimer had not been detected even by the photoirradiation with an appropriately selected wavelength.^{2,13} In present study the tricyclic dimer **3** was obtained in 71% yield with 24%

Scheme II



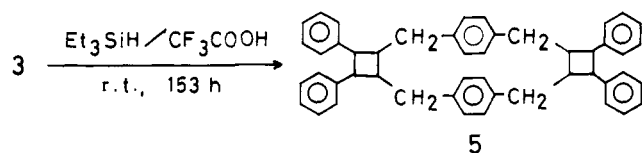
of the oligomers **4** even on the monochromatic photoirradiation with 440 nm that excites only **1**, leaving the terminal olefinic groups of **2** and **4** in the ground state. However, since we observed the formation of a significant amount of **2** during the reaction, the monophotonic mechanism is not plausible, and the unexpected formation of **3** can be explained either by significant approach between two intramolecular double bonds in **2** or by the triplet-energy transfer to the double bond in **2** from the excited species **1***.

In the final photoproduct, finely divided oligomer peaks were always observed by GPC with broad peaks of other unidentified oligomers. In addition, X-ray diffraction peaks, which are not present in either **1** or the reprecipitated crystalline sample of **3**, were seen at 10.2 and 15.3° (2θ) in the final photoproduct even though the product became nearly amorphous. These observations are interpreted by the occurrence of topochemical photocyclodimerization and photocyclooligomerization reactions at the early stage, followed by rather nontopochemical miscellaneous reactions presumably involving the photoinitiated radical species.

The total conversion and the photoproducts ratio **3**/**4** varied considerably with reaction temperature, suggesting that each elementary process in eq 1-13 was influenced to a different degree by thermal vibration in the crystal lattice. At -17 °C the reaction proceeded at a moderate rate; however, it almost ceased after the irradiation for 28 h, to give yields of about 70% of **3**, about 10% of **4**, and about 20% of **1**, respectively. On further irradiation of the above photoproducts in the sample at 28 °C for 30 h, the reaction continued to give the final photoproducts containing about 90% of **3** and about 10% of **4** with a trace amount of **1**. In contrast with the typical topochemical photodimerization, such a striking decrease of reactivity of **1** at a moderately depressed temperature suggests that more rigorous movement is required for the photoexcited species to react at a later stage. The fairly disordered photocyclodimerization of benzalacetophenone crystals has been tentatively explained by Schmidt in connection with longer lifetimes of the triplet state as compared with the singlet states in the majority of the topochemical photodimerization.²

(20) Yonezawa, N.; Yoshida, T.; Hasegawa, M. *J. Chem. Soc., Perkin Trans. 1* 1983, 1083.

Scheme III



If we assume that the reaction probability of all the elementary processes is equal in the reaction of the crystal of **1**, the statistical yields of unreacted **1**, tricyclic dimer **3**, and oligomers **4**, by simulation, should be 1.8, 37.7, and 60.5% by weight, respectively. Further, if all the photoexcited species of **2** is assumed to be converted into **3**, these yields should become 6.9, 65.6, and 27.5%. It is, therefore, rather surprising that in an extreme case of the experiment the yield of **3** was more than 90% while the amount of unreacted **1** was less than a few percent. One of the plausible mechanisms which may be suggested to explain this result is that the first formation of **3** rigorously induced the successive formation of **3** to enhance the final yield of **3**. If such an induction mechanism played an appreciable role, the optically active dimer zone may be formed at least in a micro spot of surroundings of first molecule of **3**, as illustrated below.

The yield of tricyclic dimer from bis(3,4-dichlorostyryl) ketone¹³ has been reported to be 20%, which is less than the statistical value.

Reduction of Tricyclic Dimer 3. For the purpose of preparing other new types of tricyclic cyclophanes, **3** was reduced by reaction with triethylsilane to 21,22,23,24-tetraphenyl-2(3),12(13)-diethano[4.4]paracyclophane (**5**). Racemic **5**, as well as **3**, was successfully resolved into a pair of enantiomers by chiral affinity chromatography (DAICEL Chiralpak OT).

Neither the intramolecular CT complex nor a small molecule inclusion has been observed in any of the treatments of **3** and **5**. According to the CPK molecular model, the distances between the faces of two 1,4-phenylene rings in **3** and **5** are approximately 0.7 and 0.9 Å, respectively, which would seem not to be suitable either for making the intramolecular complex or for including a small molecule in the cavity either. The attempted single crystal preparation of **5** for the X-ray crystallographic analysis has been unsuccessful so far.

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Registry No. **12**, 34838-64-7; **3**, 95462-20-7; **4** ($n = 1$), 95363-43-2; **4** ($n = 2$), 95363-44-3; **4** ($n = 3$), 95363-45-4; **4** ($n = 4$), 95363-46-5; **5**, 95363-47-6; 1,3-DCB, 55147-58-5; BCPM, 34838-75-0; DCS, 95363-41-0; 1,4-BPPB, 95363-42-1.

Kinetics of Ozonation. 3. Substituent Effects on the Rates of Reaction of Alkenes

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Abstract: We have reinvestigated structure–reactivity relationships in the ozonation of simple alkenes, measuring absolute rates of reaction by a stopped-flow technique. The polarity range of the substrates is wider than that of the earlier study, and some compounds have been included to further assess the roles of steric effects and hyperconjugation. The equation that best fits our data is $\log(k/k_0) = -0.83\sigma^* + 0.245E_s^c + 0.158(n - 3)$, where σ^* is a measure of inductive substituent effects, E_s^c is a steric parameter, and n is the number of allylic hydrogens. Additionally, we have measured absolute rates at several temperatures to determine activation parameters for the ozonation of these substrates. The energies of activation range from 2.2 kcal mol⁻¹ for vinyl acetate to 4.1 kcal mol⁻¹ for allyl cyanide. The preexponential terms range from $\log A/s = 6.1$ to 7.4.

Because of the utility of ozone in organic synthesis^{1,2} and because of the environmental hazard it poses,³ the reactions of ozone and organic and biological molecules have been the subject of frequent study. We have begun a program to bridge the gap between the chemistry of ozone in solution and its biological effects.^{4,5}

Structure–reactivity relationships are a powerful tool in organic chemistry,⁶⁻⁸ yet this technique has been infrequently applied to

(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, New York, 1978; Vol. I.

(2) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, New York, 1982; Vol. II.

(3) (a) Lee, S. D., Mustafa, M. G., Mehlman, M. A., Eds. "The Biomedical Effects of Ozone and Related Photochemical Oxidants"; Princeton Scientific Publishers, Inc.: Princeton, NJ, 1982. (b) Pryor, W. A.; Dooley, M. M.; Church, D. F. In ref 3a, pp 7–19. (c) Menzel, D. B. "Free Radicals in Biology"; Pryor, W. A. Ed.; Academic Press: New York, 1976; Vol. II, Chapter 6.

(4) Pryor, W. A.; Giamalva, D.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 6858–6861.

(5) (a) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883–2888. (b) Pryor, W. A.; Prier, D. G.; Church, D. F. *Environ. Res.* **1981**, *24*, 42–52. (c) Pryor, W. A.; Gu, J.; Church, D. F. *J. Org. Chem.*, in press. (d) Pryor, W. A.; Giamalva, D.; Church, D. F. *J. Am. Chem. Soc.* **1984**, *106*, 7094–7100. (e) Pryor, W. A.; Govindan, C. K. *J. Org. Chem.* **1981**, *46*, 4679–4682. (f) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681–7682. (g) Pryor, W. A.; Ohto, N.; Church, D. F. *Ibid.* **1982**, *104*, 5813–5814. (h) Pryor, W. A.; Govindan, C. K.; Church, D. F. *Ibid.* **1982**, *104*, 7563–7566. (i) Pryor, W. A.; Ohto, N.; Church, D. F. *Ibid.* **1983**, *105*, 3614–3622. (j) Pryor, W. A. In "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S., Ed.; Ann Arbor Science Publishers Inc.: Ann Arbor, MI, 1980; pp 3–36.

(6) Shorter, J. "Correlation Analysis of Organic Reactivity"; John Wiley and Sons: New York, Chapter 4, and references therein.

(7) Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

(8) Chapman, N. B., Shorter, J., Eds. "Advances in Linear Free Energy Relationships"; Plenum: London, 1972.