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PHOTODIMERIZATION OF 1,4-DICINNAMOYLBENZENE CRYSTAL VIA A TOPOCHEMICAL PROCESS

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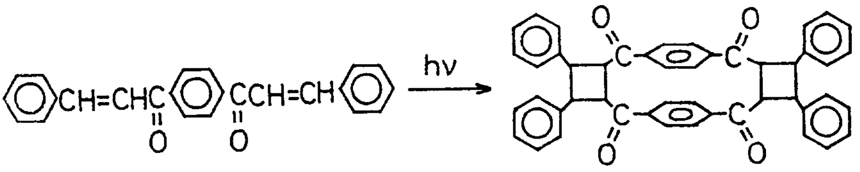
Abstract: 1,4-Dicinnamoylbenzene crystals photodimerize readily via a double [2+2] cycloaddition into the corresponding tricyclic dimer, which consists of two cyclobutane rings and a macro ring bridged by two phenylene linkages.

A number of olefinic compounds are known to photodimerize in the crystalline state.[1] This phenomena, named "topochemical reaction" by Schmidt and co-workers,[2] is controlled by the crystal lattice, and is successfully applied to the photopolymerization of diolefinic compounds in the crystalline state.[3] However, little work has been reported on double [2+2] cycloadditions of diolefinic compounds in the crystalline state except for fragmentary descriptions of bis(3,4-dichlorostyryl)ketone,[4] carbonyldiacrylic acid,[5] and its methyl ester.[6] So far as we know, the crystal structures of these starting diolefins and their dimers are unknown. In this communication we wish to report the double photocycloaddition of 1,4-dicinnamoylbenzene, a first example in which the structures of the starting crystal and the configuration of the cyclic dimer are rigorously clarified.

1,4-Dicinnamoylbenzene (1) was prepared by the condensation of 1,4-diacetylbenzene with benzaldehyde.[7] The crystals of 1 (2.00 g), recrystallized from benzene, were dispersed in heptane (400 ml) and irradiated with a 100 W high-pressure mercury lamp under an argon atmosphere at 20°C for 9 h. The starting crystals were transformed into amorphous substances during the course of the photoirradiation as determined by the x-ray powder diffraction pattern. The products were collected by filtration, and separation by silica gel column chromatography (CH_2Cl_2) gave a colorless powder (57% yield, reprecipitation from THF-hexane, mp 348-352°C) as a major product, accompanied by the starting material (7%) and a mixture of oligomers. Spectroscopic analysis[8] of the major product revealed that the crystals of 1 photodimerized



1 2

presumably via a double [2+2] cycloaddition into tricyclic 21,22,23,24-tetraphenyl-1,4,11,14-tetraoxo-2(3),12(13)-diethano[4,4]paracyclophane (2), in which there are two cyclobutane rings and a macro ring bridged by two phenylene linkages.

Next, we tried to solve the structures of 1 and 2. The failure in the preparation of crystals of 2 for x-ray analysis led us to study the coupling constants of the cyclobutane protons in 2 using modified LAOCOON III program. The derived spectrum based on calculation is shown in Fig. 1 together with the observed one. The two spectra are almost identical with each other, and high values of $J_{AA'}$, J_{AB} , and $J_{BB'}$ suggest that the configuration of the cyclobutanes in 2 is 1α, 2β, 3α, 4β, namely δ-type.[9]

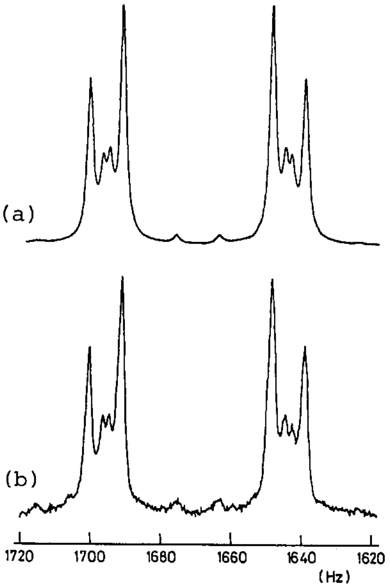


Fig. 1. (a) Calculated and (b) experimental ^{1}H-NMR spectra of cyclobutane protons of 2 at 400 MHz.

Coupling constants: $J_{AA'}$ = 9.609 Hz
J_{AB} = 9.227
$J_{AB'}$ = 0.011
$J_{BB'}$ = 9.609

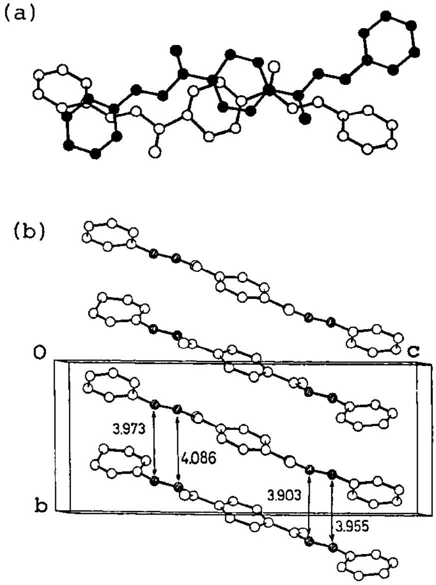
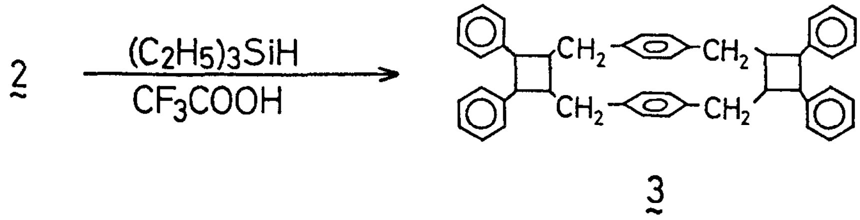


Fig. 2. The crystal structures of 1 projected onto (a) the plane of central benzene and (b) the (100) plane.

The crystal structure[10] of 1 was studied by x-ray diffraction method. The projections onto the plane of central benzene and the (100) plane are shown in Fig. 2. To our surprise, the reacted molecular pair were arranged skew to each other, and the distances between the intermolecular photoadductive carbons were 3.973 and 4.086 Å for one cyclobutane ring and 3.903 and 3.955 Å for the other. Considering that the symmetry(s) due to the parallel orientation results in general for photoadductive double bonds, the dimerization of 1 seems to be an unusual photochemical reaction since a non-parallel arrangement without any symmetry in the reacting carbon-carbon double bonds is observed.[11]

Based on the x-ray analysis of 1, the structure of the pair of reacting double bonds was found to be δ-type, which is in accord with the assignment of 2 by the computer simulation method mentioned above. These results indicate that the double photoaddition is of a widely accepted topochemical process, in which the configuration of the cyclobutane ring in the photodimerized product is governed by the crystalline structure of the starting olefinic compound.

With the aim of synthesizing a new cyclophane, the reduction of the carbonyls in 2 to methylenes was carried out in the presence of triethylsilane.[12] Thus, to a suspension of 2 (1.69 g, 2.5 mmol) in trifluoroacetic acid (42 ml) was added triethylsilane (3.52 ml, 22 mmol), and the solution was stirred at room temperature for 153 h. After neutralization, the solution was extracted with ether. Purification of the crude product by silica gel column chromatography (benzene) afforded 0.576 g (37%)[13] of 21,22,23,24-tetraphenyl-2(3),12(13)-diethano[4,4]paracyclophane (3), which is a new type of tricyclic paracyclophane, as a colorless powder, mp 254-255°C (recrystallization from 6:1 benzene/ hexane).



It should be noted that the photodimerization of 1,4-dicinnamoylbenzene crystals proceeds with remarkable ease and stereoselectivity. That is, the crystals react at a moderate rate on irradiation even at a temperature (20°C) much below the melting point (211-212°C) to give a tricyclic dimer of single configuration, suggesting that this reaction behavior is of a topochemical nature. Moreover, the reaction is considered to be a new synthetic route for tricyclic paracyclophane.

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7. To a solution of 1,4-diacetylbenzene (10.0 g) and benzaldehyde (13.1 g) in ethanol (40 ml) and dioxane (100 ml) was added aq.NaOH solution (16%, 50 ml), and the mixture was stirred 3 h at room temperature. Neutralization of the suspension with aq.HCl, followed by filtration and recrystallization gave 1. Mp 211-212°C (lit. 214°C). ^{1}H-NMR (DMSO-d_6) δ 8.31 (s, 4H), 8.00 (d, 2H, J = 16 Hz), 7.39 (m, 4H), 7.81 (d, 2H, J = 16 Hz), and 7.49 (m, 6H) ppm. IR (KBr) 1650, 1570, 760, and 700 cm^{-1}. UV (CH_2Cl_2) λmax 322 nm (ε 44,900). Mass spectrum, m/e 338 (M^+). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found, C, 84.88; H, 5.59.

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8. 2: Mp 348-352°C. ^{1}H-NMR (DMSO-d_6) δ 7.74 (pseudo-d, 4H, J = 8 Hz), 7.38 (m, 20H), 7.27 (m, 4H), 4.24(pseudo-d, 4H, J = 9 Hz), and 4.11 (pseudo-d, 4H, J = 9 Hz) ppm. IR (KBr) 1675, 915, 750, and 700 cm^{-1}. UV (CH_2Cl_2) λmax 267 (ε 25,500) and 232 (ε 19,200) nm. Mass spectrum, m/e 676 (M^+). Anal. Calcd for $C_{48}H_{36}O_4$: C, 85.18; H, 5.36. Found, C, 85.29; H, 5.42.
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10. Crystal data: $P\bar{1}$, a = 5.789(1), b = 7.923(1), c = 19.307(6) Å, α = 89.12(2), β = 82.12(2), γ = 88.67(1)°, Z = 2, V = 878.2(4) Å^3, R = 0.050. The detail of the crystal data will be published in the following paper: H. Nakanishi, M. Hasegawa, and T. Mori, *Acta crystallogr.*, *B*, in press.
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13. No products other than the reduced dimer 3 and the starting materials were detectable.

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