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Quantitative Formation of a [2.2]Paracyclophane Derivative via Topochemical Photoreaction of Crystal Complex of Ethyl and Propyl α-Cyano-4-[2-(4-pyridyl)ethenyl]cinnamates

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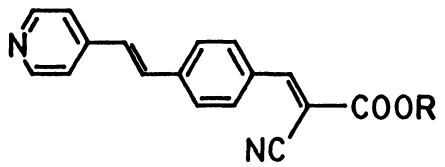
The complex with the composition ranging from 6:4 to 2:8 of ethyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate (**1**) and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate (**2**) photodimerized quantitatively into the three types of tricyclic dimer crystal, indicating a disordered sequence of **1** and **2** in the monomer crystal. The resulted dimers have a highly strained [2.2]paracyclophane unit, which is quite different from the topochemical photoproduct obtained from **1** or **2** alone.

Recently, we reported the topochemical behavior of unsymmetric diolefin crystals which gave homo- and hetero-adduct polymers and/or various types of dimers depending on the molecular arrangement in the monomer crystal.[1-4] For example, the photoreaction of ethyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamate (**1**) gave a homo-adduct polymer[3] and that of propyl α-cyano-4-[2-(4-pyridyl)-ethenyl]cinnamate (**2**) gave a photostable homo-adduct dimer in the crystalline state although their crystal structures are so similar each other.[1,5]



1 : R = Et
2 : R = Pr^n

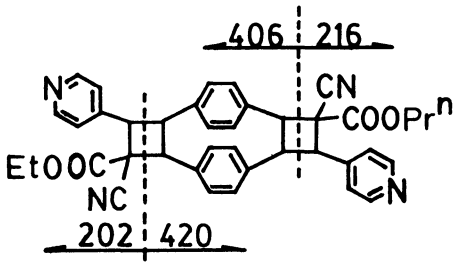
Monomers **1** and **2** were prepared from terephthalaldehyde by the successive condensation with 4-picoline and with the corresponding alkyl cyanoacetate.[6-8] The 1:1 complex was obtained by cocrystallization of equimolar mixture of **1** and **2** from ethanol. Finely powdered complex was dispersed in water/ethanol (9:1 v/v) and irradiated with a 500 W super high-pressure mercury lamp set outside of the flask for 2 h under nitrogen atmosphere at room temperature.

The IR spectrum of the photoproduct, irradiated for 2 h, showed disappearance of the olefinic bonds (1600 and 980 cm^{-1}) and shift of the carbonyl stretching to higher wave number (1730 → 1740 cm^{-1}) in comparison with that of the complex. These spectral changes indicate the transformation of unsaturated ester to saturated ester. In the ^1H NMR spectrum olefinic signals

completely disappeared and three new signals, which are assigned to the protons of cyclobutane rings, appeared at δ 4.4-5.6. The GPC curve of the photoproduct showed a single peak. The peak corresponds to the dimer since the elution time coincides with that of the photodimer of the crystal **1** characterized previously.[3] From these results, it is concluded that tricyclic dimer (**4**) was formed via "double" photocyclodimerization of the 1:1 complex.

To ascertain the substituents on the cyclobutane rings in the photoproduct, further analysis of ^{1}H NMR spectrum was carried out. The proton signals of cyclobutane rings appeared at δ 4.44, 5.36, and 5.51, which exhibited doublet (2H, J = 9.4 Hz), double doublet (2H, J_1 = 9.4 Hz, J_2 = 11.0 Hz), and doublet (2H, J = 11.0 Hz), respectively. The ABC pattern implies the formation of hetero-adduct cyclobutane rings.

In the mass spectrum, two pairs of peaks at m/e 202 and 420, and 216 and 406 were observed, which are due to the cleavage of two kinds of cyclobutane rings, respectively. These spectral evidences support the structure of hetero-adduct cyclobutane rings in dimer **4**.



Schmidt and Green described that in the "double" photodimerization of bis(3,4-dichlorostyryl)ketone,[9] the tricyclic dimer was yielded by simultaneous formation of both cyclobutane rings with one photon, since no intermediate dimer with one cyclobutane ring was detected. On the other hand, in the present study, when the monomer irradiated through a filter (cut off < 355 nm), the diolefinic dimer with one cyclobutane ring (**3**) was detected as a intermediate with λ_{max} at 317 nm, which is revealed by UV spectral change during the photoreaction (Fig. 1), in a similar manner to the photodimerization of 1,4-dicinnamoylbenzene.[10]

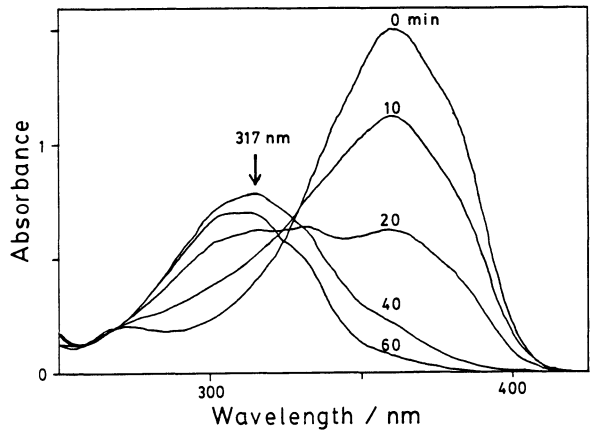
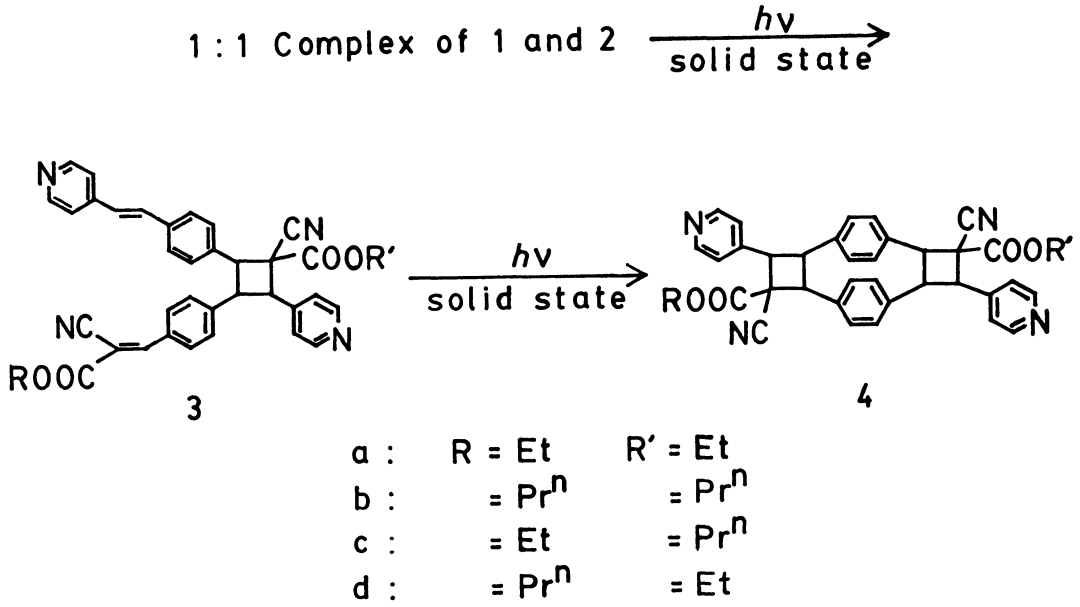


Fig.1 UV spectral change of 1:1 complex of **1** and **2** during the irradiation (> 355 nm).

In order to determine whether the crystal structure of the 1:1 complex is alternative or disordered, high-performance liquid chromatography (HPLC) of **3** was undertaken.[11] HPLC chart showed four different peaks but no peaks of the monomers. In the case of disordered sequence, dimer **3** should consist of four

structures, **3a** (R = R'= Et), **3b** (R = R'= Pr^n), **3c** (R = Et, R'= Pr^n), and **3d** (R = Pr^n, R'= Et). Therefore the analytical result by HPLC reveals the disordered crystal sequence for the 1:1 complex. Moreover, the photoproduct is concluded to be composed of three kinds of tricyclic dimers **4a-c**.



There are a few reports on double [2+2] cycloaddition of diolefinic compounds in the crystalline state[9,10,12,13] such as carbonyldiacrylic acid and its methyl ester. However, the present report is the first example of the formation of a highly strained [2.2]paracyclophane derivative and of the quantitative formation of a tricyclic dimer by the topochemical photoreaction.

X-Ray diffraction of the as-prepared dimer (**4**) showed extremely sharp peaks, indicating the photoreaction from the monomer to the dimer to be a topochemical crystal-to-crystal transformation. As reported previously, methyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate photodimerized in crystalline state quantitatively into diolefinic β-type cyclobutane dimer (corresponds to dimers 3).[4] Highly photostable behavior of the as-prepared dimer crystal has been interpreted by far distant intramolecular double bonds in the diolefinic dimer. In the present study, however, after the first cycloaddition between two molecules, the residual olefins in the resulting dimer crystal still stayed within the reactive distance, and then the second cycloaddition could occur to give the highly strained [2.2]paracyclophane. Such a striking difference of reaction behavior between extremely similar substances can not be explained by their chemical structures but by their crystal structures.

The same type of [2.2]paracyclophane derivative is formed quantitatively also from the complexes with the wide ranges of composition from 6:4 to 2:8 of **1** and **2**. This fact manifests that the crystal structure which is favorable for the cyclophane formation, exists as a stable phase in these ranges.

References

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5) Crystal data of **1** : $C_{19}H_{16}N_2O_2$ = 304.36, $P\bar{1}$, triclinic, a = 11.664(4), b = 9.151(3), c = 7.814(2) Å, α = 85.84(3), β = 104.44(4), γ = 80.05(2)°, U = 789.7 Å^3, Z = 2, D_x = 1.28 g.cm^{-3}, R = 0.082, μ(Mo-Kα) = 0.79 cm^{-1}. Crystal Data of **2** (a private communication from Prof. I. C. Paul, the University of Illinois, Urbana, Illinois, U.S.A.) : $C_{20}H_{18}N_2O_2$ = 318.38, $P\bar{1}$, triclinic, a = 8.919(2), b = 12.429(3), c = 7.781(5) Å, α = 90.24(4), β = 93.18(4), γ = 98.11(2)°, U = 852(1) Å^3, Z = 2, D_x = 1.241 g.cm^{-3}, R = 0.041, μ(Mo-Kα) = 0.76 cm^{-1}.
6) Monomer **1** : mp 172-173.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 3H), 4.35 (q, 2H), 6.95-7.45 (m, 4H), 7.50-8.05 (m, 4H), 8.15 (s, 1H), 8.53 (m, 2H) ppm.
7) Monomer **2** : mp 148-151.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3H), 1.78 (q, 2H), 4.23 (t, 2H), 6.95-7.35 (m, 4H), 7.52-7.98 (m, 4H), 8.13 (s, 1H), 8.53 (m, 2H).
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11) HPLC was performed on a steel column (4 mm x 250 mm) packed with LiChrosorb Si 60 (5 μm, Merck and Co.) at a flow rate of 0.5 mL/min using ethyl acetate as an eluent, and the absorbance at 330 nm was monitored on a Shimadzu SPD-2A spectrophotometric detector.
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