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The Formation of an Alternating Zigzag and Linear Chain Structure with Topochemical Induction into the Racemate Crystal

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Methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate crystals were highly photoreactive and formed the cycloadduct having an alternating zigzag and linear chain structures accompanied with topochemical induction of the two chiralities alternatively in the chain from the β-type achiral crystal of prochiral molecules.

Recently we found a number of unsymmetrically substituted photoreactive diolefinic crystals, exhibiting various photochemical behaviors which give such products as homo- and hetero-adduct polymers, dimers or cyclophanes.[1,2] In the present paper, we report the photoreaction behavior of methyl and ethyl α-cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**1a** and **1b**) crystals. General procedures for the synthesis and photoirradiation of the crystals are given in an earlier communication.[3]

The monomers (**1a** and **1b**) were highly photoreactive in the crystalline state and converted, by [2+2] photocyclodimerization, into the dimers (**2a** and **2b**) in high yields or into the oligomers, depending on the reaction conditions. Photoirradiation conditions of **1a** and GPC curves of their photoproducts are shown in Table 1 and in Fig. 1 respectively.

The photoproducts from the crystalline **1a**, irradiated at -40 °C, were

Table 1. Photoirradiation Conditions of Crystalline **1a**

Run	Dispersant[a]	Filter[b]	Photoirradiation Time/h	Photoirradiation Temp/°C
1	30% aqueous $CaCl_2$	none	4.5	-40
2	30% aqueous $CaCl_2$	(≥ 410 nm)	15	-40
3	water	none	2	20

a) 200 mg of the monomer crystals were dispersed in 90 ml of dispersant containing a few drops of surfactant [NIKKOL TL-10FF (polyoxyethylene laurylether)] for all runs.
b) Light source : 500 W High press. Hg lamp from the outside of flask.

amorphous and consisted of the dimer and tetramer (**2a** and **4a**) with a trace amount of residual monomer (Run 1). In Run 2 a cut-off filter (≥ 410 nm) was employed in order to excite **1a** while leaving the dimer in the ground state, and the final photoproduct was an amorphous **2a** in nearly a quantitative yield. These results in Runs 1 and 2 indicate that the photoreaction proceeded via a typical Even-numbered Polymerization Mechanism, where the excited species of **1a** reacts only with **1a** but the excited **2a** does not react with **1a**. Furthermore, it is obvious that the crystal lattice control worked during the whole course of photoreaction, although the starting crystal was transformed into the amorphous product at the final stage. In contrast, when the photoreaction was carried out at 20 °C without filter (Run 3), although the predominant product was **2a**, an appreciable amount of the trimer was seen in the photoproducts, indicating a certain deterioration of the topochemical process. The photochemical behavior of **1b** was similar to that of **1a**, except that the Even-numbered Mechanism was not maintained as strictly as in the case of **1a**.

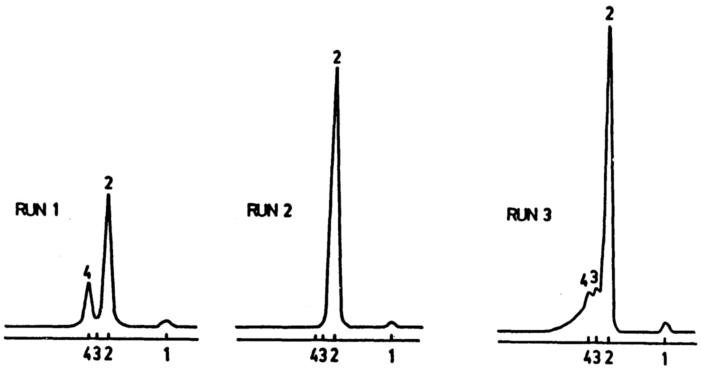


Fig. 1. GPC curves of the photoproducts from **1a** crystal.

It was confirmed from NMR and MS analysis that all the reactions of **1a** or **1b** carried out in the present study gave only one type of the dimer (**2a** or **2b**) which had a hetero-adduct type head-to-head cyclobutane structure. The dimer structure was also easily predictable from the crystal structures of **1a** and **1b**, according to the topochemical principle by Schmidt, although the reacting olefinic bonds were not exactly in parallel. In the crystals of **1a** and **1b**, every pair of two reactive molecules was arranged in β-type packing, with the other neighboring molecules being too far away to react. Finally, the chemical structures of **2a** and **2b** were definitely determined by their crystal structures.4)

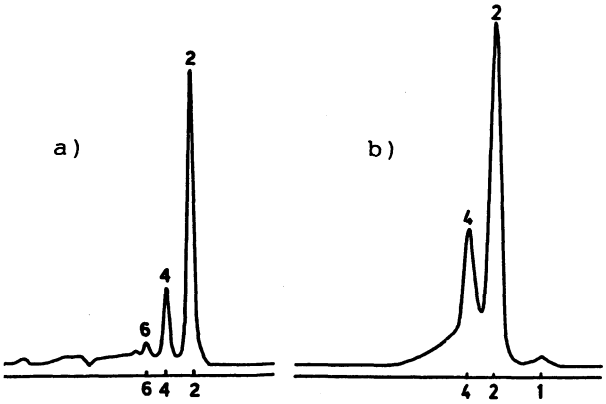
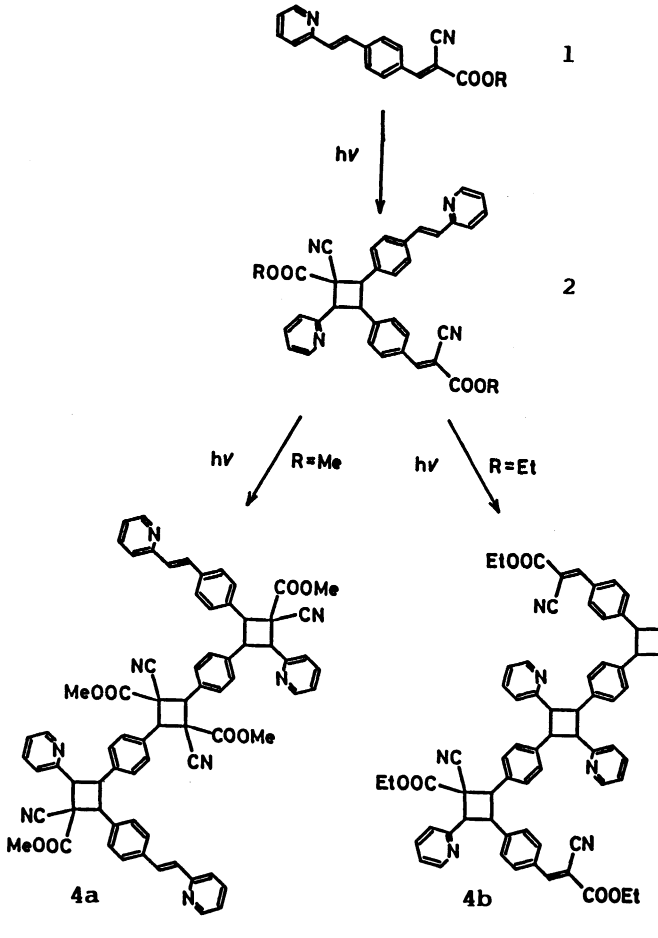


Fig. 2. GPC curves of the photoproducts from a) **2a** (recryst.), irradiated at 10 °C/4 h and b) **2a** (as-prepared amorph.), irradiated at -40 °C/11 h.

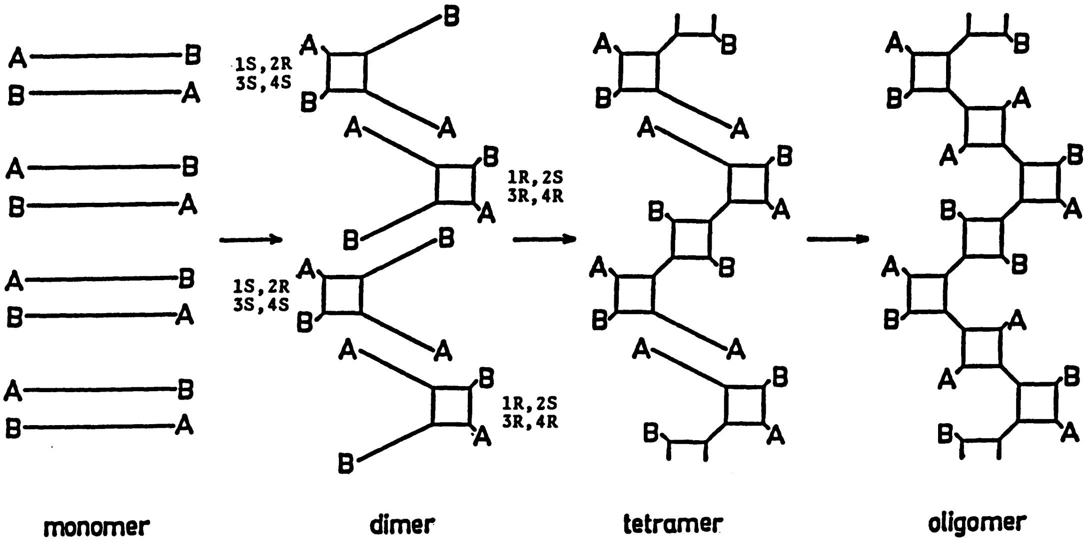
Photochemical behaviors of the crystalline and amorphous dimers (**2a** and **2b**), were also investigated. On photoirradiation, the recrystallized and as-prepared amorphous **2a** behaved essentially in the same manner to result in the oligomeric products, as are seen in Fig. 2. It is concluded from the result of Fig. 2 that the molecules in the as-prepared amorphous dimer **2a** were arranged in a similar manner to those in the recrystallized crystal, which is highly favorable for successive photocyclodimerization. In the photoproducts of **2b**, ^{1}H NMR spectra of the two isolated tetramers (**4b**), one derived from the crystalline dimer and the other from the amorphous, were exactly the same, confirming the identical structure of these tetramers. This suggested that the as-prepared amorphous **2b** has a molecular orientation very close to that of the crystalline **2b**.



Scheme 1.

The structures of **4a** and **4b** were readily predicted from the crystal structures of the corresponding dimers (**2a** and **2b**), in which the two reacting molecules were related with a centrosymmetry and gave a homo-adduct type head-to-tail cyclobutane ring, as are shown in Scheme 1. The two facing olefinic bonds are parallel and separated by 3.867(9) Å for the methyl ester side of **2a** and 4.0368 Å for the 2-pyridyl side of **2b**, and these distances are within those of normal reactive bonds. Other intermolecular distances of double bonds, 4.481(9) Å for the 2-pyridyl side of **2a** and 5.7269 Å for the ethyl ester side of **2b** seemed to be too long to form a photocycloadduct. The structures of **4a** and **4b**, which were predicted from the crystal structures of **2a** and **2b** respectively, were definitely shown to coincide with those determined by means of ^{1}H NMR spectral analysis.$^{5)}$ From the NMR spectral results in which the numbers of cyclobutane protons were eight for **4a** (4.72-5.13 ppm) and ten for **4b** (4.57-5.15 ppm), it was concluded that **4a** was formed by the addition of ester side olefins and **4b**, 2-pyridyl sides. It should be noted that the tetramer contains three cyclobutane rings of head-to-head, head-to-tail and head-to-head structures and that the head-to-head cyclobutanes have opposite chiralities alternatively in the polymer chain. No attempts to prepare the high-molecular-weight polymer has yet been successful from **2**, even though the octamer was clearly identified in the GPC curve. The present result is the first example of topochemical polymerization affording a polymer structure other than that predicted from the crystal structure of the starting compound but of an alternating zigzag and linear main chain structure, with a repeating unit of the tetramer, as is illustrated in Scheme 2.

Furthermore, this result implies that the [2+2] photocyclodimerization in **1a** and **1b** does not proceed at random, but that the induction of a non-random, alternating arrangement of both enantiomers occurs during the reaction of prochiral molecules in the achiral crystals. Although such an induction phenomenon is very common in the crystallization process of racemates, this is the first demonstration through the topochemical reaction of prochiral molecules.



Scheme 2.

References

1) M. Hasegawa, Pure Appl. Chem., 58, 1179 (1986).

2) M. Hasegawa, Y. Maekawa, S. Kato, and K. Saigo, Chem. Lett., 1987, 907.

3) S. Kato, M. Nakatani, H. Harashina, K. Saigo, and M. Hasegawa, Chem. Lett., 1986, 847. **1b**: mp 134-135 °C; ^{1}H NMR ($CDCl_3$) δ=1.41(3H, t), 4.40(2H, q), 7.19-7.71(7H, m), 8.02(2H, d), 8.23(1H, s), 8.65(1H, s).

4) Crystal data of **1b**: $C_{19}H_{16}N_2O_2$ = 304.36, $P\bar{1}$, triclinic, a = 7.628(2), b = 16.807(2), c = 7.474(2) Å, α = 88.04(2), β = 113.90(2), γ = 113.58(2)°, U = 793.0 Å^3, Z = 2, D_x = 1.27 g.cm^{-3}, R = 0.066, μ(Cu Kα) = 0.64 mm^{-1}; **2a**: $C_{36}H_{28}N_4O_4$ = 580.62, $A_{2/a}$, monoclinic, a = 33.52(4), b = 6.542(5), c = 29.372(14) Å, β = 107.34(6)°, U = 6147.9 Å^3, Z = 8, D_x = 1.25 g.cm^{-3}, R = 0.11, μ(Cu Kα) = 0.64 mm^{-1}; **2b**: $C_{38}H_{32}N_4O_4$ = 608.72, $P\bar{1}$, triclinic, a = 15.261(1), b = 8.831(1), c = 13.669(1) Å, α = 106.34(1), β = 109.11(1), γ = 73.88(1)°, U = 1635.1 Å^3, Z = 2, D_x = 1.24 g.cm^{-3}, R = 0.085, μ(Cu Kα) = 0.62 mm^{-1}.

5) **4a**: ^{1}H NMR($CDCl_3$) δ = 3.26(6H, s), 3.54(6H, s), 4.72(2H, d), 4.89(2H, s), 4.94(2H, d), 5.13(2H, t), 6.99-7.74(32H, m), 8.62(4H, d).
4b: ^{1}H NMR($CDCl_3$) δ = 0.92(6H, t), 1.38(6H, t), 3.95(4H, m), 4.36(4H, q), 4.57(4H, d), 4.70(2H, t), 4.86(2H, d), 5.15(2H, t), 6.83-7.73(28H, m), 8.12(2H, s), 8.38(2H, d), 8.60(2H, d).

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