Topochemical Reaction of 7-Bromoethoxycarbonyl-7-cyano-1,4-benzoquinone Methide in the Solid State

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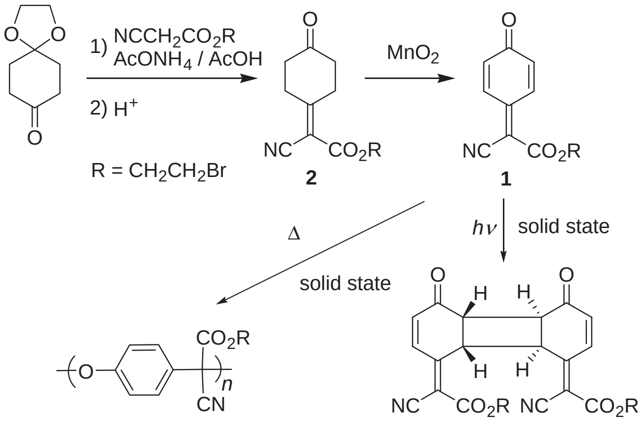
Topochemically controlled [2 + 2] photocycloaddition took place at the quinoid double bond of the 7-bromoethoxycarbonyl-7-cyano-1,4-benzoquinone methide (**1**) to afford its cyclobutane dimer.

Solid-state organic reactions have attracted much attention as an environment-friendly synthetic method because of solvent-free processes, and also solid-state reactions under topochemical control are more attractive in the points of providing products with specific structures in a high conversion and selectivity. Until now, enormous solid-state organic reactions have been reported.[1] There are a large number of the organic reactions under topochemical control for the low molecular product formation, but monomers that can be polymerized topochemically are limited to derivatives of diacetylene,[2] 2,5-distyrylpyrazine,[3] triene and triacetylene,[4] and muconic acid and sorbic acid.[5] Recently, we found that polymerization reactions of 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes proceed topochemically and we explained the relationship between topochemical polymerization reactivity and the monomer packing in the crystals.[6] To find a general rule to predict this relationship for the quinoid compounds, we expanded the investigation of the solid-state polymerizations to quinine methides as a member of the quinoid family.[7a] In the course of the research, we found that a cyclobutane dimer of 7-bromoethoxycarbonyl-7-cyano-1,4-benzoquinone methide (**1**) might be formed by the topochemically controlled [2 + 2] photocycloaddition reaction (Scheme 1). Here, we report the synthesis of **1** and its solid-state reaction.

7-Bromoethoxycarbonyl-7-cyano-1,4-benzoquinone methide (**1**) was prepared by the method reported previously.[7] Knoevenagel condensation of 1,4-cyclohexanedione monoethylene ketal with bromoethyl cyanoacetate followed by deprotection of the ketal afforded 4-[cyano(bromoethoxycarbonyl)methylene]-cyclohexanone (**2**) (55% yield) as white needles. Oxidation of **2** with activated manganese dioxide in the refluxing benzene gave **1** (41% yield), which was recrystallized from a mixture of dichloromethane and hexane to afford orange needles.



Scheme 1.

The crystals of **1** were heated at 60 °C, lower than its melting point (81.4 °C), in the dark in vacuo, or irradiated using a 400 W high-pressure Hg lamp at 30 °C (Table 1).

On the thermally induced reaction, **1** retained the crystal shape except for the color change from orange to pale yellow, and the white solids with M_n of 85,000 (GPC, polystyrene standard, THF eluent) were isolated in 84% yield by the dissolution–reprecipitation treatment. The isolated product was characterized by ^1H and ^{13}C NMR and IR spectroscopies and elemental analysis, and it was found to be a homopolymer of **1** with chemical structures similar to the polymers obtained by the solution polymerizations of substituted quinone methides.[7b] The change in crystallinity during the reaction was investigated by the powder XRD measurement. The powder XRD pattern for the **1** crystals showed very sharp peaks: at 41% conversion it showed the coexistence of monomer crystal phase and the polymer amorphous phase, and at 84% conversion it became broad and there were no significant peaks, indicating that the monomer crystals collapsed with a progress of polymerization and amorphous polymers might be formed. On the other hand, on the photoinduced reaction at 30 °C, **1** retained the crystal shape during the irradiation, but it turned orange to pale orange after a few hours. GPC measurement of the reaction mixture showed two components, corresponding to unreacted **1** and the reaction product with the molecular weight of 540, and the conversions to the reaction product determined by ^1H NMR were to be 90% for 4 days and 94% for 59 days, respectively. The reaction products were isolated in 77 and 84% yields as pale yellow powders by

Table 1. Thermally induced and photoinduced reactions of **1** in the solid state in vacuo

Light source	Temp /°C	Time /days	Conv.[a] /%	M_n
dark	60	28	84	85,000
Hg lump	30	4	77	540
Hg lump	30	59	84	540

[a]Isolated yield.

Table 2. Crystallographic data for crystals of **1** and dimer

Compound	**1**	Dimer (1:1 complex)
formula	$C_{11}H_8BrNO_3$	$C_{28}H_{22}Br_2N_2O_6$
fw	282.09	642.30
crystal system	triclinic	triclinic
space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)
a/Å	4.108(1)	7.821(1)
b/Å	11.388(2)	11.178(2)
c/Å	11.496(2)	17.083(3)
α/deg	90.96(2)	72.91(2)
β/deg	94.58(2)	89.72(2)
γ/deg	90.96(2)	76.71(2)
V/Å^3	535.0(2)	1386.0(5)
Z	2	2
D_{calcd}/g cm^{-3}	1.751	1.539
unique reflecns	1803	4654
no. obsd reflens	5727	13615
R_1	0.067	0.078
R, R_w	0.101, 0.213	0.108, 0.228
GOF	1.9	1.91
$2\theta_{\text{max}}$/deg	136.5	136.5
temp/°C	−180	−60

the dissolution–reprecipitation treatment (repeated three times) using dichloromethane as a solvent and hexane as a precipitant. The isolated reaction product was characterized by ^{1}H and ^{13}C NMR, IR spectroscopies and elemental analysis, and determined to be the cyclobutane dimer.[8] And also, single-crystal structure analysis of the reaction product crystals, obtained by recrystallization from benzene, supported the cyclobutane dimer structure, though it was a 1:1 complex of the dimer with benzene (Table 2). This indicates that the photoinduced [2 + 2] cycloaddition took place at the double bond of the quinoid ring of **1** in the solid state.

On contrast, when **1** was irradiated in toluene solution at 30 °C for 4 days, no cyclobutane dimer was obtained and instead its homopolymer with M_n of 5,100 was obtained in 82% yield. Therefore, the dimer formation is regarded as the specific reaction in the solid state.

To clarify the relationship of the reaction product with the molecular packing mode of **1** in the crystals, we investigated the crystal structures of **1** by X-ray crystallography. The single crystals were prepared successfully by slow solvent evaporation from a mixture solution of hexane with dichloromethane. The crystallographic data of **1** are summarized in Table 2 together with the data of the cyclobutane dimer, and the crystal structure of **1** is shown in Figure 1. The **1** molecules stack along a-axis to form a columnar structure, which is similar to the molecular packing of 7-cyano-7-propoxycarbonyl-1,4-benzoquinone methide, where an amorphous polymer was formed in the solid-state polymerization.[7a] However, as in Figure 1 two nearest-neighboring molecules lie in parallel with the double bonds oriented in the same direction with a maximal distance between the reacting quinoid double bonds of 3.5 Å, conditions of which allowed to form a cyclobutane dimer by photodimerization. It is considered, therefore, that in the photoinduced reaction the cyclobutane dimer was formed by topochemically controlled [2 + 2] cycloaddition and in the thermally induced reaction amorphous polymer was obtained. Further studies on the relationship of the reactions in the solid state and crystal structures for the quinoid family are now in progress.

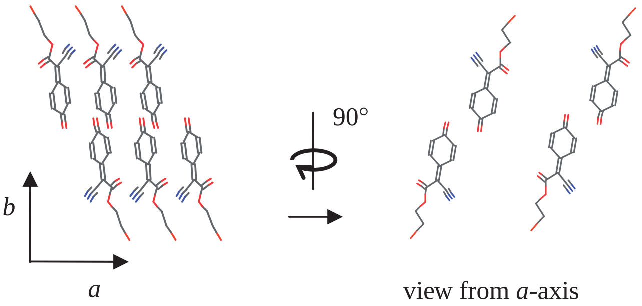


Figure 1. Crystal structure of **1**.

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8 Mp 45–46 °C; IR (KBr): 2966, 2222, 1728, 1678, 1247, 1146, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.59 (d, $J = 10.88$ Hz, 1H), 7.78 (d, $J = 10.56$ Hz, 1H), 6.69 (d, $J = 10.56$ Hz, 1H), 6.57 (d, $J = 10.56$ Hz, 1H), 5.28 (dd, $J = 8.57$, 8.57 Hz, 1H), 4.52–4.61 (m, 4H), 4.39–4.50 (m, 1H), 3.58 (t, $J = 5.28$ Hz, 4H), 3.35 (d, $J = 8.25$ Hz, 1H), 3.27 (d, $J = 8.90$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 195.2, 160.8, 158.2, 158.1, 140.2, 137.2, 136.6, 135.0, 114.9, 113.1, 109.0, 106.5, 65.6, 47.6, 45.7, 45.4, 43.2, 27.7, 27.3; Anal. Calcd for $C_{22}H_{16}Br_2N_2O_6$: C, 46.84; H, 2.86; N, 4.97%. Found: C, 47.03; H, 2.95; N, 4.84%.

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