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Photoreaction of 2,3-Bis[2-(4-chlorophenyl)ethenyl]pyrazine in the Crystalline State and in Acetonitrile Solution

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The photoreaction behaviors of 2,3-bis[2-(4-chlorophenyl)ethenyl]pyrazine (**1**) in the crystalline state as well as in acetonitrile solution were examined mechanistically. In the crystalline state, stepwise [2+2] cycloadditions occurred between two facing molecules under the crystal lattice control to give a [2.2]orthocyclophane derivative in 74% yield. Photoirradiations of **1** in acetonitrile solution were also performed. In this case, products distributions were changed depending on the cut off wavelength.

It has been reported that many diolefin compounds, which have 1,4-divinylarene structure, underwent [2+2] photocycloaddition in the crystalline state and gave polymers, oligomers, dimers or cyclophanes.[1] However, the photoreaction of meta- or ortho-substituted type diolefin compounds in the crystalline state have been rarely investigated.[2] Recently, we have found that a quite number of ortho- or meta-substituted type diolefin compounds also exhibited photoreactivity in the crystalline state. Among such type of compounds, we report the photoreaction behaviors of 2,3-bis[2-(4-chlorophenyl)ethenyl]pyrazine (**1**) both in the crystalline state and in solution.

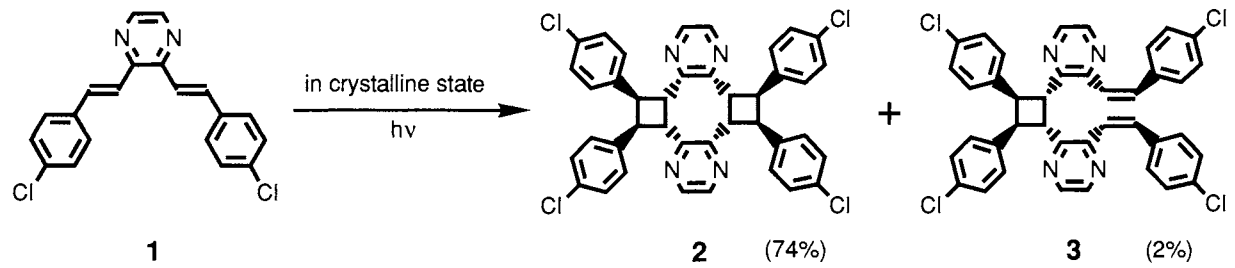
1 was prepared by the condensation of 2,3-dimethylpyrazine with *p*-chlorobenzaldehyde in refluxing butyric anhydride (36%). Yellow needle crystals of **1** were obtained by recrystallization from ethanol solution.[3]

In the first place, we investigated the photoreaction of **1** in the crystalline state. Powdered crystals of **1** were suspended in water and were irradiated with a 100 W high-pressure mercury lamp for 5 h under nitrogen atmosphere at room temperature. Separation of the products by silica gel chromatography gave colorless powder **2** as a major product (74%, based on the initial weight of **1**),[4] pale yellow powder **3** (2%), a mixture of oligomers, and a trace amount of starting material **1** (1%).

The main product **2** consisted with dimeric structure from GPC and MS analysis. Its ^{1}H-NMR spectrum showed no olefinic protons, but a couple of cyclobutane protons (4.56, 5.06 ppm) instead. Pyrazine protons appeared as a sharp singlet at 8.26 ppm, which implied a symmetrical structure. The ratio of cyclobutane, phenylene (7.07, 7.17 ppm), and pyrazine protons was 2:4:1. According to these observations, the main product **2** was assigned to be a [2.2]orthocyclophane derivative, 3,4,13,14-tetrakis(4-chlorophenyl)-7,10,17,20-tetraazapentacyclo[14.4.0.0^{2,5}.0^{6,11}.0^{12,15}]icosa-6,8,10,16,18,20(1)-hexaene.

^{1}H-NMR spectrum of the second product (pale yellow powder) **3** showed olefin and cyclobutane protons in the same ratio. As the elution time in GPC analysis was nearly the same as that of **2**, the pale yellow product

3 was considered to be the monocyclic dimer as shown in Scheme 1. The isolation of an intermediate monocyclic dimer **3** indicates that **2** was formed through stepwise [2+2] photocycloadditions between two molecules of **1**.



Scheme 1.

In order to obtain further informations on the reaction pathways and the structure of main product **2**, single crystal X-ray analyses of **1** and **2** were carried out. Figure 1 shows a crystal structure of **1**.[5] The molecules of **1** were piled up along the shortest crystal axis (c-axis) to form a parallel plane-to-plane stack. The double bonds between intrastack molecules were parallel and existed within a photoreactive range (4.008(3) Å).[6] The single crystals of **2** were prepared by slow evaporation of benzene solution and included the solvent molecules. Its molecular structure is shown in Fig. 2.[7] Based on the crystal structure of **1**, mirror-symmetric dimer or zigzag-type oligomer (or polymer) was anticipated to arise from the photoirradiation. However, dimer **2** was formed in much higher yield than oligomers experimentally, which is explained as follows. The molecular mortion accompanying with the first step photocycloaddition within a crystal lattice facilitates the subsequent *intramolecular* photoreaction. Then, owing to the faster second step reaction, the yield of the intermediate monocyclic dimer **3** was lowered. This tendency is different from the solid state synthesis of [2.2]paracyclophane.[8] Furthermore rather high conversion of starting material **1** would imply that the topochemical induction process[10] plays an important role during this reaction.

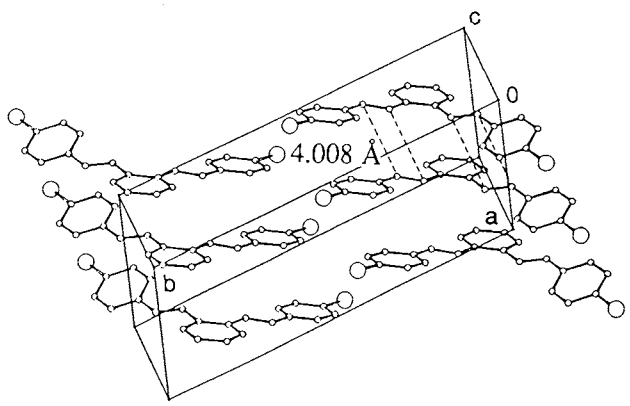


Fig. 1. Perspective view for the crystal structure of **1**.

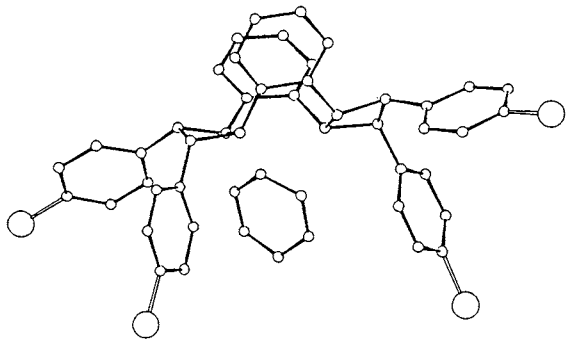


Fig. 2. Molecular structure of **2**.

Next, the photoreaction of **1** in solution was investigated. A degassed acetonitrile solution of **1** (1.0×10^{-3} mol/l) was irradiated with a 100 W high-pressure mercury lamp through a uranium glass filter (cut off < 320 nm) for 4 h under nitrogen atmosphere. Separation of the products by column chromatography gave **2** (40%), another type of cycloadduct **4** (25%), 4,4'-dichlorostilbene (4%), and a small amount of undefined products. From the ^{1}H-NMR, MS,and GPC analysis, **4** was concluded to be a geometrical isomer of **3**, namely a head-to-tail type monocyclic dimer, while the configuration of cyclobutane ring has not been determined yet. Formation of the same main product as in the crystalline state may be explained by aggregation of **1** in solution. In fact, in the fluorescence spectrum of **1** measured in concentration more than 5×10^{-4} mol/l, a new emission peak appeared at longer wavelengths (Fig. 3). The appearance of this fluorescence peak is considered to be caused by the aggregation of **1** in the ground state.

Irradiation of **1** without filter for 1.5 h, otherwise in the same conditions, afforded another cyclophane **5** (19%) as a main product[11] with appreciable amount of undefined products. In ^{1}H-NMR spectrum of **5**, olefinic signals were not observed at all. The signals attributable to the cyclobutane protons (8H, 4.2-5.1 ppm) were complicated and four pyrazine protons (4H, 7.8-8.3 ppm) were not equivalent. The molecular weight was the same as that of **2** from the GPC and MS analysis. Based on these results, the main product **5** was tentatively assigned to be an epimer of **2**, as shown in Scheme 2.[12]

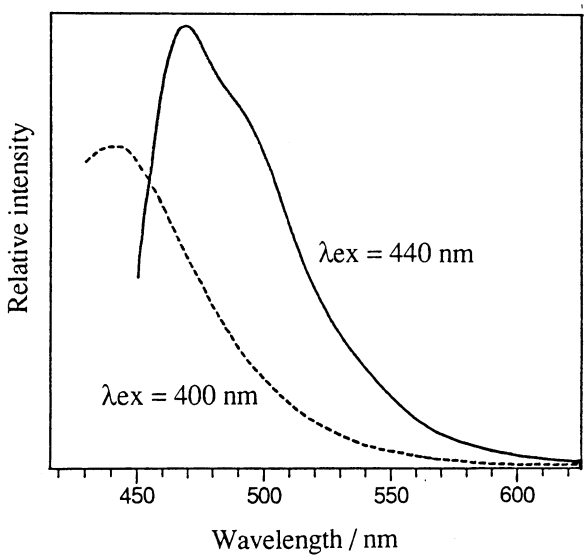
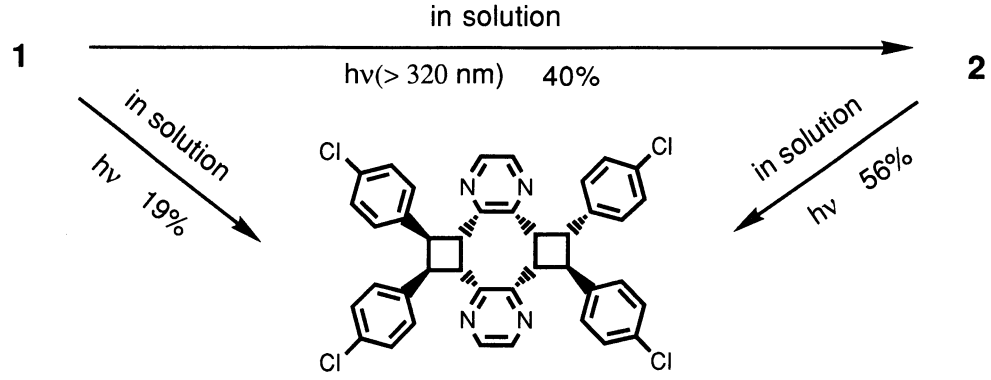


Fig. 3. Fluorescence emmission spectrum of **1** in acetonitrile (5×10^{-4} mol/l). Excitation: 400 nm (------), and 440 nm (——).



Scheme 2.

Cyclophane **2** was also photoirradiated in acetonitrile solution (1.5×10^{-3} mol/l) without filter for 2 h to give **5** as a main product (56%), 4,4'-dichlorostilbene (1%), and undefined products. This result indicates the

intermediacy of **2** in the formation of epimer **5**. Namely, by the irradiation of **1** in acetonitrile solution without filter, **2** was initially formed through [2+2] photocycloadditions as mentioned above, followed by photoepimerization induced by light of shorter wavelength to afford epimer **5**.

References

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2) F. Nakanishi, H. Nakanishi, M. Hasegawa, and Y. Yamada, *J. Polym. Sci., A-1*, **13**, 2499 (1975); H. G. Bührer, R. Aeschbach, T. Phillipou, J. J. Parnaud, and H. G. Elias, *Makromol. Chem.*, **157**, 13 (1972).
3) Monomer **1** : mp 208-209 °C (EtOH); ^{1}H-NMR ($CDCl_3$) δ 7.38 (d, J=8.54 Hz, 2H), 7.44 (d, J=15.6 Hz, 2H), 7.56 (d, J=8.55 Hz, 4H), 7.80 (d, J=15.6 Hz, 2H), 8.44 (s, 2H).
4) Cyclophane **2** : mp 225-228 °C (C_6H_6); ^{1}H-NMR ($CDCl_3$) δ 4.56 (m, 4H), 5.06 (m, 4H), 7.07 (d, J=8.55 Hz, 8H), 7.17 (d, J=8.55 Hz, 8H), 8.26 (s, 4H).
5) Crystal data of **1** : $C_{20}H_{14}N_2Cl_2$=353.25, $P2_1/n$, monoclinic, a=18.476(10), b=23.155(13), c=4.008(3) Å, ß=91.97(5)°, V=1713 Å^3, Z=4, Dx=1.369 g cm^{-3}, R=0.062, μ(Cu-Kα)=34.7 cm^{-1}.
6) G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).
7) Crystal data of **2** : $C_{46}H_{34}N_4Cl_4$=784.61, $P2_1/a$, monoclinic, a=20.372(10), b=14.366(8), c=13.835(8) Å, ß=102.38(5)°, V=3955 Å^3, Z=4, Dx=1.318 g cm^{-3}, R=0.067, μ(Cu-Kα)=30.6 cm^{-1}.
8) In the case of the solid state synthesis of [2.2]paracyclophane,[9] the intermediate monocyclic dimers could be isolated in almost quantitative yields by the exclusive photoexcitation of the monomers. Whereas **3** was formed only in low yields under a variety of reaction conditions.
9) C.-M. Chung, F. Nakamura, Y. Hashimoto, and M. Hasegawa, *Chem. Lett.*, **1991**, 779; C.-M. Chung, A. Kunita, K. Hayashi, F. Nakamutra, K. Saigo, and M. Hasegawa, *J. Am. Chem. Soc.*, in press.
10) M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara, and H. Nakanishi, *J. Am. Chem. Soc.*, **107**, 2788 (1985).
11) Cyclophane **5** : mp 281-282 °C; ^{1}H-NMR ($CDCl_3$) δ 4.20 (m, 2H), 4.53Å (m, 1H), 4.83 (m, 3H), 5.05 (m, 2H), 6.95 (d, J=8.23 Hz, 2H), 7.11 (d, 8.24 Hz, 2H), 7.20 (s, 4H), 7.22 (s, 4H), 7.29 (d, J=8.24 Hz, 2H), 7.54 (d, J=8.55 Hz, 2H), 7.79 (d, J=2.75 Hz, 1H), 7.93 (d, 2.75 Hz, 1H), 8.21 (d, 2.75 Hz, 1H), 8.30 (d, J=2.45 Hz, 1H).
12) From NMR data, the structure of **5** is assumed to be the unsymmetric cyclophane in which one or three *p*-chlorophenyl substituents of **2** epimerized.

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