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Photochemical Reaction of 2,3-Di[(*E*)-styryl]pyrazine Derivatives in the Crystalline State and in Solution1)

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The photoreaction of 2,3-di[(*E*)-styryl]pyrazine derivatives was carried out in the crystalline state and in solution. Among them, 2,3-di(*p*-chlorostyryl)pyrazine and 2,3-di(*p*-cyanostyryl)pyrazine were photoreactive in the crystalline state and gave, upon photoirradiation, [2.2]orthocyclophanes in 76 and 58% yields, respectively. Such a topochemical photo-behavior was interpreted on the basis of X-ray crystallographic analyses of the crystals. The photoirradiation of 2,3-distyrylpyrazine in solution gave [2.2]orthocyclophane and *anti* head-to-tail type monocyclic dimer as the major products. The yields of the products varied depending on the solvent; with decreasing the polarity of the solvent, the yield of the cyclophane decreased, whereas the yield of the monocyclic dimer increased. In a similar manner, the photoirradiation of the other 2,3-distyrylpyrazine derivatives in acetonitrile/chloroform (10/1) or acetonitrile gave the corresponding [2.2]orthocyclophanes and monocyclic dimers, respectively, as major products through two types of excimers.

It has been reported from our laboratory that a large number of 1,4-diethenylaromatic compounds underwent [2+2] photocycloaddition in the crystalline state and gave dimers, cyclophanes, oligomers, and/or polymers, depending on their molecular arrangement in the crystal.2) However, the [2+2] photocycloaddition of 1,2- and 1,3-diethenylaromatic compounds in the crystalline state has not been thoroughly investigated.3) Moreover, there have been only a few reports concerning the *intermolecular* photoreaction of fully conjugated diolefin compounds in solution.4,5)

Recently, we found that a few types of 1,2-diethenylaromatic compounds also exhibited photoreactivity in both the crystalline state and in solution.1) In the present paper, we report in detail on the photochemical behavior of 2,3-di[(*E*)-styryl]pyrazine derivatives (Chart 1) in both the crystalline state and in solution.

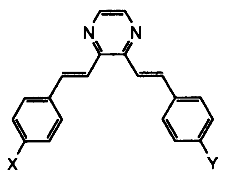

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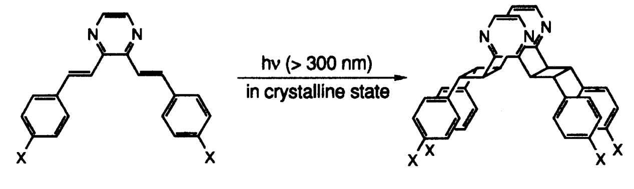
Chart 1.

Results and Discussion

Photoreaction in the Crystalline State. 2,3-Di[(*E*)-styryl]pyrazine derivatives (**1a**—**f**; see Table 1) were prepared by the aldol-type condensation of 2,3-dimethylpyrazine with the corresponding aldehydes. Among these compounds, **1b** and **1c** were photoreactive in the crystalline state. When powdered crystals of **1b** and **1c** were suspended in water and irradiated with a 500-W super-high-pressure mercury lamp through a cut-off filter (wavelengths>300 nm) for 5 h under a nitrogen atmosphere at room temperature, the morphology of the crystals gradually changed from the crystalline phase into the amorphous phase, and [2.2]orthocyclophanes **2b** and **2c** were isolated as major products in 76 and 58% yields, respectively, accompanied by oligomers and small amounts of unidentified products (Scheme 1). In the photoreaction of **1b**, however, the monocyclic dimer **3b** was also obtained, although its yield was quite low (ca. 1%). The structure of **2b** was directly determined by an X-ray crystallographic analysis (Fig. 1),6) and the structure of **2c** was confirmed by a comparison of its ^{1}H NMR spectrum with

Table 1. Photoreactivity of 2,3-Di[(*E*)-styryl]pyrazine Derivatives in the Crystalline State

1	X=	Y=	Photoreactivity in the crystalline state
1a	H	H	No
1b	Cl	Cl	Yes
1c	CN	CN	Yes
1d	NO$_2$	NO$_2$	No
1e	CH$_3$	CH$_3$	No
1f	CN	OCH$_3$	No



1b : X = Cl
1c : X = CN

2b : X = Cl (76% yield)
2c : X = CN (58% yield)

Scheme 1.

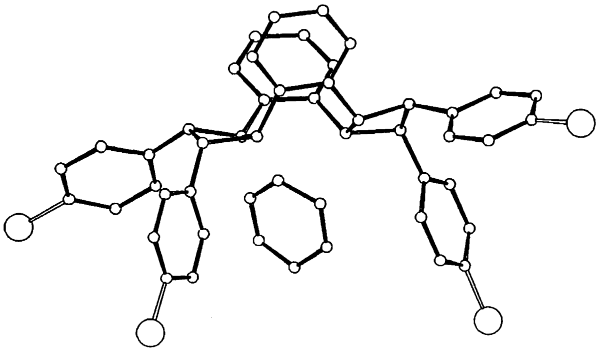


Fig. 1. ORTEP drawing of **2b**·benzene.

that of **2b**; the peak patterns of the cyclobutane protons and pyrazine protons of **2c** were quite similar to those of **2b**, and the A_2B_2 patterns of **2b** and **2c** arising from the 1,4-disubstituted benzenes were also similar to each other, although the chemical shifts were different due to the influence of the para-substituents. Moreover, the structure of **3b** was determined by a comparison of its ^{1}H NMR spectrum with that of **3a**, of which the structure was directly solved by X-ray crystallography (vide infra); the chemical shifts and peak patterns in the ^{1}H NMR spectra of **3a** and **3b** were similar to each other, especially concerning the cyclobutane (around 5 ppm), olefin (around 7.2 and 7.6 ppm), and pyrazine protons (around 8.3 and 8.4 ppm).

In order to explain the difference in the photoreactivity between these 2,3-di[(*E*)-styryl]pyrazine derivatives, X-ray crystallographic analyses were performed for the typical photoreactive and photostable compounds. The crystal structures of photoreactive **1b** and photostable **1a,e** are shown in Fig. 2.[7]

The molecules of **1b** are piled up along the shortest crystal axis (*c*-axis) to form a parallel plane-to-plane stack (Fig. 2b), in which the molecules of **1b** are almost completely overlapped with each other. The carbon–carbon double bonds in the intrastack molecules are parallel to each other, and the distance is 4.008(3) Å, which is within the limit allowed for topochemical [2+2] photocycloaddition.[8] Since a topochemical reaction proceeds with a minimum of the atomic and molecular movement, **2b** would be formed by a double [2+2] photocycloaddition between the two facing molecules of **1b** under crystal lattice control.

The crystal structure of photoreactive **1c** was not solved, since a single crystal suitable for an X-ray crystallographic analysis could not be obtained. However, the photochenical behavior of **1c** was similar to that of **1b** in the crystalline state, indicating that the molecular arrangement of **1c** in the crystal would be similar to that of **1b**.

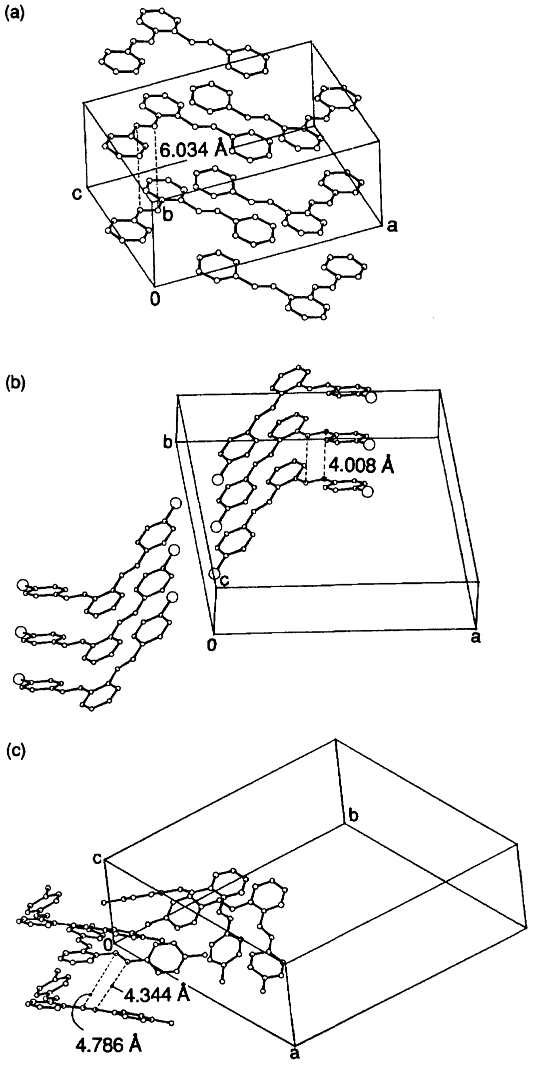


Fig. 2. The crystal structures of (a) **1a**, (b) **1b**, and (c) **1e**.

In contrast, there might exist no pair of carbon-carbon double bonds for [2+2] photocycloaddition in the crystals of the other photostable compounds. This explanation is, for example, definitely supported by the case of the crystal of **1a** (Fig. 2a). The intermolecularly nearest carbon–carbon double bonds are located along the *b*-axis, but the distance is 6.034(1) Å, which is over the limit of the photoreactive range.[8]

The introduction of chloro substituents brought about a dramatic change in the crystal structure, as can be seen by a comparison of the crystal structure of **1a** with that of **1b**. This phenomenon could be explained in terms of the effect of chlorine-chlorine interaction in the crystal.[9] Figure 3 shows the relative position of two molecules of **1b**. In the crystal of **1b**, the chlorine atoms are located closely; the distance of Cl···Cl is 3.45 Å and the angle of C–Cl···Cl is 146° to form plane ribbons, indicating the presence of an intraplanar Cl···Cl interaction.[10] Moreover, by an interplanar C···C interaction, the ribbons are piled up with only a slight displacement along the shortest axis (*c*-axis) at a distance of about 4 Å, as observed for the crystals of planar chloro-substituted aromatics,[9] resulting in the location of the carbon–carbon double bonds in a face-to-

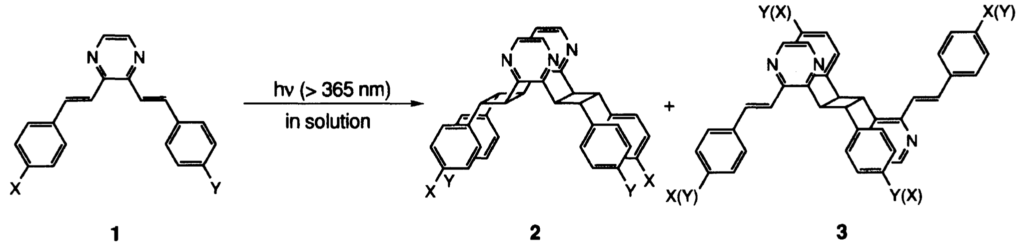


Chart 2.

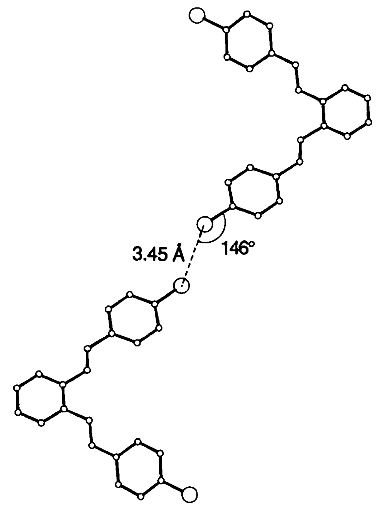


Fig. 3. The relative position of two molecules of **1b**.

face configuration and within a photoreactive distance. On the other hand, in the crystal of **1a**, since such an intraplanar interaction as the Cl···Cl interaction does not exist, a C···C interaction might work, not only interplanarly, but also intraplanarly, resultig in a pile-up of the molecules with a greater displacement. Subsequently, the distance between the neighboring carbon–carbon double bonds in **1a** molecules is made longer than that of **1b**. These facts indicate that the Cl···Cl and C···C interactions in the crystal of **1b** play an important role in determining the distance between the carbon–carbon double bonds.

In order to confirm this interpretation, an X-ray crystal structure analysis of **1e**, in which the size of the methyl substituent is comparable to that of chlorine substituent,[9] was also performed (Fig. 2c). In the crystal of **1e**, the distances between the neighboring carbon–carbon double bonds are 4.344 and 4.786 Å, and the carbon–carbon double bonds are unparallel and distorted about 27.2°, making **1e** photostable in the crystalline state. This structure also explains the photoreactivity of the crystal of **1b**, which is attributed to the molecular arrangement influenced by the Cl···Cl and C···C interactions.

Photoreaction in Solution. As mentioned above, the photoreaction of **1b** crystals dispersed in water gave monocyclic dimer **3b**, although the yield was very low. Monocyclic dimer **3b**, however, would not arise through the topochemical process, since the carbon-carbon double bond in a molecule of **1b** is too far away from the carbon–carbon double bond in the neighboring molecule to give **3b**. The formation of **3b** may thus be explained as follows: 1) The [2+2] photocycloaddition of **1b**, which was slightly dissolved in water, took place in solution, and/or 2) **1b** molecules photoreacted without any crystal lattice control, since **1b** gradually changed from the crystalline phase into the amorphous phase upon the progress of the photoreaction.

Table 2. Photoreaction (>365 nm) of **1a** in Solution[a)]

Solvent	Concentration	Reaction time	Yield/%	
	mol dm^{-3}	h	**2a**	**3a**
Acetonitrile	3.7×10^{-3}	22	21	18
Benzene			15	25
Hexane			6	35[b)]

a) The reaction was performed until reaching to the stationary state, and yields given are isolated yields after chromatography and recrystallization. b) Most of **3a** was obtained as a white precipitate.

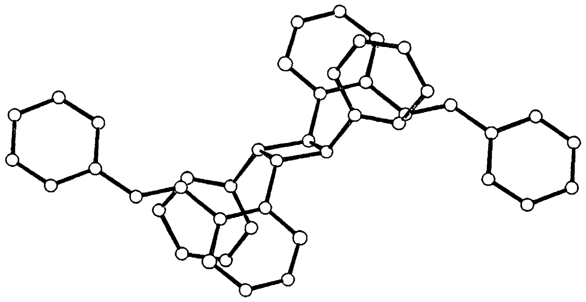


Fig. 4. ORTEP drawing of **3a**.

This consideration led us to investigate the photoreaction of **1** in solution. When a solution of **1a** was irradiated with a 500-W supper-high-pressure mercury lamp through a cut-off filter (wavelengths>365 nm) under a nitrogen atmosphere for 22 h, [2.2]orthocyclophane **2a** and monocyclic dimer **3a** were isolated as major products among the photoproducts; the structure of **2a** was determined by a comparison of its ^{1}H NMR spectrum with that of **2b**, and the structure of **3a** was directly solved by an X-ray crystallographic analysis (Fig. 4).[11)] The yield of **2a** decreased with decreasing the polarity of the solvent, whereas the yield of **3a** increased (Chart 2, Table 2).

Table 3. Photoreaction (>365 nm) of **1b**, **1e** and **1f** in Solution[a]

Substrate	Solvent	Concentration	Reaction time	Yield/%	
		mol dm^{-3}	h	**2**	**3**
1b	Acetonitrile /Chloroform[b]	3.3x10^{-3}	5	35	11
1e	Acetonitrile	3.5x10^{-3}	7	10	10
1f		2.9x10^{-3}		37	—[c]

a) The reaction was performed until reaching to the stationary state, and yields given are isolated yields after chromatography and recrystallization. b) Acetonitrile/chloroform=10/1. c) Other products were complex and not identified.

Table 4. Photoreaction (>365 nm) of **1a** in the Presence of a Triplet Sensitizer or Quencher[a]

Solvent	Additive[a]	Wavelengths for irradiation/nm	Reaction time	Yield/%	
			h	**2a**	**3a**
Acetonitrile	Perylene	>440	36	No reaction	
	Rhodamine B			No reaction	
	Acriflavine			0	0
	Azulene	>365	22	23	8
	None			21	18
Hexane	Azulene			22	35
	Fluoranthene			13	23
	None			6	35

a) The reaction was performed until reaching to the stationary state, and yields given are isolated yields after chromatography and recrystallization. The amount of the additive was 7 mg/50 ml.

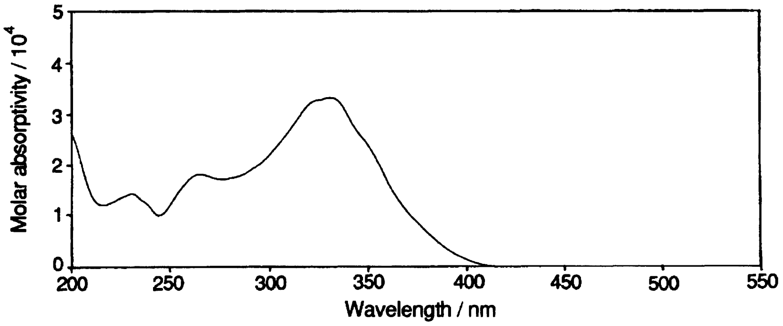


Fig. 5. The UV-spectrum of **1a** in acetonitrile.

The photoreaction of **1b,e,f** was also carried out in acetonitrile/chloroform (10/1) or acetonitrile, but the photoreaction of **1c** and **1d** was not conducted because of poor solubility in usual solvents at room temperature. In all of the reactions carried out, the corresponding [2.2]orthocyclophane was obtained as a major product in moderate yield (Table 3).

In the photoreaction of the unsymmetrically substituted derivative **1f**, there is a possibility to form two types of [2.2]orthocyclophanes, head-to-tail and head-to-head **2f**. It is noteworthy that the photoreaction of **1f** in acetonitrile predominantly gave the head-to-tail type [2.2]orthocyclophane (head-to-tail-**2f**) and no head-to-head type [2.2]orthocyclophane was isolated. The exclusive formation of the head-to-tail-**2f** suggests that there exists a strong charge-transfer interaction between the methoxyphenyl group and the cyanophenyl group in the molecules of **1f**.

In order to visualize the photoexcited species in the reaction of 2,3-di[(*E*)-styryl]pyrazine derivatives in solution, the photoreaction of **1a** was carried out in the presence of a triplet sensitizer or quencher (Table 4). From the UV-absorption of **1a** (Fig. 5) and from the fact that no reaction proceeded upon irradiation with wavelengths longer than 440 nm, the singlet energy of **1a** was estimated to be 65—70 kcal mol^{-1}.

When perylene (E_S = 65 kcal mol^{-1}, E_T = 36 kcal mol^{-1}) or rhodamine B (E_S=49 kcal mol^{-1}, E_T=43 kcal mol^{-1}) was added in an acetonitrile solution of **1a**, no reaction proceeded upon irradiation with wavelengths longer than 440 nm. On the other hand, when acriflavine (E_S=59 kcal mol^{-1}, E_T=51 kcal mol^{-1}) was

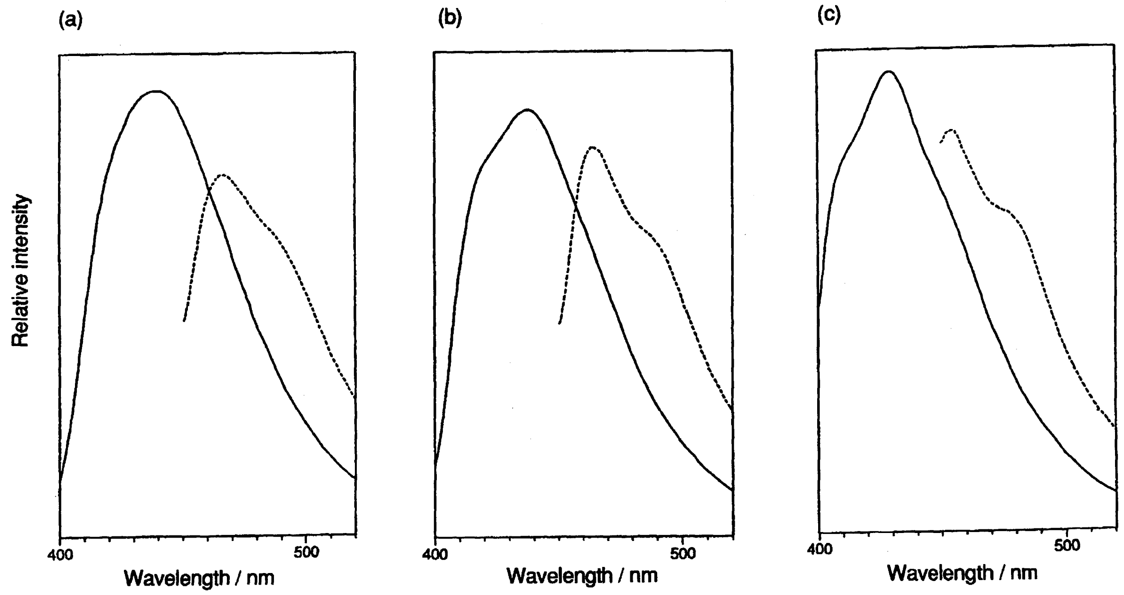


Fig. 6. The fluorescence spectra of **1a** (a) in acetonitrile, (b) benzene, and (c) hexane. Excitation: 365 nm (at which **1a** can be excited) (——). 440 nm (at which **1a** cannot be excited) (- - -).

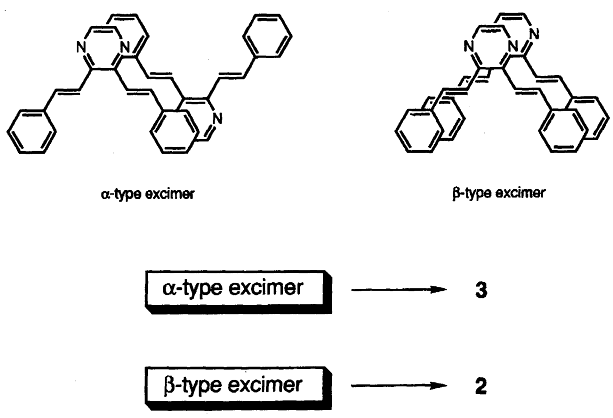


Fig. 7. Schematic drawings for two types of excimers in solution.

added and the solution was irradiated with wavelengths longer than 440 nm, the reaction proceeded. However, neither **2a** nor **3a** was detected, but stilbene was obtained as a major product; stilbene would be formed through an intramolecular [2+2] photocycloaddition, followed by the cleavage of the cyclobutane ring, as observed for the photoreaction of 1,2-distyrylbenzene derivatives.[4a,12] On the basis of these results, it is suggested that a triplet excited state of **1a** exists between 43 and 51 kcal mol^{-1}, and that through the triplet state the intermolecular photoreactions, giving **2a** and **3a**, do not proceed although the intramolecular photoreaction occurs.

The photoreaction (wavelengths>365 nm) in the presence of azulene ($E_S=81$ kcal mol^{-1}, $E_T=33$—37 kcal mol^{-1}) gave an equal quantity of **2a** as that in the absence of azulene, whereas the yield of **3a** was depressed. This decrease in the yield of **3a** would be attributable to a side reaction of **3a** with azulene in acetonitrile; this assumption is supported by the fact that the yield of **3a** was not affected when the reaction was carried out in hexane. These results indicate that the photoreaction was not essentially affected by the addition of azulene. Moreover, the photoreaction (wavelengths>365 nm) in the presence of fluoranthene ($E_S=80$ kcal mol^{-1}, $E_T=53$ kcal mol^{-1}) in hexane also gave **2a** and **3a**. These results indicate that both **2a** and **3a** are produced through a singlet excited state.

In the next stage, the fluorescence spectra were measured for **1a**. When **1a** in solution (5.0×10^{-3} mol dm^{-3}) was excited at a wavelength of 440 nm, at which **1a** had almost no absorption in the UV spectrum, an emission peak appeared at a longer wavelength than that of **1a**, itself (Fig. 6), indicating that the reaction proceed through other species different from the excited **1a**, itself.

The results on the excited species and fluorecence spectra suggest that **2a** and **3a** are produced through two types of singlet excited states: An α-type excimer which gives monocyclic dimer **3a**, and a β-type excimer which gives [2.2]orthocyclophane **2a** (Fig. 7).

The fully overlapping β-type excimer would be more stable than the α-type excimer; in fact, the photoreaction of 1,2-di[(*E*)-styryl]benzene in a nonpolar solvent, hexane, gave the corresponding [2.2]orthocyclophane as a major product ([2.2]orthocyclophane/monocyclic dimer=78/22).[5] In contrast, a monocyclic dimer **3a** was predominantly obtained when the photoreaction of **1a** was performed in a nonpolar solvent ([2.2]orthocyclophane/monocyclic dimer=37/63 and 15/85 in benzene and in hexane, respectively; see Table 2). This

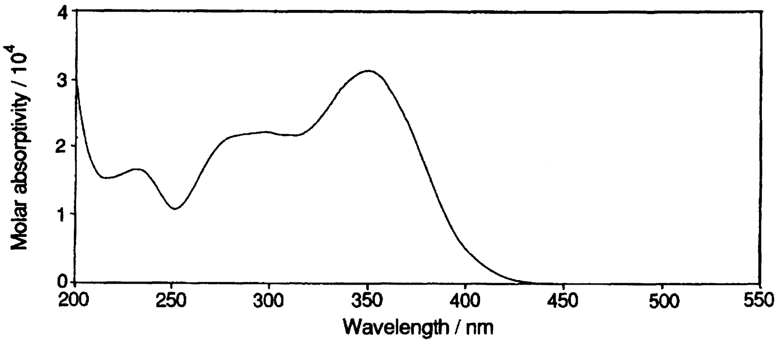


Fig. 8. The UV-spectrum of **1f** in acetonitrile.

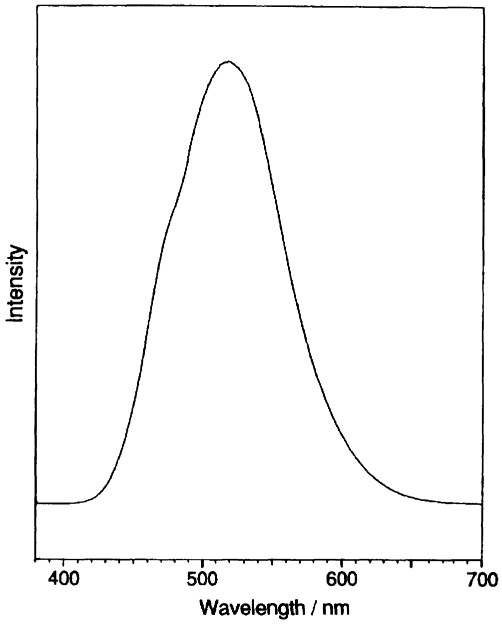


Fig. 9. The fluorescence spectrum of **1f** in acetonitrile (5×10^{-3} mol dm^{-3}). Excitation: 365 nm.

phenomenon would be attributable to a charge-transfer-like intermolecular interaction between the phenyl group and the pyrazinylene group, which generally appears stronger in a nonpolar solvent than in a polar solvent. Considering a similar intermolecular interaction, the fact that head-to-tail-**2f** was exclusively formed in the photoreaction of **1f** in acetonitrile can be explained as follows: A relatively strong charge transfer-like interaction exists between the methoxyphenyl group and the cyanophenyl group in the molecules of **1f** and significantly overcomes the charge transfer-like interactions between the pyrazinylene group and the substituted phenyl group to form β-type excimer predominantly, resulting in the exclusive formation of head-to-tail-**2f**. The UV absorption end of **1f** was shifted to about 445 nm and the fluorescence peak appeared around 520 nm (Figs. 8 and 9; compare with Figs. 5 and 6), indicating the existence of a charge-transfer interaction in the ground state as well as a bathochromic effect due to the cyano- and methoxy-substituents, although no fluorescence peak, which was attributable to the charge transfer complex, could be detected. On the basis of these observations, it is concluded that 2,3-di[(*E*)-styryl]pyrazine derivatives exist in α- and β-type excimers upon photoirradiation and that the ratio of the α-type excimer/β-type excimer increases with a decrease in the polarity of the solvent.

To our surprise, the highest yield of **2a** was achieved (41%) among the present experiments, when the photoirradiation (wavelengths>365 nm) was carried out for a transparent, solidified benzene solution of **1a** (3.7×10^{-3} mol dm^{-3}), which was obtained by cooling the solution to 0 °C with stirring. In contrast, the crystal of **1a**, which was prepared by slow evaporation of a benzene solution, was quite photostable. The result may be explained in the following terms, that the aggregated molecules, which give β-type excimer predominantly, are frozen while keeping the relative positions, and that a crystal-like photoreaction can occur.

In conclusion, the photoreaction of 2,3-di[(*E*)-styryl]pyrazine derivatives **1** was examined in the crystalline state and in solution. In the crystalline state, photoreactivity is largely dependent on the crystal structure and, for the photoreactive derivatives **1b** and **1c**, the exclusive formation of [2.2]orthocyclophanes **2b** and **2c** was observed under crystal-lattice control. In contrast, the photoirradiaiton of 2,3-di[(*E*)-styryl]pyrazine derivatives **1** in solution gave [2.2]orthocyclophane **2** and *anti* head-to-tail type monocyclic dimer **3** as major products. These two products would arise from different excimers, and the product distribution was influenced by the polarity of the solvent employed.

Experimental

Measurements. The infrared spectra and ^{1}H NMR spectra were recorded on a JASCO IR-810 spectrophotometer and a JEOL GX-400 instrument, respectively. The melting points were measured by a Laboratory Devices Mel-Temp and are uncorrected. Fluorescence spectra were measured by a Hitachi Fluorescence Spectrophotometer Model 850. Intensity data for an X-ray crystallographic analysis were measured on a Mac-Science MXC-18 or a Phillips PW1100 four-circle diffractometer with graphite monochromated Cu *K*α radiation.

Preparation of 1a. Butyric anhydride (76 ml) was added to a mixture of 2,3-dimethylpyrazine (9.9 ml, 92 mmol) and benzaldehyde (29.7 g, 280 mmol); the mixture was refluxed for 37 h under a nitrogen atmosphere. After dichloromethane (50 ml) was added, the reaction mixture was washed with an 8 mol dm^{-3} aqueous sodium hydroxide solution (3×50 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated by an evaporator under reduced pressure. The black oil, thus obtained, was roughly purified by short silica-gel column chromatography (ethyl acetate/hexane=1/1 v/v). The crude product was recrystallized from hexane to give 5.58 g (21%) of pure 2,3-di[(*E*)-styryl]pyrazine (**1a**) as yellow needle crystals: Mp 117—119 °C; IR (KBr) 1630, 1450, 1390, 980, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.35 (t, 2H, J=7 Hz), 7.42 (t, 4H, J=7 Hz), 7.51 (d, 2H, J=16 Hz), 7.64 (d, 4H, J=7 Hz), 7.85 (d, 2H, J=16 Hz), 8.44 (s, 2H).

Found: C, 84.41; H, 5.68; N, 10.07%. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85%.

Preparation of 1b. Butyric anhydride (47 ml) was added to a mixture of 2,3-dimethylpyrazine (6.1 ml, 58 mmol) and *p*-chlorobenzaldehyde (24.4 g, 174 mmol); the mixture was refluxed for 36 h under a nitrogen atmosphere. Upon cooling the reaction mixture to room temperature, yellow crystals were deposited. After 8 mol dm^{-3} aqueous sodium hydroxide solution (50 ml) and dichloromethane (50 ml) were added to the suspension, the suspension was vigorously stirred, giving the crude precipitate. The crude precipiatate was recrystallized from ethanol to give 7.33 g (36%) of 2,3-bis[(*E*)-*p*-chlorostyryl]pyrazine (**1b**) as yellow needle crystals: Mp 207—209 °C; IR (KBr) 1495, 1410, 1100, 1080, 965, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.38 (d, 4H, J=9 Hz), 7.44 (d, 2H, J=16 Hz), 7.56 (d, 4H, J=9 Hz), 7.80 (d, 2H, J=16 Hz), 8.44 (s, 2H).

Found: C, 68.20; H, 4.09; N, 7.70; Cl, 20.50%. Calcd for $C_{20}H_{14}N_2Cl_2$: C, 68.00; H, 3.99; N, 7.93; Cl, 20.07%.

In a similar manner, **1c** was prepared and recrystallized from ethanol. By using acetic anhydride instead of butyric anhydride, **1d** and **1e** were also prepared, and recrystallized from chloroform and ethanol, respectively.

1c: Yellow needle crystals: Mp 278—280 °C; IR (KBr) 2230, 1600, 1415, 1395, 965, 850, 815, 555 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.57 (d, 2H, J=16 Hz), 7.71 (s, 8H), 7.89 (d, 2H, J=16 Hz), 8.51 (s, 2H).

Found: C, 78.76; H, 4.39; N, 16.49%. Calcd for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76%.

1d: Yellow needle crystals: Mp>310 °C (decomposed before melting); IR (KBr) 1595, 1520, 1345, 1110, 965, 860, 750 cm^{-1}; ^{1}H NMR (CF_3CO_2D) δ=7.83 (d, 2H, J=16 Hz), 7.96 (d, 4H, J=9 Hz), 8.17 (d, 2H, J=16 Hz), 8.42 (d, 4H, J=8 Hz), 9.05 (s, 2H).

Found: C, 63.95; H, 3.78; N, 15.22%. Calcd for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97%.

1e: Yellow needle crystals: Mp 130—132 °C; IR (KBr) 2930, 1630, 1510, 1440, 1395, 1190, 980, 975, 810, 480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.39 (s, 6H), 7.21(d, 4H, J=8 Hz), 7.44 (d, 2H, J=16 Hz), 7.53 (d, 4H, J=8 Hz), 7.80 (d, 2H, J=16 Hz), 8.40 (s, 2H).

Found: C, 84.40; H, 6.45; N, 9.12%. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97%.

Preparation of 1f. Acetic anhydride (18 ml) was added to a mixture of 2,3-dimethylpyrazine (3.8 ml, 36 mmol) and *p*-anisaldehyde (24.6 g, 181 mmol); the mixture was refluxed for 43 h under a nitrogen atmosphere. After dichloromethane (50 ml) was added, the reaction mixture was successively washed with 8 mol dm^{-3} aqueous sodium hydroxide solution (3×50 ml) and 2 mol dm^{-3} aqueous $NaHSO_3$ solution (3×100 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated by an evaporator under reduced pressure. The resulting black oil was purified by silica-gel column chromatography (dichloromethane), followed by recrystallization from ethanol, to give 1.69 g (21%) of pure 2-[(*E*)-*p*-methoxystyryl]-3-methylpyrazine as yellow needle crystals: Mp 122—124 °C; IR (KBr) 1630, 1605, 1515, 1465, 1420, 1400, 1305, 1260, 1180, 1120, 1080, 1020, 975, 870, 850, 820, 540, 510, 460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.68 (s, 3H), 3.84 (s, 3H), 6.93 (d, 2H, J=9 Hz), 7.15 (d, 2H, J=16 Hz), 7.56 (d, 2H, J=9 Hz), 7.79 (d, 2H, J=16 Hz), 8.28 (d, 2H, J=2 Hz), 8.37 (d, 2H, J=2 Hz).

Acetic anhydride (2 ml) was added to a mixture of the monoolefinic pyrazine derivative (1.76 g, 7.8 mmol) and *p*-cyanobenzaldehyde (2.55 g, 19.4 mmol); the mixture was refluxed for 6 h under a nitrogen atmosphere. After dichloromethane (50 ml) was added, the reaction mixture was successively washed with 6 mol dm^{-3} aqueous sodium hydroxide solution (2×10 ml) and 2 mol dm^{-3} aqueous $NaHSO_3$ solution (3×50 ml). The organic layer was dried over anhydrous Na_2SO_4 and concentrated by an evaporator under reduced pressure. After the crude mass was purified by silica-gel column chromatography (dichloromethane/hexane=1/5), recrystallization from ethanol was carried out to give pure 2-[(*E*)-*p*-cyanostyryl]-3-[(*E*)-*p*-methoxystyryl]pyrazine (**1f**) as yellow needle crystals: Mp 188—189.5 °C, IR (KBr) 2225, 1605, 1260, 1240, 1180, 975, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.86 (s, 3H), 6.95 (d, 2H, J=9 Hz), 7.33 (d, 1H, J=16 Hz), 7.59 (d, 2H, J=9 Hz), 7.60 (d, 1H, J=15 Hz), 7.70 (s, 4H), 7.83 (d, 1H, J=16 Hz), 7.83 (d, 1H, J=16 Hz), 8.42 (d, 1H, J=2 Hz), 8.46 (d, 1H, J=2 Hz).

Found: C, 77.57; H, 5.17; N, 12.46%. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38%.

Photoreaction in the Crystalline State. Finely powdered crystals of **1b** or **1c** (100 mg) were dispersed in 100 ml of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated from outside the flask with a 500-W super-high-pressure mercury lamp (Ushio USH 500D) through an optical filter (Kenko UV-32(cut off<300 nm)) with vigorous stirring under a nitrogen atmosphere. The products were separated and purified by preparative TLC (dichloromethane).

Photoreaction in Solution. In a quartz cell, a degassed solution (50 ml) of **1** was placed and irradiated with a 500-W super-high-pressure mercury lamp (Ushio USH 500D-0) through an optical filter (Kenko L-40 (cut off <365 nm)), or with a 500-W xenon short arc lamp (Ushio UXL 500D-0) through an optical filter (Kenko Y-46 (cut off<440 nm)), with vigorous stirring under a nitrogen atmosphere. The products were roughly purified by preparative TLC and quantitated by ^{1}H NMR.

The structures of isolated **2b** and **3a** were directly determined by X-ray crystallographic analyses. The structures of other photoproducts **2** and **3** were determined by comparison of their ^{1}H NMR spectra with those of **2b** and **3a**, respectively. **2a**: ^{1}H NMR ($CDCl_3$) δ=4.67—4.70 (m, 4H), 5.11—5.13 (m, 4H), 7.06—7.17 (m, 20H), 8.26 (s, 4H). **2b**: ^{1}H NMR ($CDCl_3$) δ=4.56—4.57 (m, 4H), 5.06—5.07 (m, 4H), 7.07 (d, 8H, $J=9$ Hz), 7.17 (d, 8H, $J=9$ Hz), 8.26 (s, 4H). **2c**: ^{1}H NMR ($CDCl_3$) $\delta=4.62$—4.64 (m, 4H), 5.22—5.24 (m, 4H), 7.24 (d, 8H, $J=8$ Hz), 7.49 (d, 8H, $J=8$ Hz), 8.30 (s, 4H). **2e**: ^{1}H NMR ($CDCl_3$) $\delta=2.24$ (s, 12H), 4.60—4.61 (m, 4H), 5.02—5.04 (m, 4H), 6.98 (d, 8H, $J=8$ Hz), 7.05 (d, 8H, $J=8$ Hz), 8.23 (s, 4H). head-to-tail-**2f**: ^{1}H NMR ($CDCl_3$) $\delta=3.76$ (s, 6H), 4.28 (dd, 2H, $J=10$, 4 Hz), 4.81 (t, 2H, $J=10$ Hz), 5.03 (t, 2H, $J=10$ Hz), 5.15 (dd, 2H, $J=10$, 4 Hz), 6.77 (d, 4H, $J=8$ Hz), 7.14 (d, 4H, $J=9$ Hz), 7.15 (d, 4H, 8 Hz), 7.42 (d, 4H, $J=8$ Hz), 8.20 (d, 2H, $J=2$ Hz), 8.33 (d, 2H, $J=3$ Hz). **3a**: ^{1}H NMR ($CDCl_3$) $\delta=4.86$—4.91 (m, 2H), 5.30—5.39 (m, 2H), 7.00 (t, 2H, $J=7$ Hz), 7.05 (t, 4H, $J=7$ Hz), 7.14 (d, 4H, $J=7$ Hz), 7.29 (d, 2H, $J=16$ Hz), 7.37 (t, 2H, $J=7$ Hz), 7.45 (t, 4H, $J=7$ Hz), 7.62 (d, 2H, $J=15$ Hz), 7.62 (d, 4H, $J=7$ Hz), 8.26 (d, 2H, $J=2$ Hz), 8.39 (d, 2H, $J=2$ Hz). **3b**: ^{1}H NMR ($CDCl_3$) $\delta=4.75$—4.79 (m, 2H), 5.25—5.30 (m, 2H), 7.01 (d, 4H, $J=9$ Hz), 7.05 (d, 4H, $J=9$ Hz), 7.17 (d, 2H, $J=16$ Hz), 7.41 (d, 4H, $J=8$ Hz), 7.53 (d, 4H, $J=9$ Hz), 7.58 (d, 2H, $J=16$ Hz), 8.31 (d, 2H, $J=2$ Hz), 8.40 (d, 2H, $J=2$ Hz). **3e**: ^{1}H NMR ($CDCl_3$) $\delta=2.14$ (s, 6H), 2.42 (s, 6H), 4.76—4.83 (m, 2H), 5.27—5.33 (m, 2H), 6.84 (d, 4H, $J=8$ Hz), 7.04 (d, 4H, $J=8$ Hz), 7.23 (d, 2H, $J=16$ Hz), 7.25 (d, 4H, $J=7$ Hz), 7.52 (d, 4H, $J=8$ Hz), 7.57 (d, 2H, $J=16$ Hz), 8.24 (d, 2H, $J=2$ Hz), 8.37 (d, 2H, $J=2$ Hz).

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6) Crystal data of **2b**·benzene: Chemical formula $C_{40}H_{28}N_4Cl_4\cdot C_6H_6$; formula weight 784.61; crystal system monoclinic; space group $P2_1/a$; $Z=4$; $a=20.372(10)$, $b=14.366(8)$, $c=13.835(8)$ Å; $\beta=102.38(5)°$; $V=3955$ Å^3; $D_c=1.32$ g cm^{-3}; $R=0.067$ (used 6734 reflections).

7) Crystal data of **1a**: Chemical formula $C_{20}H_{16}N_2$; formula weight 284.36; crystal system monoclinic; space group $P2_1/c$; $Z=4$; $a=16.792(2)$, $b=6.034(1)$, $c=15.639(2)$ Å; $\beta=101.47(1)°$; $V=1552.9(4)$ Å^3; $D_c=1.22$ g cm^{-3}; $R=0.059$; $R_w=0.053$ (used 2583 reflections). Crystal data of **1b**: Chemical formula $C_{20}H_{14}N_2Cl_2$; formula weight 353.25; crystal system monoclinic; space group $P2_1/n$; $Z=4$; $a=18.476(10)$, $b=23.155(13)$, $c=4.008(3)$ Å; $\beta=91.97(5)°$; $V=1713$ Å^3; $D_c=1.37$ g cm^{-3}; $R=0.062$ (used 2583 reflections). Crystal data of **1e**: Chemical formula $C_{22}H_{20}N_2$; formula weight 312.41; crystal system orthorhombic; space group $P2_12_12_1$; $Z=8$; $a=21.459(3)$, $b=22.154(3)$, $c=7.384(1)$ Å; $V=3510.4(7)$ Å^3; $D_c=1.18$ g cm^{-3}; $R=0.054$; $R_w=0.061$ (used 2632 reflections).

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