Topochemical Photopolymerization of 4-[2-(Unsubstituted and Methyl-Substituted Pyrazinyl)ethenyl]cinnamates and -thiocinnamates in the Crystalline State

Kazuhiko Saigo,* Makoto Sukegawa, Yasunari Maekawa, and Masaki Hasegawa*,†

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

†Department of Materials Science and Technology, Faculty of Engineering, Toin University of Yokohama, Kurogane-cho, Aoba-ku, Yokohama 225

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Topochemical photopolymerization of 4-[2-(unsubstituted and methyl-substituted pyrazinyl)ethenyl]-cinnamates and -thiocinnamates were carried out in the crystalline state. Upon photoirradiation, ethyl 4-[2-(unsubstituted and methyl-substituted pyrazinyl)ethenyl]cinnamates and *S*-ethyl 4-[2-(unsubstituted and methyl-substituted pyrazinyl)ethenyl]thiocinnamates gave α-hetero-type crystalline linear polymers, whereas methyl 4-[2-(methyl-substituted pyrazinyl)ethenyl]cinnamates afforded mixtures of β-type oligomers. The X-ray crystallographic analyses of the monomers revealed that the thioesters were more favorable monomers than the corresponding esters from the viewpoint of close packing in a crystal. The following factor(s) would play an important role in determining their molecular arrangements: 1) The close contact between the central 1,4-phenylene ring and the alkoxy oxygen of the ester group or the alkylthio sulfur of the thioester group, 2) the hydrogen bond between the interstacked pyrazinyl groups, and/or 3) the gearing of the alkyl group in the ester moiety with the methylpyrazinyl group.

Topochemical [2+2] photoreaction has increasingly been attracting attention from the viewpoints of organic and polymer syntheses related to regio- and/or stereoselectivity that arise from the highly ordered environment of a crystal lattice.[1] For recent decade, we have reported that unsymmetrically substituted diolefin compounds, alkyl 4-(2-azaarenylethenyl)cinnamates, displayed various types of topochemical [2+2] photocycloadditions; their photochemical behavior greatly varied, depending not only on slight modifications of the molecular structure but even on the crystallization process of the same compound. For example, alkyl 4-[2-(4-pyridyl)ethenyl]cinnamate crystals showed "kaleidoscopic" photochemical behavior upon varying the ester alkyl moiety to give a linear high polymer from the methyl ester, an optically active dimer from a chiral crystal of the ethyl ester, and two types of dimers from a single crystal of the propyl ester.[2] The azaarenyl part of alkyl 4-(2-azaarenylethenyl)cinnamates also greatly influenced the topochemical photobehavior; ethyl 4-(2-pyrazinylethenyl)cinnamate[3] showed high photoreactivity to yield a crystalline linear polymer with high molecular weight, whereas the corresponding 4-pyrimidinyl derivative[4] showed no topochemical photoreactivity.

In many topochemical [2+2] photoreactions, the structures of photoproducts are reasonably interpreted on the basis of the X-ray crystal structure analyses of the starting compounds, since the topochemical photoreaction proceeds with a minimum movement of atoms and molecules. However, the determining factor of the crystal structures of photoreactive compounds is so sophisticated that it is rather difficult to predict the structures of photoproducts from the chemical structures of reactants.

In this paper we describe the influence in topochemical behavior of 4-[2-(2-pyrazinyl)ethenyl]cinnamate crystals upon replacing the ester group by a thioester group and/or introducing a methyl substituent in the pyrazinyl group.

Results and Discussion

S-Ethyl 4-(2-pyrazinylethenyl)thiocinnamate (**1**),[5] *S*-ethyl 4-[2-(6-methyl-2-pyrazinyl)ethenyl]thiocinnamate (**2**), *S*-ethyl 4-[2-(3-methyl-2-pyrazinyl)ethenyl]-thiocinnamate (**3**), ethyl 4-[2-(6-methyl-2-pyrazinyl)ethenyl]cinnamate (**5**), ethyl 4-[2-(3-methyl-2-pyrazinyl)-ethenyl]cinnamate (**6**), methyl 4-[2-(6-methyl-2-pyrazinyl)ethenyl]cinnamate (**8**), and methyl 4-[2-(3-methyl-2-pyrazinyl)ethenyl]cinnamate (**9**) were synthesized by aldol-type reactions of methyl 4-formylcinnamate with pyrazine derivatives, transesterification of the resulting methyl cinnamate derivatives, or hydrolysis of the methyl cinnamate derivatives, followed

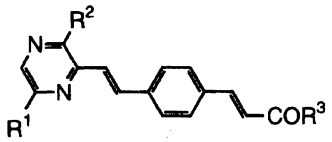


Table 1. Photoreaction of **1**—**9**

Compound	R^1	R^2	R^3	Light source[a)]	Reaction time/h	Morphology of photoproducts	η_{inh}[b)] / dL g^{-1}
1	H	H	SEt	500 W	24	Crystalline	1.6
2	Me	H	SEt	100 W	4	Crystalline	1.1
3	H	Me	SEt	100 W	4	Crystalline	1.8
4[3)]	H	H	OEt	500 W	5	Crystalline	8.2
5	Me	H	OEt	500 W	8	Crystalline	0.8
6	H	Me	OEt	500 W	8	Crystalline	2.5
7[3)]	H	H	OMe	500 W	5	Crystalline	3.9
8	Me	H	OMe	100 W	8	Amorphous	—[c)]
9	H	Me	OMe	500 W	8	Amorphous	—[c)]

a) A 100-W high-pressure mercury lamp set inside of the flask or a 500-W super-high-pressure mercury lamp set outside of the flask. b) 0.3 g dL^{-1} in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 30 °C. c) The photoproduct comprised a mixture of oligomers, as determined by gel permeation chromatography (eluent: *N*,*N*-dimethylformamide).

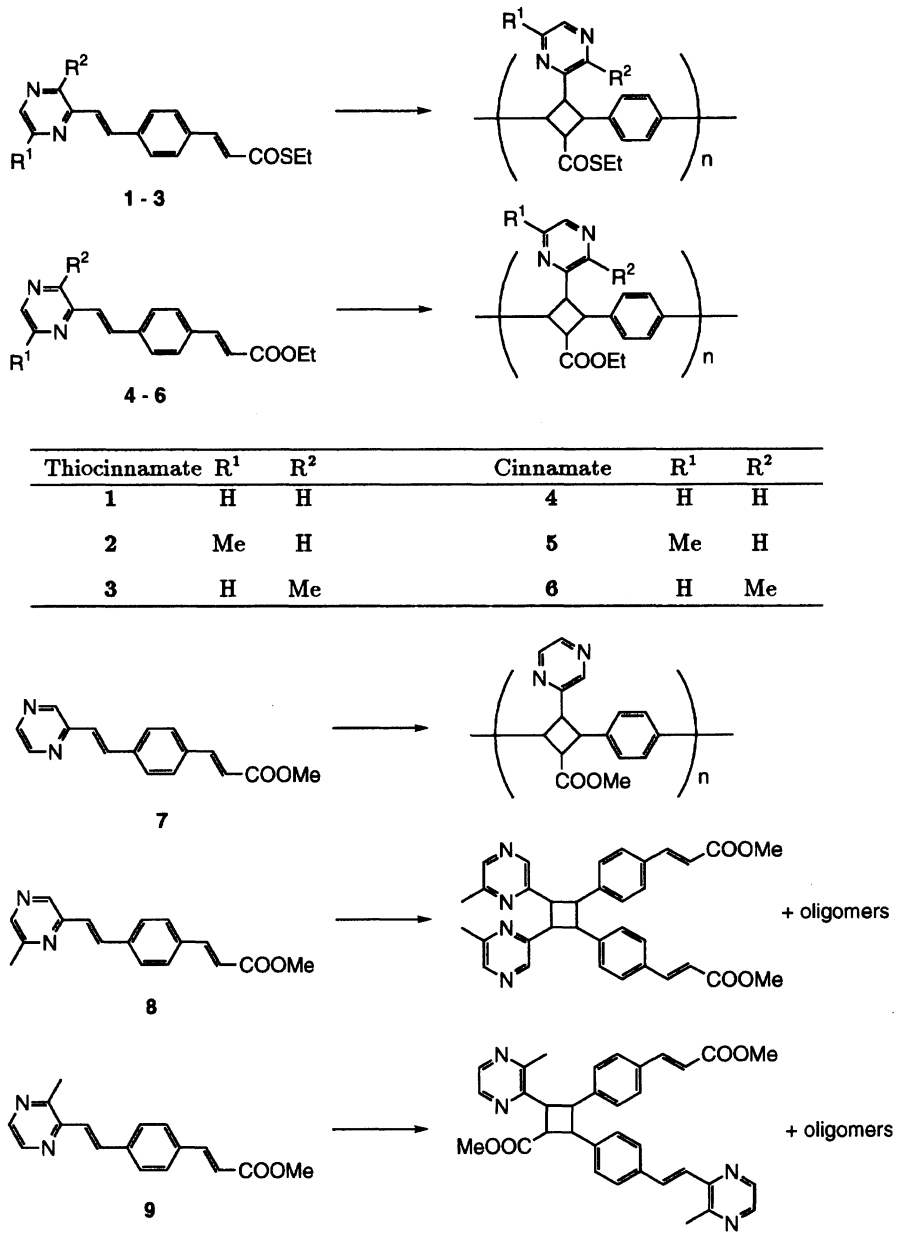
Table 2. Crystal Data and Details of Refinement of **1**, **2**, **5**, and **8**

Compounds	**1**	**2**	**5**	**8**
Formula	$C_{17}H_{16}N_2OS$	$C_{18}H_{18}N_2OS$	$C_{18}H_{18}N_2O_2$	$C_{17}H_{16}N_2O_2$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pna2_1$	$Pna2_1$	$P2_1/a$
a/Å	21.279(6)	7.788(3)	7.656(1)	18.539(8)
b/Å	9.489(4)	9.568(2)	9.681(1)	4.834(2)
c/Å	7.500(2)	21.922(7)	21.342(3)	17.197(12)
β/deg	97.65(6)			104.40(3)
V/Å^3	1500.9(3)	1636(1)	1581.8(4)	1493(1)
Z	4	4	4	4
Crystal dimensions/mm	0.8×0.15×0.05	0.4×0.3×0.1	0.3×0.2×0.1	0.6×0.4×0.15
D_c	1.31	1.26	1.23	1.25
μ/cm^{-1}	17.98	16.69	5.74	5.87
$2\theta_{max}$/deg	130	130	130	120
Unique reflections	2244	1409	1197	2506
Observed reflections	2019	1135	964	1853
R	0.061	0.058	0.053	0.100
R_w	0.097	0.061	0.065	0.120
Largest shift/esd	0.67	0.20	0.17	0.03
Largest peak/e Å^{-3}	0.50	0.23	0.19	0.63

by thioesterification. Their topochemical behavior was compared to each other as well as to that of unsubstituted 4-(2-pyrazinylethenyl)cinnamate derivatives, ethyl 4-(2-pyrazinylethenyl)cinnamate (**4**) and methyl 4-(2-pyrazinylethenyl)cinnamate (**7**), which have been already reported from our laboratory.[3)] The irradiation conditions and the photoproducts are shown in Table 1 and Scheme 1.

From the comparison of the X-ray diffraction pattern and ^{1}H NMR spectrum of poly-**1** with those of poly-**4**,[3)] an alternating structure of an α-hetero-type cyclobutane ring and 1,4-phenylene skeleton in the main chain has been confirmed for poly-**1**.[5)] On the basis of a similar comparison, in the present study, it was found that irradiation of each of the monomers having a thioester group, **2** and **3**, gave a crystalline polymer (η_{inh}=1.1 and 1.8 dL g^{-1}, respectively) of the same skeleton as those of poly-**1** and poly-**4**, even though a methyl substituent was introduced to the pyrazinyl moiety. The formation of a crystalline polymer having α-hetero-type cyclobutane rings in the main chain was also achieved upon photoirradiation of methyl-substituted ethyl esters, **5** and **6**.

On the other hand, irradiation of the corresponding methyl ester having a methylpyrazinyl group, **8** or **9**, at room temperature gave only an amorphous mixture of oligomers accompanying a small amount of a dimer, suggesting the occurrence of a different type of [2+2]



Thiocinnamate	R^1	R^2	Cinnamate	R^1	R^2
1	H	H	4	H	H
2	Me	H	5	Me	H
3	H	Me	6	H	Me

Scheme 1.

photoreaction in the crystals of **8** and **9**. In order to confirm the structure of the cyclobutane ring in the dimer and oligomers, photoirradiations of **8** and **9** were carried out with wavelengths longer than 410 nm to give the corresponding dimers as main products, respectively. On the basis of the spectral data of the dimers thus obtained, it was confirmed that the cyclobutane ring in the photoproducts from **8** was a β-homo-type whereas that from **9** was a β-hetero-type.

In conclusion, all of 4-(2-pyrazinylethenyl)cinnamates used in the present study showed photoreactivity in the crystalline state, while the photoproducts varied, greatly depending on the alkyl group in the esters and on the methyl-substituent on the pyrazinyl moiety. *S*-Ethyl thioesters **1**—**3** gave the corresponding crystalline polymers, respectively, of which the fundamental skeletons were the same as those derived from esters **4**—**6**. The introduction of a methyl group to the pyrazinyl group has no influence in polymerizability in the cases of *S*-ethyl thioesters **2** and **3**, and of ethyl esters **5** and **6**, whereas methyl esters **8** and **9** having a methyl substituent on the pyrazinyl group showed no polymerizability and arranged in β-type packings to give only mixtures of oligomers, respectively.

In order to elucidate, in further detail, the contribution of a sulfur atom in the thioester group and of a methyl group on the pyrazinyl ring to crystal packing, the X-ray crystal structure analyses of **1**, **2**, **5**, and **8** were carried out. The results are summarized in Table 2.[6] Since single crystals of **3**, **6**, and **9** suitable for an X-ray crystal structure analysis could not be obtained, the influence of a methyl group at 3-position

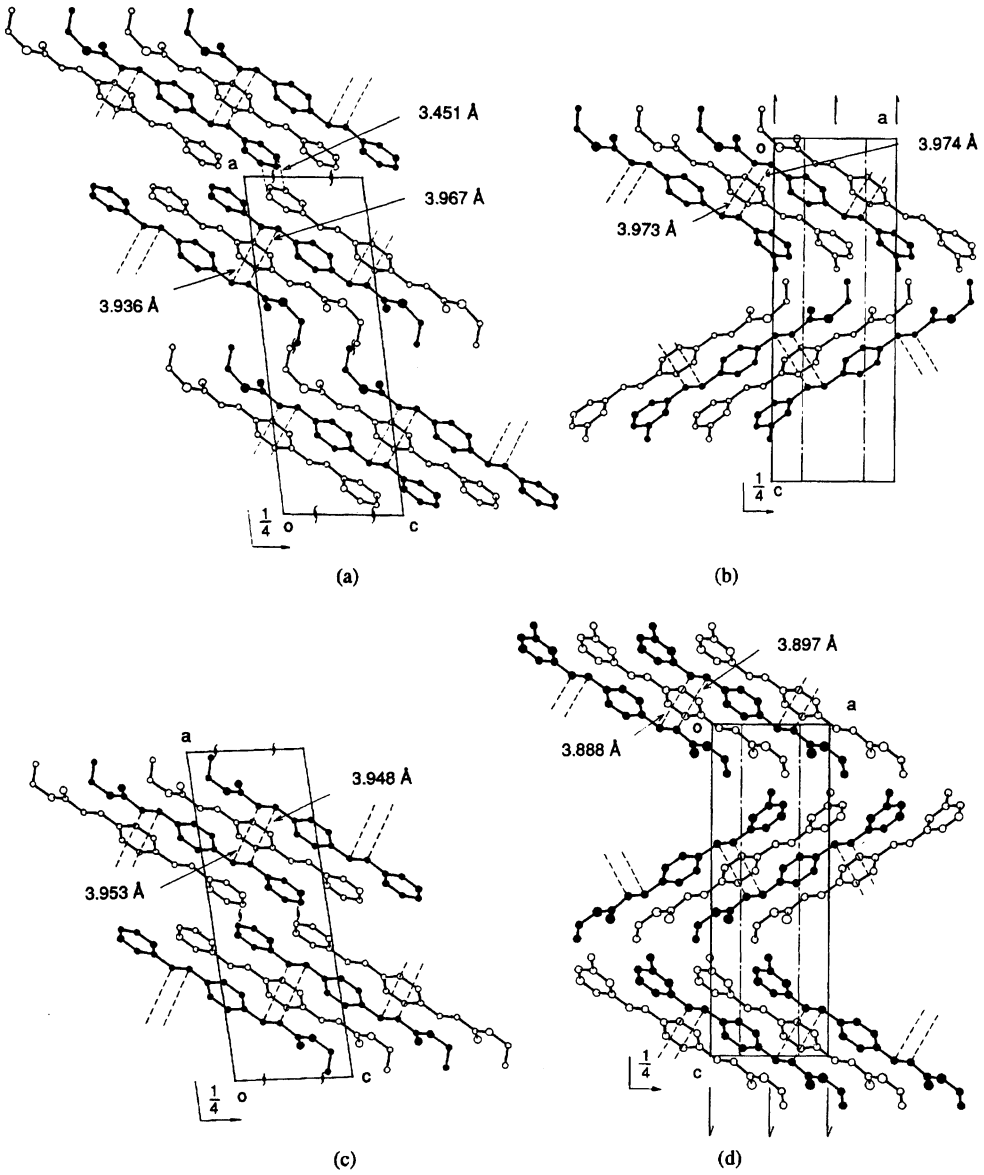


Fig. 1. Crystal structures of (a) **1**, (b) **2**, (c) **4**,[3] and (d) **5**.

of the pyrazinyl group on the molecular arrangement could not been clarified in the present work.

Figure 1 shows the crystal structures of **1** (a), **2** (b), and **5** (d), as well as that of **4** (c) reported previously.[3] In each crystal, the molecules are stacked in the relation of a translation symmetry (along the *c*-axis for **1** and along the *a*-axis for **2** and **5**) with replacement by a half of a molecule (an α-translation-type packing) as well as **4**. The shortest double bonds are related by a translation symmetry and are separated by distances of 3.936 Å (C(7)···C(15)) and 3.967 Å (C(8)···C(16)) for **1**, 3.974 Å (C(8)···C(16)) and 3.973 Å (C(9)···C(17)) for **2**, and 3.888 Å (C(8)···C(16)) and 3.897 Å (C(9)···C(17)) for **5** (the numbering atoms, see Fig. 2). The distances between the double bonds are within allowance for topochemical [2+2] photoreaction. These molecular arrangements demonstrate that in cases of **1**, **2**, and **5**, the double bonds react with each other to form a linear polymer with α-hetero-type cyclobutane rings. The crystal structures of thioesters **1** and **2** are quite similar to those of the corresponding esters **4** and **5**, respectively. In the crystals **1**, **2**, **4**, and **5**, the pyrazinyl (methylpyrazinyl) and ester groups are

Table 3. Parameters of Molecular Packing in Crystals **1**, **2**, **4**, and **5**

Compound	d/Å[a]	Sum of van der Waals radii (W/Å)[b]	$d-W$/Å
1	3.643	3.65	0.01
2	3.631	3.65	−0.02
4	3.421	3.32	0.10
5	3.526	3.32	0.21

a) *d*: The distance between the least square plane of the phenylene ring and the oxygen or the sulfur atom. b) Van der Waals radii; C: 1.80 Å, O: 1.52 Å, S: 1.85 Å.

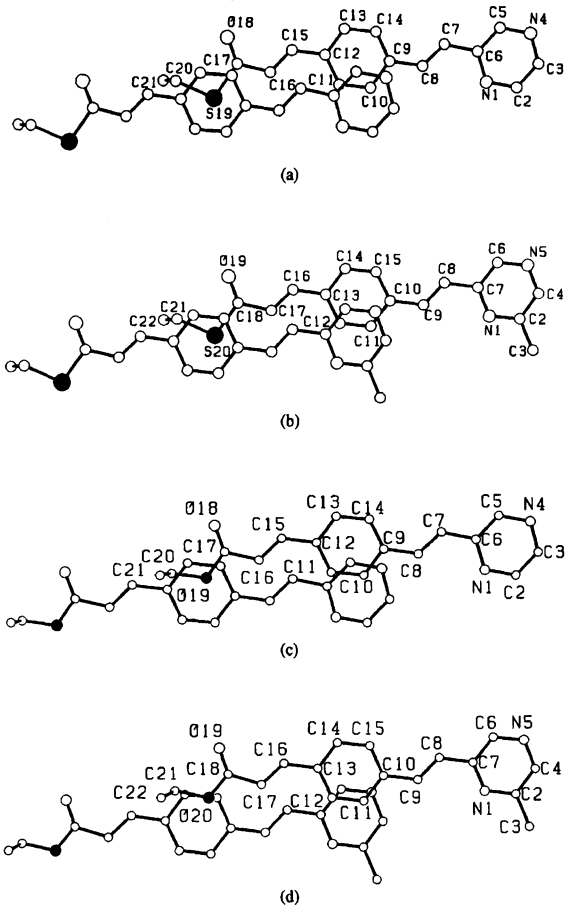


Fig. 2. Overlapping of neighboring molecules viewed perpendicular to the average plane of the phenylene rings with the numbering atoms for (a) **1**, (b) **2**, (c) **4**, and (d) **5**.

intracolumnarly stacked over the same group (a translation-type). However, the methylpyrazinyl rings are directed to the ester groups of a neighboring column in the crystals of **2** and **5**, whereas the same groups, the pyrazinyl rings or the ester groups, face each other at the intercolumnar boundary in the crystals of **1** and **4**.

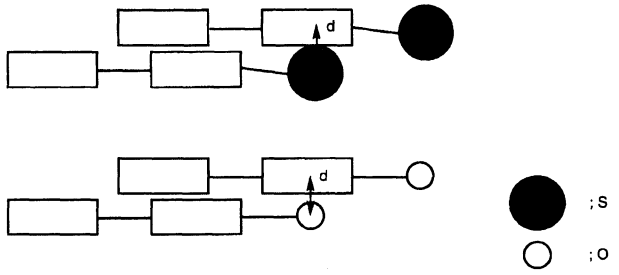


Fig. 3. Schematic molecular arrangement of (a) thioester group and (b) ester group.

Figure 2 shows the reacting molecules of **1** (a), **2** (b), **4** (c),[3] and **5** (d) viewed perpendicular to the average plane of the central 1,4-phenylene rings with the numbering atoms. In each case, the alkoxy oxygen of the ester group or the alkylthio sulfur of the thioester group closely contacts with the central 1,4-phenylene ring. Nakanishi and his co-workers[7] pointed out that symmetrically substituted diolefin compounds, 3,3′-(1, 4-phenylene)diacrylate derivatives, had a close contact between the alkoxy oxygen of the ester group and the central 1,4-phenylene ring to make intermolecular double bonds in the crystal suitable for [2+2] photoreaction. In crystals of unsymmetrically substituted diolefin compounds taking an α-translation-type packing, the same close contact was commonly observed between the central 1,4-phenylene ring and the alkoxy oxygen of the ester group of a reacting molecule pair.[3,8] These results indicate that this close contact is one of the important factors making the reacting molecules pack in an α-translation.

As listed in Table 3, the distance (d) between the least square plane of the central 1,4-phenylene ring and the sulfur atom of the thioester group (**1**: 3.643 Å and **2**: 3.631 Å) is slightly larger than that between the plane of the central 1,4-phenylene and the oxygen atom of the ester group (**4**: 3.421 Å and **5**: 3.526 Å). However, the difference ($d - W$) between the sulfur–phenylene distance (d) and the van der Waals contact of sulfur-sp^2

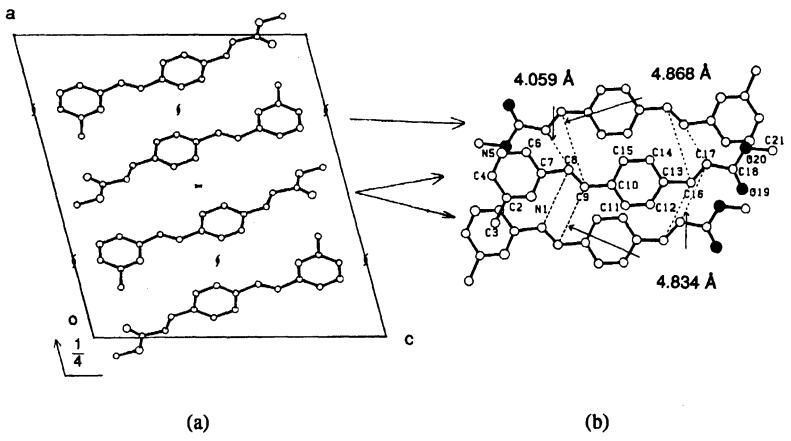


Fig. 4. (a) Crystal structure and (b) overlapping of neighboring molecules viewed perpendicular to the average plane of the phenylene rings with the numbering atoms for **8**.

carbon (**1**: 0.01 Å and **2**: −0.02 Å) is smaller than that between the oxygen–phenylene distance (d) and the van der Waals contact of oxygen-sp^2 carbon (**4**: 0.10 Å and **5**: 0.21 Å), taking account that the sum of the van der Waals radii is 3.65 Å (1.85+1.80 Å) for sulfur atom and sp^2 carbon, and 3.32 Å (1.52+1.80 Å) for oxygen atom and sp^2 carbon.[9,10] From the viewpoint of the closest-packing of molecules in a crystal, the contact between the sulfur and the phenylene may be more favorable than that between the oxygen and the phenylene. Figure 3 shows schematic molecular arrangements of the molecules having an ester group or a thioester group.

In the crystal of **1**, the pyrazinyl nitrogen (N4) atom makes a weak hydrogen bond with the pyrazinyl hydrogen (H2) of the interstacked molecule related by a two-fold axis perpendicular to the glide plane (Fig. 1a), while the methylpyrazinyl groups of the interstacked molecules of **2** can not make a hydrogen bond with each other, since **2** has a methyl group in the pyrazinyl ring (Fig. 1b). The relationship in molecular arrangement between **4** and **5** is the same as that between **1** and **2**. These molecular arrangements indicate that a weak hydrogen bond between the interstacked pyrazinyl groups plays a significant role in determining the molecular arrangement at the intercolumnar boundary.

Figure 4 shows the crystal structure of **8** (a) and the neighboring molecules of **8** viewed perpendicular to the average plane of the central 1,4-phenylene rings with the numbering atoms (b). Two intramolecular double bonds in **8** exist in a cisoid conformation across the central 1,4-phenylene ring, and there is no intermolecular double bond pair in parallel and within 4.5 Å, which allowed for normal [2+2] photocycloaddition in the crystalline state. If we take account of the formation of a β-homo-type dimer from **8** upon irradiation, the translationally related double bonds at the methylpyrazinyl side, which are separated by a distance of 4.834 Å, should react at first with each other, although this distance is quite longer than the photoreactive range accepted for the topochemical reaction.

For methylpyrazinyl ethyl and *S*-ethyl esters **2** and **5**, α-translation-type packing (polymerizable) is maintained by gearing of the ethoxy groups with the methylpyrazinyl rings probably to solve the steric hindrance of the methyl substituent on the pyrazinyl group (Figs. 1b and 1d). However, methylpyrazinyl methyl ester **8** takes β-translation-type packing, in which the molecules are superimposed without displacement in the direction of the long molecular axis (Fig. 4). This molecular arrangement would arise from the spatial mismatching between the small methoxy group and the bulky methylpyrazinyl ring; the mismatching interferes with the molecular arrangement in an α-translation-type packing.

Experimental

Measurements. The infrared spectra were measured on a JASCO IR-810 spectrophotometer, and the ^{1}H NMR spectra were measured by a JEOL PMX-60SI or a JEOL GX-400 instrument. The mass spectra were measured on a Shimadzu GCMS-QP2000 instrument. The melting points were measured by a Laboratory Devices MEL-TEMP and are uncorrected. Gel permeation chromatography (GPC) was performed at 40 °C by using Shodex GPC (AD 800/P+AD 805/S+AD 803/S+AD 802/S+AD 802/S) columns (DMF solution).

Preparation of Monomers. Methyl 4-[2-(6-Methyl-2-pyrazinyl)ethenyl]cinnamate (8): To a solution of lithium diisopropylamide (25 mmol), prepared from 16 ml of 1.58 M n-BuLi solution (1M=1 mol dm^{-3}) in hexane (25 mmol) and diisopropylamine (3.7 ml, 27 mmol), was added a solution of 2,6-dimethylpyrazine (2.4 g, 22 mmol) in THF (18 ml) at −78 °C; then the mixture was stirred for 20 min at 0 °C. To the mixture was added trimethylsilyl chloride (3.4 ml, 27 mmol) at −78 °C, and this reaction mixture was stirred at −78 °C for 3 h. The reaction was quenched by adding water, and the mixture was extracted with ethyl acetate (200 ml). The extract was dried over Na_2SO_4. After evaporation of the solvent, 2-methyl-6-(trimethylsilylmethyl)pyrazine (2.8 g, 70% yield) was obtained upon purification by column chromatography (Merck Kiesel gel 60, ethyl acetate–hexane 1 : 5). To the resulting pyrazine derivative (2.8 g, 16 mmol) in THF (40 ml) was added 10 ml of 1.58 M n-BuLi solution in hexane (16 mmol) at −78 °C. After being stirred for 15 min at 0 °C, the reaction mixture was added to a solution of methyl 4-formylcinnamate (4.4 g, 23 mmol) in THF (90 ml) at −78 °C; then the mixture was stirred for 2 h. 4-Formylcinnamic acid was prepared according to the literature procedure,[11] and esterification was carried out by refluxing for 3 h with methanol saturated with HCl. Water was added to the reaction mixture in order to quench the reaction, and the resulting mixture was extracted with CH_2Cl_2 (500 ml). After evaporation of the solvent, the residue was purified by column chromatography (Merck Kiesel gel 60, ethyl acetate–hexane 1 : 3). Pure **8** was obtained by recrystallization from methanol: Yield 31%; mp 133—134.5 °C; IR (KBr) 1720, 1640, 1210, 1170, 970, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.60 (s, 3H), 3.82 (s, 3H), 6.47 (d, 1H, J=16 Hz), 7.18 (d, 1H, J=16 Hz), 7.55 (d, 2H, J=9 Hz), 7.61 (d, 2H, J=9 Hz), 7.69 (d, 1H, J=16 Hz), 7.74 (d, 1H, J=16 Hz), 8.31 (s, 1H), 8.46 (s, 1H). Found: m/z 280.1188. Calcd for $C_{17}H_{16}N_2O_2$: M, 280.1211.

Methyl 4-[2-(3-Methyl-2-pyrazinyl)ethenyl]cinnamate (9): 2-Methyl-3-(trimethylsilylmethyl)pyrazine (63% yield) was prepared from 2,3-dimethylpyrazine in a similar manner to the preparation of 2-methyl-6-(trimethylsilylmethyl)pyrazine. The reaction of 2-methyl-3-(trimethylsilylmethyl)pyrazine with methyl 4-formylcinnamate, followed by recrystallization from methanol, gave pure **9**: Yield 40%; mp 138—139 °C; IR (KBr) 1710, 1640, 1200, 1180, 980, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.71 (s, 3H), 3.82 (s, 3H), 6.47 (d, 1H, J=16 Hz), 7.34 (d, 1H, J=16 Hz), 7.56 (d, 2H, J=8 Hz), 7.63 (d, 2H, J=8 Hz), 7.70 (d, 1H, J=16 Hz), 7.83 (d, 1H, J=16 Hz), 8.34 (d, 1H, J=2 Hz), 8.41 (d, 1H, J=2 Hz). Found: C, 72.69; H, 5.77; N, 9.99%. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99%.

Ethyl 4-[2-(6-Methyl-2-pyrazinyl)ethenyl]cinnamate (5): A CH_2Cl_2 (15 ml) solution of **8** (0.44 g, 1.6 mmol) was added into 0.21 M sodium ethoxide solution in

ethanol (22 ml) at 0 °C, and the reaction mixture was stirred for 10 h at room temperature. Water was added to the reaction mixture, and the resulting mixture was extracted with CH_2Cl_2. After evaporation of the solvent, recrystallization from methanol gave pure **5**: Yield 46%; mp 106—107 °C; IR (KBr) 1700, 1630, 1310, 1200, 1180, 980, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (t, 3H, J=7 Hz), 2.60 (s, 3H),4.28 (q, 2H, J=7 Hz), 6.47 (d, 1H, J=16 Hz), 7.19 (d, 1H, J=16 Hz), 7.55 (d, 2H, J=8 Hz), 7.61 (d, 2H, 8 Hz), 7.69 (d, 1H, J=16 Hz), 7.73 (d, 1H, J=16 Hz), 8.31 (s, 1H), 8.46 (s, 1H). Found: C, 73.51; H, 6.12; N, 9.52%. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%.

Ethyl 4-[2-(3-Methyl-2-pyrazinyl)ethenyl]cinnamate (6): Transesterification of **9** in a similar manner to the preparation of **5**, followed by recrystallization from methanol, gave pure **6**: Yield 59%; mp 140—141.5 °C; IR (KBr) 1710, 1630, 1200, 1180, 980, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (t, 3H, J=7 Hz), 2.71 (s, 3H), 4.28 (q, 2H, J=7 Hz), 6.47 (d, 1H, J=16 Hz), 7.35 (d, 1H, J=16 Hz), 7.56 (d, 2H, J=8 Hz), 7.63 (d, 2H, J=8 Hz), 7.69 (d, 1H, J=16 Hz), 7.83 (d, 1H, J=16 Hz), 8.34 (d, 1H, J=2 Hz), 8.41 (d, 1H, J=2 Hz). Found: C, 73.57; H, 6.17; N, 9.46%. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%.

***S*-Ethyl 4-(2-Pyrazinylethenyl)thiocinnamate (1):** Thioester **1** was prepared according to the previously reported method:[5] Yield 62%; mp 165—166 °C; IR (KBr) 1660, 1620, 1060, 1030, 980, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (t, 3H, J=7 Hz), 3.02 (d, 2H, J=7 Hz), 6.73 (d, 1H, J=16 Hz), 7.20 (d, 1H, J=16 Hz), 7.56 (d, 2H, J=8 Hz), 7.59 (d, 1H, J=16 Hz), 7.60 (d, 2H, J=8 Hz), 7.74 (d, 1H, J=16 Hz), 8.42 (bs, 1H), 8.55 (bs, 1H), 8.64 (s, 1H).

***S*-Ethyl 4-[2-(6-Methyl-2-pyrazinyl)ethenyl]thiocinnamate (2):** A mixture of **8** (1.3 g, 4.8 mmol) and 85% KOH in ethanol (4.8 ml) and water (1.0 ml) was stirred at room temperature for 20 h. After the mixture was neutralized with 1 M HCl, the precipitated acid was collected by filtration and dried under vacuum. To the resulting crude acid in benzene (150 ml) were successively added DMF (2 ml) and $SOCl_2$ (10 ml); then the mixture was refluxed for 3 h to give a homogeneous solution. After concentration of the solution under reduced pressure, residual $SOCl_2$ was removed as benzene azeotrope (two times) under argon to give crude 4-[2-(6-methyl-2-pyrazinyl)ethenyl]cinnamoyl chloride. To a solution of the resulting crude chloride in CH_2Cl_2 (150 ml) was added a solution of ethanethiol (1.5 ml, 21 mmol) and pyridine (1.5 ml) in CH_2Cl_2 (60 ml) over a period of 30 min; then the reaction mixture was stirred for an additional 30 min at 0 °C under argon. After evaporation of the solvent, water was added, and the reaction mixture was extracted with CH_2Cl_2 (150 ml). After evaporation of the solvent, the residue was purified by column chromatography (Merck Kiesel gel 60, CH_2Cl_2). Pure **2** was obtained by recrystallization from methanol: Yield 41%; mp 125—126 °C; IR (KBr) 1660, 1610, 1420, 1030, 980, 820 cm^{-1}; ^1H NMR (TFA-d) δ=1.41 (t, 3H, J=7 Hz), 2.99 (s, 3H), 3.16 (q, 2H, J=7 Hz), 7.00 (d, 1H, J=16 Hz), 7.50 (d, 1H, J=16 Hz), 7.7—7.8 (m, 5H), 8.20 (d, 1H, J=16 Hz), 8.85 (s, 1H), 9.38 (s, 1H). Found: C, 69.47; H, 5.81; N, 9.07%. Calcd for $C_{18}H_{18}N_2OS$: C, 69.65; H, 5.84; N, 9.02%.

***S*-Ethyl 4-[2-(3-Methyl-2-pyrazinyl)ethenyl]thiocinnamate (3):** Thioester **3** was prepared by the hydrolysis of **9**, followed by esterification with ethanethiol, in a similar manner to the preparation of **2**. Pure **3** was obtained by recrystallization from methanol: Yield 46%; mp 131—132.5 °C; IR (KBr) 1660, 1610, 1420, 1030, 980, 750 cm^{-1}; ^1H NMR (TFA-d) δ=1.41 (t, 3H, J=7 Hz), 3.09 (s, 3H), 3.16 (q, 2H, J=7 Hz), 7.00 (d, 1H, J=16 Hz), 7.54 (d, 1H, J=16 Hz), 7.7—7.8 (m, 5H), 8.17 (d, 1H, J=16 Hz), 8.68 (s, 1H), 9.14 (s, 1H). Found: C, 69.46; H, 5.81; N, 9.26%. Calcd for $C_{18}H_{18}N_2OS$: C, 69.65; H, 5.84; N, 9.02%.

Preparation of Dimers. Finely powdered crystals (100 mg) of **8** or **9** were dispersed in water (90 ml) and irradiated with a 500-W high-pressure mercury lamp (Ushio USH-500D), set outside of the flask, through a Kenko L42 filter (cut off<410 nm) at room temperature with vigorous stirring. The dimer was separated from oligomers by preparative TLC (silica gel, CH_2Cl_2–CH_3OH 100:0.5).

Dimer of 8: 27%; ^1H NMR ($CDCl_3$) δ=2.42 (s, 6H), 3.78 (s, 6H), 4.7—4.8 (m, 2H), 4.8—4.9 (m, 2H), 6.33 (d, 2H, J=16 Hz), 7.17 (d, 4H, J=8 Hz), 7.30 (d, 4H, J=8 Hz), 7.56 (d, 2H, J=16 Hz), 8.09 (s, 2H), 8.11 (s, 2H); MS m/z 560 (M^+).

Dimer of 9: 20%; ^1H NMR ($CDCl_3$) δ=2.63 (s, 3H), 2.66 (s, 3H), 3.41 (s, 3H), 3.75 (s, 3H), 4.05 (dd, 1H, J=10 and 7 Hz), 4.52 (dd, 1H, J=10 and 7 Hz), 4.66 (dd, 1H, J=10 and 7 Hz), 4.80 (dd, 1H, J=10 and 7 Hz), 6.31 (d, 1H, J=16 Hz), 7.02 (d, 2H, J=8 Hz), 7.07 (d, 2H, J=8 Hz), 7.19 (d, 1H, J=16 Hz), 7.29 (d, 2H, J=8 Hz), 7.41 (d, 2H, J=8 Hz), 7.55 (d, 1H, J=16 Hz), 7.72 (d, 1H, J=16 Hz), 8.29 (d, 1H, J=2 Hz), 8.35 (d, 1H, J=3 Hz), 8.37 (d, 1H, J=2 Hz), 8.42 (d, 1H, J=2 Hz); MS m/z 560 (M^+), 382, 178, (unsymmetrically cleaved product), and 147 (unsymmetrically cleaved product $-OCH_3$).

Photoirradiation. Photoreaction was carried out as follows:

Method 1) Finely powdered crystals (100 mg) were dispersed in 300 ml of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a 100-W high-pressure mercury lamp (Eikousha EHB WF-100), set inside of the flask, through a Pyrex glass fiter. Vigorous stirring continued under a nitrogen atmosphere.

Method 2) Finely powdered crystals (100 mg) were dispersed in 90 ml of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a 500-W super-high-pressure mercury lamp (Eikousha EHB WF-500), set outside of the flask, through a Kenko UV30 filter (cut off<280 nm). Vigorous stirring continued under a nitrogen atmosphere.

Poly-1: ^1H NMR (TFA-d) δ=0.9—1.1 (bs, 3H), 2.7—2.9 (m, 2H), 4.59 (bs, 1H), 4.85 (bs, 1H), 5.00 (bs, 2H), 7.1—7.3 (bs, 2H), 7.3—7.5 (bs, 2H), 8.61 (bs, 1H), 8.66 (bs, 1H), 9.38 (bs, 1H).

Poly-2: ^1H NMR (TFA-d) δ=1.01 (s, 3H), 2.7—2.8 (m, 2H), 2.90 (s, 3H), 4.64 (bs, 1H), 4.75 (bs, 1H), 4.88 (bs, 1H), 4.98 (bs, 1H), 7.22 (bs, 2H), 7.36 (bs, 2H), 8.3—8.7 (bs, 2H); MS m/z 314 (unsymmetrically cleaved product), 245 (unsymmetrically cleaved product –SEt), and 184 (unsymmetrically cleaved product $-(SEt)_2$).

Poly-3: ^1H NMR (TFA-d) δ=1.09 (bs, 3H), 2.84 (bs, 3H), 2.92 (bs, 2H), 4.39 (bs, 1H), 4.92 (bs, 1H), 5.10 (bs, 1H), 5.33 (bs, 1H), 7.24 (bs, 2H), 7.38 (bs, 2H), 8.52 (bs, 1H), 9.32 (bs, 1H); MS m/z 314 (unsymmetrically cleaved product), 245 (unsymmetrically cleaved product –SEt), and 184 (unsymmetrically cleaved product $-(SEt)_2$).

Poly-5: ^{1}H NMR (TFA-*d*) δ=1.0—1.2 (m, 3H), 2.88 (bs, 3H), 4.0—4.1 (m, 2H), 4.51 (bs, 1H), 4.74 (bs, 2H), 4.89 (bs, 1H), 7.2—7.3 (m, 2H), 7.3—7.4 (m, 2H), 8.38 (bs, 1H), 8.47 (bs, 1H).

Poly-6: ^{1}H NMR (TFA-*d*) δ=1.0—1.2 (m, 3H), 2.78 (bs, 3H), 3.9—4.0 (m, 2H), 4.20 (bs, 1H), 4.83 (bs, 1H), 4.99 (bs, 1H), 5.22 (bs, 1H), 7.1—7.2 (m, 2H), 7.2—7.3 (m, 2H), 8.41 (bs, 1H), 9.23 (bs, 1H).

X-Ray Structure Determination. Intensity data were measured by 2θ–ω scan with graphite monochromated Cu $K\alpha$ radiation on a Mac Science four-circle diffractometer (MXC-18). Accurate cell dimensions were obtained by a least-squares refinement of 20 reflections in the range $40° < 2\theta < 60°$. Data were collected with three check reflections. The observed reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the solutions and refinements; no absorption correction was made. The structures were solved by a direct method with the MULTAN 78 program and refined by a full-matrix least-squares method with the SHELXS 76 program. The positions of hydrogen atoms were obtained from a difference map. Final refinements were performed with the anisotropic thermal parameters for the non-hydrogen atoms and with isotropic ones for the hydrogen atoms.

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