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Photoisomerization and Photodimerization of 3-(1- and 2-Naphthyl)acrylate in Bichromophoric Systems

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The photochemical *trans-cis* isomerization of methyl 3-(1- and 2-naphthyl)acrylate (**1Me** and **2Me**) and the intramolecular (2+2) cycloaddition of ethylene bis[3-(1- and 2-naphthyl)acrylates] (**1E** and **2E**) have been studied in cyclohexane and methanol. The quantum yield of the *trans-cis* isomerization of **2Me** and **2E** in methanol was larger than that in cyclohexane, while the yield of the cyclization of **2E** showed the reverse. The isomerization is thought to occur *via* the triplet state, while the cyclization is *via* the singlet excited state. The triplet yield of **2Me** in the polar solvent has been estimated to be larger than in nonpolar solvent. The cyclization of **1E** was much slower than that of **2E**, and the quantum yield of the reaction of **1Me** and **1E** did not appreciably depends on the polarity of the solvent.

The Photodimerization of cyclic α,β-unsaturated carbonyl compounds has been studied extensively, but the acyclic ones have not, due to the rapid *trans-cis* isomerization making quantitative analysis of the dimerization impossible.[1–4] The quantum yield of dimerization is usually very small compared with that of the isomerization, and most of the dimerization occurs from the equilibrium mixture of *trans* and *cis* isomers.[5,6] In the crystalline state or in the solid monolayer assemblies the *trans-cis* isomerization is greatly diminished and the dimerization proceeds more efficiently.[7,8] In solution, however for example, methyl cinnamate or ethyl cinnamylideneacetate does not dimerize but rapidly isomerizes.[9] In dimerization, the distance between the chromophores is an important factor. If two cinnamate groups are incorporated in the same molecule, namely, in the bichromophoric system, the cinnamate groups dimerize intramolecularly in solution.[10,11] Bichromophoric systems are recently attracting wide interest because they provide a method for controlling bimolecular reactions—model systems for polymer photochemistry such as DNA, and give information on chain dynamics.[12] Several bichromophoric systems bearing photodimerizable chromophores have been reported recently and most of them are cyclic compounds such as coumarin,[13] anthracene,[14] maleimides,[15] and thimine.[16]

In this study, the photoisomerization and photodimerization of 3-(1- and 2-naphthyl)acrylate have been studied in bichromophoric systems; ethylene bis[3-(1-naphthyl)acrylates] (**1E**) and ethylene bis[3-(2-naphthyl)acrylates] (**2E**) have been studied along with methyl 3-(1-naphthyl)acrylate (**1Me**) and methyl 3-(2-naphthyl)acrylate (**2Me**).

Results and Discussion

trans-cis *Isomerization.* In a previous paper, the solvent effect on the *trans-cis* isomerization and fluorescence of **2Me** was reported.[17] The quantum yield of the *trans-cis* isomerization, ϕ_{t-c} of **2Me** increased with increase in the solvent polarity, while the fluorescence quantum yield, ϕ_f decreased remarkably.

Table 1 shows the ϕ_{t-c} for **1Me** and **2Me** in cyclohexane and methanol. The ϕ_{t-c} of **1Me** in methanol is only slightly larger than that in cyclohexane and the dependency on solvent polarity for **1Me** is much smaller than that for **2Me**.

Table 2 shows the quantum yield of the fluorescence in cyclohexane and methanol where solvent dependency was observed for **2Me**, but not for **1Me**.

The solvent polarity effect on *trans-cis* isomerization has been demonstrated for stilbenes having electron-withdrawing and electron repelling groups.[18–22] For molecules having large dipole moments in the ground state, the quantum yield of the *trans* to *cis* isomerization was small in polar solvents due to stabilization of the excited trans isomer. Here the opposite tendency was observed— the quantum yield of the *trans* to *cis* isomerization of **2Me** was large in polar solvents and small in nonpolar solvents.

The isomerization was little affected by aerobic oxygen but enhanced by pure oxygen. The enhancement of the isomerization by oxygen has been observed

Table 1. The quantum yield of isomerization and cyclization

		In cyclohexane			In methanol			In methanol–*n*-PrBr
		Argon	Air	Oxygen	Argon	Air	Oxygen	Air
1E	ϕ_{cy}	0.0075	0.010		0.0085	0.013		0.001
	ϕ_{t-c}	0.19	0.18		0.22	0.22		0.19
trans-**1Me**	ϕ_{t-c}	0.19	0.18		0.22	0.22		0.19
2E	ϕ_{cy}	0.22	0.17	0.08	0.11	0.10	0.09	0.01
	ϕ_{t-c}	0.09	0.09	0.09	0.25	0.26	0.23	0.21
trans-**2Me**	ϕ_{t-c}	0.22	0.24	0.31	0.37	0.37	0.37	0.40
cis-**2Me**	ϕ_{c-t}	0.16			0.14			

TABLE 2. THE QUANTUM YIELD OF THE FLUORESCENCE

	In cyclohexane		In methanol		In methanol–n-PrBr
	Argon	Air	Argon	Air	Air
1E	0.021	0.015	0.0090	0.0083	
trans-**1Me**	0.052	0.043	0.052	0.038	0.028
2E	0.22	0.13	0.17	0.17	0.094
trans-**2Me**	0.61	0.25	0.39	0.38	0.097
cis-**2Me**	0.041		0.030		

more remarkably in the case of styrylnaphthalenes.[23,24] The explanation for this has been that $O_2(^3\Sigma_{-g})$ increased the population of the triplet state by quenching the excited singlet state which has been attributed to direct intermolecular exchange interaction or the inhomogeneous field of the O_2 triplet ground state. As shown in Table 2, oxygen and heavy atom solvents, *e.g.*, propyl bromide strongly quenched the fluorescence. The heavy atom solvent remarkably increased the ϕ_{t-c} and the intensity of the phosphorescence of **2Me** by quenching the fluorescence suggesting that the isomerization takes place from the triplet state. The corrected fluorescence spectra for **2Me** in cyclohexane and methanol are shown in Fig. 1.

The fluorescence spectrum of **2Me** in cyclohexane is a good mirror image of the absorption spectrum and therefore, the lowest singlet excited state is thought to lie near 355 nm (28169 cm^{-1}). This resembles the ^1L_b state of naphthalene in the weakness of the absorption and the long-lifetime of the fluorescence (107 ns in cyclohexane from the quenching of the fluorescence by aerobic oxygen). In methanol and in other polar solvents, a large Stokes' shift is observed and the maximum of the fluorescence shifts to 400 nm indicating that the dipole moment of the fluorescence state in polar solvents is larger than in cyclohexane. The separation between the singlet and triplet state may be small in polar solvent. The above solvent effects lead to the conclusion that the isomerization occurs from the triplet state, and that the triplet yield in polar solvents may be larger than in nonpolar solvents due to the small separation between the singlet and triplet states. The enhancement of ϕ_{t-c} by oxygen has been observed only in nonpolar solvents; in polar solvents, the triplet yield is sufficiently large before enhancement by oxygen.

Phosphorescence of **2Me** was too weak to be observed in EPA [ether–isopentane–ethanol (5 : 5 : 2) mixed solvent] at 77 K, but was observed in propyl bromide–ethanol (1 : 1 mixed solvent). The phosphorescence spectrum has three peaks at 544, 593, and around 650 nm as shown in Fig. 1, the first peak rising from 533 nm (53.5 kcal/mol).

For *cis*-**2Me** the fluorescence was very weak and the measurement was always interfered from by the strong fluorescence of the *trans*-**2Me** which was produced during the measurement. No phosphorescence was observed in the heavy atom solvent.

That the fluorescence yield of the *cis*-**2Me** is markedly smaller than the *trans* form (Table 2) implies that the singlet excited state of the *trans* and *cis* form may be different from each other, *i.e.* there may exist an energy barrier between the two excited singlet states.

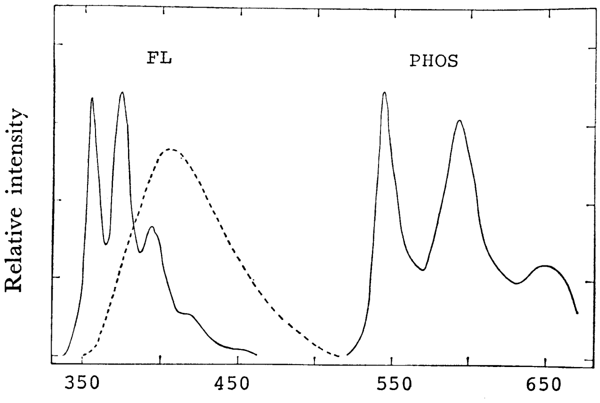


Fig. 1. Corrected fluorescence (—— in cyclohexane, ---- in methanol) and phosphorescence (in propyl bromide-ethanol 1 : 1 mixed solvent) spectra of **2Me**.

If the *trans* to *cis* isomerization of **2Me** occurs only from the triplet state, the triplet yield can be estimated using the following equation:

$$\frac{\phi_{\rm isc}}{\phi^{\rm s}_{\rm isc}} = \frac{\phi_{\rm t-c}}{\phi^{\rm s}_{\rm t-c}}, \qquad (1)$$

where $\phi^{\rm s}_{\rm t-c}$ is the quantum yield of the *trans* to *cis* isomerization for sensitized reaction and $\phi^{\rm s}_{\rm isc}$ is the triplet yield of the sensitizer. ($\phi^{\rm s}_{\rm isc}$ is known for Michler's ketone in several solvents.[25]) The triplet energy of Michler's ketone is 72 kcal/mol in cyclohexane, 61 kcal/mol in ethanol.[26] Since the triplet energy of **2Me** has been estimated to be 53.6 kcal/mol from the phosphorescence spectrum, the energy transfer from Michler's ketone to **2Me** is considered to be a diffusion controlled process. The concentration of **2Me**, 5×10^{-4} mol/l is sufficiently large to completely accept the energy from Michler's ketone within the lifetime (20—40 μs). Therefore, under the experimental conditions, the energy transfer from Michler's ketone to **2Me** occurs with an efficiency of nearly unity. Thus the $\phi_{\rm isc}$ of **2Me** has been estimated to be 0.41 in cyclohexane and 0.81 in ethanol by measuring $\phi_{\rm t-c}/\phi^{\rm s}_{\rm t-c}$. The radiationless deactivation of the singlet excited state cannot be ignored, and consequently the sum of $\phi_{\rm f}$ and $\phi_{\rm isc}$ should be less than unity, but here the sum becomes 1.02 in cyclohexane, 1.06 in ethanol. This may be caused by an impurity or incomplete degassing which would decrease $\phi^{\rm s}_{\rm isc}$, and thus $\phi_{\rm isc}$ of **2Me** might have been overestimated. The value obtained however are thought to be qualitatively reliable.

The quantum yield of the *cis* to *trans* isomerization, $\phi_{\rm c-t}$ of *cis*-**2Me** is small as shown in Table 1.

The fluorescence yield of **1Me** is far smaller than that of **2Me** and is not appreciably diminished by aerobic oxygen as found for **2Me**, suggesting that the lifetime of the excited state of **1Me** is much shorter than that of **2Me** and that the triplet yield does not depend on solvent polarity.

The difference in oxygen effect between **1Me** and **2Me** is analogous to the results between 1- and 2-styrylnaphthalene. The $\phi_{\rm f}$ of 2-styrylnaphthalene

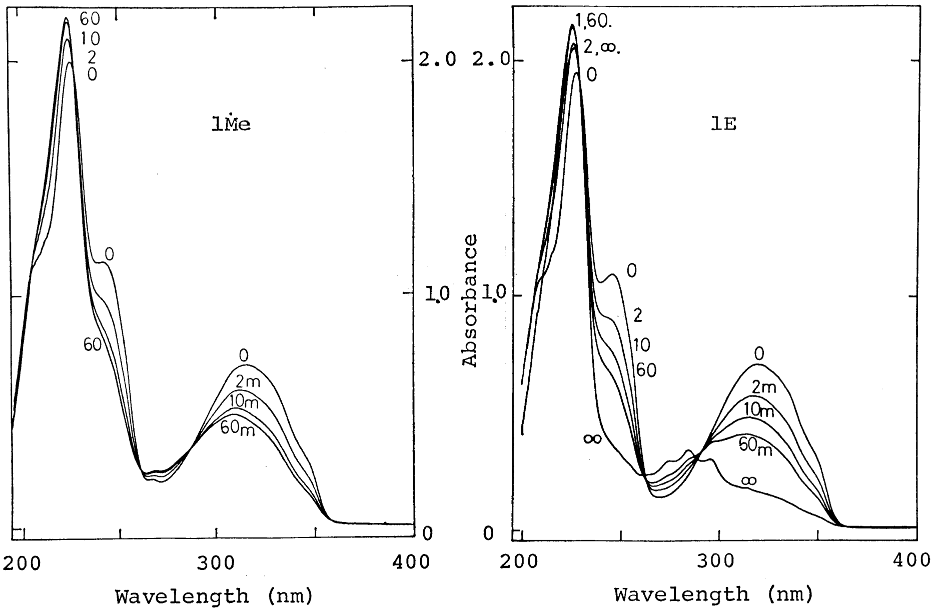
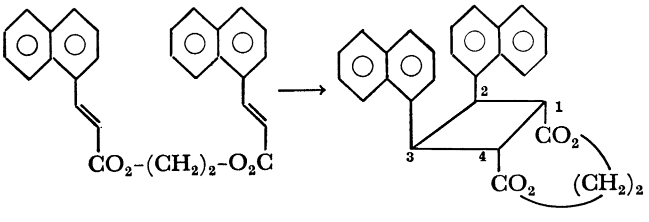


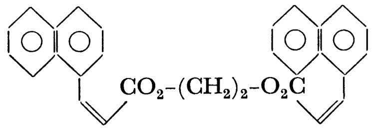
Fig. 2. UV absorption spectral change of **1Me** (0.31×10^{-4} mol/l) and **1E** (0.15×10^{-4} mol/l) in cyclohexane on the irradiation with 313 nm light.

decreased to one third, and ϕ_{t-c} doubled when aerobic oxygen was used, while ϕ_f and ϕ_{t-c} of 1-styrylnaphthalene changed very little.[24] The lifetime of the fluorescence of the former is 20 ns and that of the latter is 2 ns.[27]

Photochemical Reactions of 1E and 2E. The photochemical reaction of **1E** in solution was a rapid *trans-cis* isomerization followed by a slow intramolecular (2+2) cycloaddition giving *cis,cis*-**1E** (18%) and **1ED** (53%) as final products. The photoproduct *cis,cis*-**1E** was assinged on the basis of the NMR spectrum and **1ED** on the basis of the NMR, UV, and IR spectra.



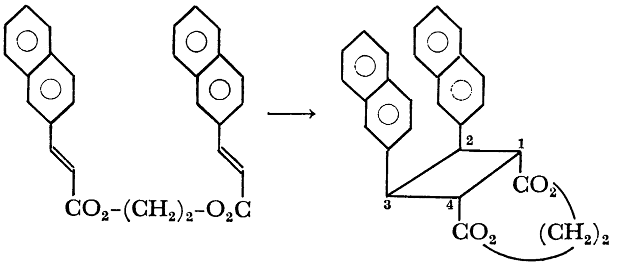
trans,trans-**1E** **1ED**



cis,cis-**1E**

Figure 2 shows that UV absorption spectral change of *trans,trans*-**1E** and -**1Me** when irradiated with 313 nm light. A rapid *trans-cis* isomerization occurs and isosbestic points are observed at 260 and 290 nm until the equilibrium state is attained since cyclization proceeds very slowly. In the equilibrium state, the *cis* isomers predominate (approximately 70% *cis*, 30% *trans*) under the irradiation conditions since the *cis* isomer has an absorption maximum at a shorter wavelength (296 nm) and a smaller extinction coefficient. In the ^{1}H NMR spectrum, the peak for the methylene protons of *cis,cis*-**1E** shift to a higher field (3.58 ppm) compared with 4.54 ppm for *trans,trans*-**1E** suggesting that the methylene chain of the *cis,cis*-**1E** is more strongly affected by the naphthalene nuclei than the *trans,trans*-**1E**. The Stuart molecular model shows that the double bond of the *cis* isomer is twisted out of the two naphthalene nuclei and therefore the methylene chain may possibly interfere in the accessability of the two double bonds on dimerization. A further consequence of the steric hindrance, is that *cis,cis*-**1E** is considered to be poorly photocyclizable. In the photo-stationary mixture, the *cis,cis*-**1E** probably photocyclizes *via* the *trans,trans*-**1E**. Thus **1ED** may be largely formed from the photo-stationary mixture.

The photochemical reaction of **2E** was a slow *trans-cis* isomerization followed by a rapid intramolecular (2+2) cycloaddition of 3-(2-naphthyl)acrylate giving a single product, **2ED**. The structure of **2ED** was assinged by the method analogous with that for **1ED**. Figure 3 shows the UV absorption spectral changes of **2E** and **2Me** on irradiation with 313 nm light. The cyclization is so rapid that the reaction is considered to take place from the original *trans,trans*-**2E**.



2E **2ED**

The quantum yield of the cyclization, ϕ_{cy}, and the isomerization, ϕ_{t-c}, of **1E** and **2E** are shown in Table 1. Taking into consideration the large triplet yield of **2Me** in methanol, the fact that **2E** in cyclohexane cyclized with a larger quantum yield than in methanol

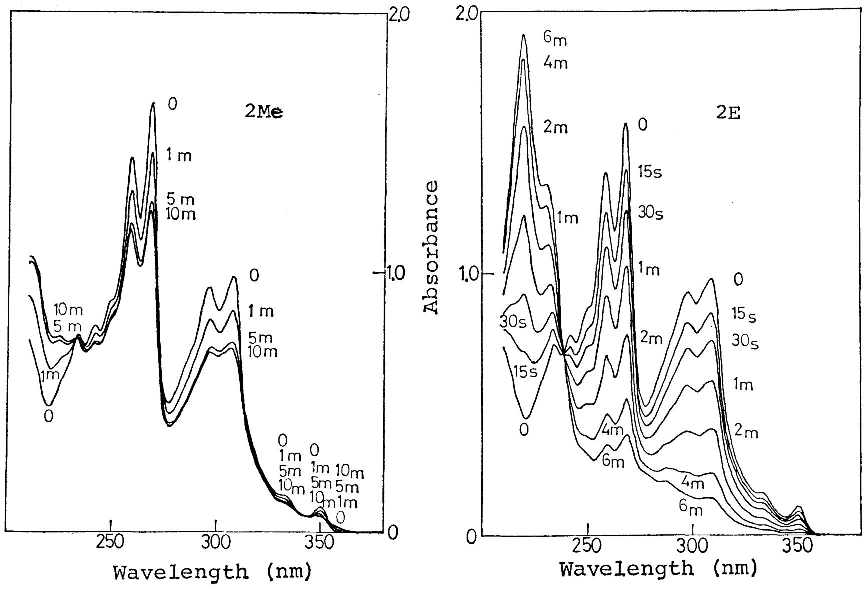


Fig. 3. UV absorption spectral change of **2Me** (0.39×10^{-4} mol/l) and **2E** (0.20×10^{-4} mol/l) in cyclohexane on the irradiation with 313 nm light.

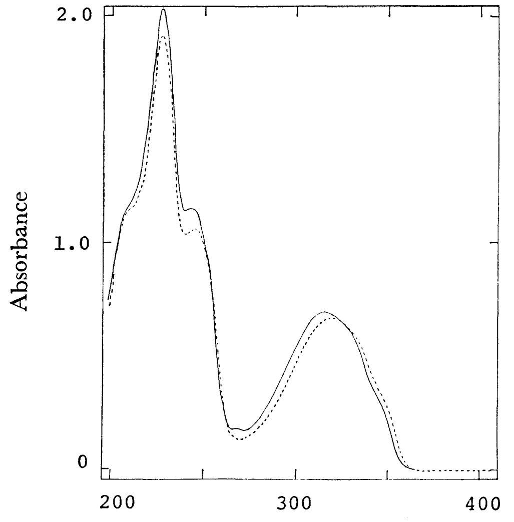


Fig. 4. UV absorption spectra of **1Me** (——, 0.29×10^{-4} mol/l) and **1E** (----, 0.14×10^{-4} mol/l) in cyclohexane.

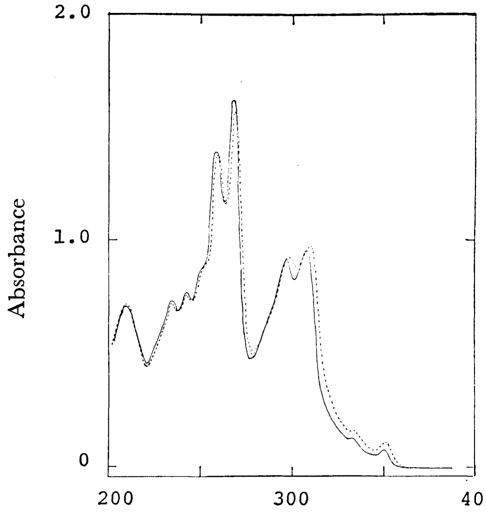


Fig. 5. UV absorption spectra of **2Me** (——, 0.39×10^{-4} mol/l) and **2E** (----, 0.20×10^{-4} mol/l) in cyclohexane.

suggests that the reactive state for the cyclization is the excited singlet state. Accordingly the cyclization was depressed while the *trans-cis* isomerization was accelerated by the heavy atom solvent which strongly quenches the fluorescence and accelerates intersystem crossing of the excited singlet state of **2Me**

In the case of **1E**, the solvent dependency of ϕ_{cy} is very small. The difference in the reactivity between **1E** and **2E** has been interpreted as follows : firstly, in the bichromophoric system, the quantum yield of the fluorescence was reduced to about half that of the corresponding methylesters and the amount of the decreased fluorescence is attributed to the cyclization. From Table 2, the difference in ϕ_f between **1Me** and **1E** is 0.03, while that between **2Me** and **2E** is 0.39 in cyclohexane the former being one tenth of the latter coinciding with the difference in the quantum yield of the cyclization. Secondly the lifetime of the fluorescence of **2Me** has been estimated from the quenching by aerobic oxygen to be much longer than that of **1Me** and because of this it is thought the two chromophores of **2E** cyclize more rapidly than **1E**, and the *trans-cis* isomerization proceeds slowly. A further consequence of the long-lifetime is that the cyclization of **2E** is susceptible to quenching by oxygen, while **1E** is not. In methanol, the lifetime of the fluorescence of **2Me** has been estimated to be shorter than in cyclohexane and consequently, the cyclization in methanol is not appreciably quenched by oxygen.

The above discussion demonstrates that the difference in reactivity between **1E** and **2E** can be explained by the difference in quantum yield and lifetime of the fluorescence between **1Me** and **2Me**. The excited state of **1Me** is considered to be more rapidly deactivated by radiationless transitions than that of **2Me**. 1-Substituted naphthalene derivatives are considered to be sterically hindered owing to the protons at the 8 position in the naphthalene nucleus, which causes the rapid radiationless deactivations resulting in the short lifetime of the fluorescence.

The absorption spectra of the bichromophoric molecules, **1E** and **2E**, are shifted slightly into the red compared to the corresponding monochromophoric molecules as shown in Figs. 4 and 5 indicating the existence of a slight interaction between the chromophores in the ground state. The fluorescence spectra of **1E** and **2E** were accordingly shifted slightly into the red from those of **1Me** and **2Me**. Excimer fluorescence in the long wavelength side of the fluorescence spectra, frequently observed for aromatic bichromophoric molecules, was not observed for **1E** and **2E**.[14)]

Experimental

Instrumentation. IR spectra were recorded on a JASCO model IR-S using KBr discs and UV absorption spectra on a Shimadzu model UV-300 and UV-200. NMR spectra were measured in $CDCl_3$ (otherwise indicated) with tetramethylsilane as an internal standard on a Hitachi model R-24A for ^1H, and a varian model NV-14 for ^{13}C. Emission spectra were recorded on a Hitach model MPF-1, and corrected for the photomultiplier (Hamamatsu TV Co. R446) response. Mass spectra were recorded on a Shimdzu model LKB-9000. High speed liquid chromatography was performed on a Waters Associate model equipped with a column, Michrobonda pack C-18 and a UV detector.

For the photolysis on a preparative scale, an immersion well type photoreactor was used. A naphthalene–ethanol solution ($\lambda > 320$ nm) or cinnamylideneacetic acid–ethanol solution ($\lambda > 360$ nm) was used as a filter.

For the photolysis on a analytical scale, a 4 ml rectangular cell equipped with an inlet tube about 10 cm was used. Pure argon or oxygen was bubbled through the tube for 5 min and immediately bottled. The period of bubbling (5 min) has been shown to be sufficient to change the air in the solution by measuring the intensity of the fluorescence. The light source was a 500 W high pressure mercury arc lamp (Ushio Electric Co.) with a monochromator (Nikon G250). Potassium ferioxalate system was used for actinometry.

Materials. *3-(1- and 2-Naphthyl)acrylic Acid*: 3-(1- and 2-Naphthyl)acrylic acid were synthesized by the Knoevenagel condensation from the corresponding naphthaldehyde and recrystallized from methanol. 3-(1-Naphthyl)-acrylic acid, mp 206.0 °C (lit, 205.0 °C[21)]). 3-(2-Naphthyl)-acrylic acid, mp 189.5 °C (lit, 196.0 °C[21)])

*Methylesters (**1Me** and **2Me**)*: The acrylic acids were esterified in refluxing dry methanol with a trace of *p*-toluenesulfonic acid. Methyl 3-(2-naphthyl)acrylate (**2Me**), mp 91.0 °C. Methyl 3-(1-naphthyl)acrylate (**1Me**) was an oil at room temperature.

*Ethylene Bis[3-(1-naphthyl)acrylates] (**1E**) and Ethylene Bis-[3-(2-naphthyl)acrylates] (**2E**)*: **1E** and **2E** were synthesized from the corresponding acid chloride and ethylene glycol by heating in benzene with a trace amount of pyridine. ***1E***, mp 114—115 °C. ^1H NMR (ppm), 4.54(s, 4H, methylene), 6.51 (d, J=5.6, 2H, vinyl), 8.53 (d, J=15.6, 2H, benzyl), 7.2—8.2 (m, 14H, aromatic). IR (cm^{-1}), 1700 (s, carbonyl), 1620 (s, double bond), 1296, 1245, 1160, 1350, 770, 795, UV, λ_{max}=323 nm, ε=4.80×10^4. MS, 422.

Found: C, 79.96; H, 5.2%. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.21%.

2E, mp 148.0 °C. ^1H NMR (ppm), 4.60 (s, 4H, methylene), 6.60 (d, J=16.0, 2H, vinyl), 7.3—8.1 (m, 16H, aromatic and benzyl). IR (cm^{-1}), 1700 (s, carbonyl), 1630 (s, double bond), 1360, 1290, 1250, 1170, 1180, 860, 820. UV, λ_{max}=307 nm, ε=5.00×10^4. MS, 422.

Found: C, 79.24, H, 5.25%. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.21%.

*Photolysis of **1E***: **1E** (0.9 g) in acetone (990 ml) was irradiated with light ($\lambda > 320$ nm) under nitrogen for 11 h and the solution concentrated in a rotary evaporator. On adding hexane, crystals precipitated out from the solution which were recrystallized from acetone–hexane to give **1ED**. 0.48 g, 53%. Concentration of the filtrate gave 0.16 g (18%) of *cis,cis*-**1E**.

1ED, mp 205—210.5 °C. ^1H NMR (ppm), 4.64 (s, 4H, methylene) 4.15—4.30 (d, 2H, cyclobutane), 5.45—5.65 (d, 2H, cyclobutane), 7.0—8.2 (m, 14H, aromatic). ^{13}C NMR (ppm), 65.20 (methylene C), 49.28 (carbon 1 and 4 on cyclobutane), 41.18 (carbon 2 and 3 on cyclobutane). IR (cm^{-1}), 1750 (s, carbonyl), 1603, 1250, 1225, 777. UV, λ_{max} 220 and 285 nm. MS, 422.

Found: C, 79.20; H, 5.30%. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.21%.

cis,cis-***1E***, mp 107.0—108.0 °C ^1H NMR (ppm), 3.85 (s, 4H, methylene), 6.05 (d, J=11.7, 2H, vinyl), 7.0—8.5 (m, 16H, aromatic and benzyl). IR(cm^{-1}), 1723 (s, carbonyl), 1635 (s, double bond), 1180, 1214, 1420, 829, 814, 790. UV, λ_{max}=296 nm ε=2.32×10^4. MS 422.

*Anhydride of **1ED** (**1EA**)*: **1ED** (0.21 g) was heated in 1M aqueous sodium hydroxide (50 ml) for 3 h at 60—70 °C. After filtration the filtrate was acidified. The precipitate (0.17 g 81%) was dried over P_2O_5 and refluxed in acetyl chloride (20 ml) for 3 h. Concentration of the solution gave crystals of **1EA** 0.10 g (48%). ***1EA***, mp 214.0—215.0 °C. ^1H NMR (ppm) in C_5D_5N, 4.63 (d, 2H, cyclobutane), 5.97 (d, 2H, cyclobutane), 7.0—8.0 (m, 14H, aromatic). IR (cm^{-1}), 1870 and 1795 (five membered ring anhydride), 1603, 1245, 1214, 1065, 903, 780, MS, 378.

Found: C, 78.35; H, 4.93%. Calcd for $C_{26}H_{18}O_3$: C, 80.53; H, 4.79%.

*Photolysis of **2E***: **2E** (1 g) was irradiated in the same way as **1E** for one hour and the reactant solution concentrated in a rotary evaporator. The addition of hexane precipitated crystals of **2ED**, 0.75 g in 75% yield. **2ED**, mp 190.0 °C. ^1H NMR (ppm), 4.62 (s, 4H, methylene), 4.1—4.8 (m, 4H, cyclobutane), 6.85 and 7.0, 7.2—8.2 (m, 14H, aromatic). ^{13}C NMR (ppm), 65.03 (methylene C), 49.02 (carbon 1 and 4 on cyclobutane), 44.63 (carbon 2 and 3 on cyclobutane).

*Anhydride of **2ED**, (**2EA**)*: **2ED** was converted into the anhydride (**2EA**) in the same way as **1ED**. **2EA**, mp 165.0—168.0 °C. ^1H NMR (ppm), 4.1 and 4.6 (m, 4H, cyclobutane), 6.84 and 6.97, 7.20—8.00 (14H, aromatic). IR(cm^{-1}), 1855 and 1775 (five-membered ring anhydride), 1235, 1210, 1060, 900. MS, 378.

Found: C, 79.45; H, 4.82%. Calcd for $C_{26}H_{18}O_3$: C, 80.53; H, 4.79%.

*Dimethyl Ester of **2ED** (**2EM**)*: The dicarboxylic acid of **2ED** was esterified by diazomethane. **2EM** mp 108.0—109.0 °C. ^1H NMR (ppm), 3.80 (s, 6H, methyl), 4.10 and 4.80 (m, 4H, cyclobutane), 6.90 and 7.07, 7.2—8.0 (14H, aromatic). IR (cm^{-1}), 1730 (s, carbonyl), 1600, 1430, 1270, 1200. MS, 378.

*Photolysis of a Concentrated Solution of **2Me**.* **2Me** (1 g) in 50 ml of benzene was irradiated with light ($\lambda > 320$ nm) for 24 h. After irradiation, evaporation of the solvent gave crystals. Thin layer chromatography and NMR methyl signals showed the presence of at least two kind of products and HLC retention times indicated that one product was **2EM**.

Identification of 1ED and 2ED : The compound **1ED** was assigned the proposed cyclobutane structure based on NMR, UV, and IR spectra. ^{13}C NMR spectrum of **1ED** showed a single peak at 65.20 ppm for the methylene carbons, 49.29 ppm for carbons 1 and 4, 41.18 ppm for carbons 2 and 3 on the cyclobutane ring. The hydrolyzed product of **1ED** gave an acid anhydride (**1EA**) in boiling acetyl chloride. **1EA** has IR peaks at 1795 and 1870 cm^{-1}, characteristic of a five-membered ring anhydride. The all-*cis* structure presumably can be neglected since the hydrolyzed product of **1ED** gave *trans*-3-(1-naphthyl)acrylic acid upon irradiation with 253.7 nm light. The structure of **2ED** was assigned by an analogous method. The ^{13}C NMR spectrum has a peak at 65.03 ppm for the methylene carbons, 49.02 ppm for carbons 1 and 4, 44.63 ppm for carbons 2 and 3 on the cyclobutane ring. The hydrolyzed product of **2ED** gave an anhydride (**2EA**) in boiling acetyl chloride. **2EA** has IR peaks at 1780 and 1855 cm^{-1}, characteristic of a five-membered ring anhydride. Photolysis of **2EM** by 253.7 nm light or thermolysis above 250 °C in a gas chromatograph gave *trans*-**2Me**. These facts support the proposed structure for **2ED**.

Quantum Yield Measurements. A) The quantum yield of *trans* to *cis* isomerization of **1Me** and **2Me** was calculated from the decrease in the UV absorbance. Molar extinction coefficients used are shown below.

	In methanol			In cyclohexane
trans-**1Me**	$\lambda_{\max}=323$ nm	$\varepsilon=2.40$ ($\times 10^4$)	$\varepsilon_{313}=2.36$ ($\times 10^4$)	$\varepsilon_{313}=2.36$ ($\times 10^4$)
cis-**1Me**	$\lambda_{\max}=296$ nm	$\varepsilon=1.16$	$\varepsilon_{313}=0.933$	$\varepsilon_{313}=0.933$
trans-**2Me**	$\lambda_{\max}=307$ nm	$\varepsilon=2.52$	$\varepsilon_{313}=1.80$	$\varepsilon_{313}=1.48$
cis-**2Me**	$\lambda_{\max}=298$ nm	$\varepsilon=1.11$	$\varepsilon_{313}=0.779$	$\varepsilon_{313}=0.967$

B) The quantum yield of the cyclization and *trans-cis* isomerization of **1E** and **2E** was calculated from the peak area in the HLC chart. Usually a 2×10^{-5} mol/l reactant solution in 4 ml rectangular cell was irradiated for 30 or 60 s with 313 nm light.

C) The fluorescence quantum yield was calculated by using 2-(1-naphthyl)-5-phenyloxazole (α**NPO**) in cyclohexane as standard,[22] $\phi_f=0.70$.

D) Michler's ketone photosensitized isomerization of **2Me**. A solution of Michler's ketone (1.1×10^{-3} mol/l) and **2Me** (5×10^{-4} mol/l) in cyclohexane or ethanol was purged with argon for 10 min and irradiated with light of wavelength 365 nm or 405 nm respectively. A solution of **2Me** of the same concentration without Michler's ketone was irradiated with 313 nm light. The ratio of *trans*- and *cis*-**2Me** was measured by HLC.

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