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Thermostable Intramolecular Coupling Products from Some *p*-Xylylenebis(anthrylcarboxylate)s and the Relationship between Their Thermal Stability and Relative Distortion Energy

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The thermal stability of intramolecular coupling products from three kinds of *p*-xylylenebis(anthrylcarboxylate)s are evaluated. Upon near-UV irradiation, two anthracene moieties in each derivative react at the 9–9′ and 10–10′ positions. The derivatives then from intramolecular coupling products. These coupling products are identified by means of ^{1}H NMR and a linear combination of the atomic orbital coefficients for the highest occupied molecular orbital and the lowest unoccupied molecular orbital from analogues of each derivative. After keeping for 1000 h at a temperature of 60 °C, the coupling products from 2 species of *p*-xylylenebis(anthrylcarboxylate)s do not revert to the original *p*-xylylenebis(anthrylcarboxylate)s and are thermostable. However, these thermostable coupling products are reversed to the *p*-xylylenebis(anthrylcarboxylate)s by UV (260 nm) irradiation. The thermal stability of these coupling products can be explained on the basis of the magnitude of the relative distortion energy.

Many kinds of photochromic compounds such as spiropyran,[1–6] azobenzene,[7–10] fulgide,[11–14] diarylethene,[15–18] and anthracene[19–21] derivatives have been studied in order to develop erasable optical memory media and optical devices. It is necessary for memory media, that many data can be written, read or erased; for devices, the ON–OFF states of the photosignal can be regulated by photoinduced reversible absorption changes of these compounds. The data-storage stability of the memory media and the ON–OFF state stability of the devices are two of the most important characteristics for practical use. To improve ths stability of photochromic compounds, their isomers, which are produced by light irradiation, should be thermostable. Anthracene derivatives, which are a kind of photochromic compound, can be coupled by near-UV (ca. 300—400 nm) irradiation, while their coupling products can be cleaved to anthracene derivatives by UV (ca. 240—270 nm) irradiation.[19–22] The coupling products are also cleaved thermally. Studies[19,20,22] have suggested that the cleavage of coupling products might be related to their intramolecular structural strain. We consider that the structural strain can be estimated from the distortion energy. In this paper, we report on some new *p*-xylylenebis(anthrylcarboxylate)s which can be changed into thermostable intramolecular coupling products. To investigate the cause of their thermal stability, we identify their coupling product structures, and discuss the relationship between their thermal stability and distortion energy. To measure both their absorption spectra and thermal stability conveniently, some samples that comprise were polymer membranes containing the respective compounds prepared. For the polymer, poly(vinyl chloride) (PVC) was chosen because *p*-xylylenebis(anthrylcarboxylate)s are very soluble in it.

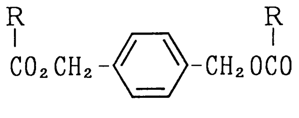

Fig. 1. Structures of compounds **1**—**3**. **1**: R; 1-substituted anthracene, **2**: R; 2-substituted anthracene, **3**: R; 9-substituted anthracene.

Experimental

Materials. PVC (polymerization degree 1100) was used without further purification. Diethyl adipate (DEA) and tetrahydrofuran (THF) were of extra-pure reagent grade.

1,4-Phenylenebis(methylene) Bis(1-anthracenecarboxylate) (1). Compound **1** was prepared by the condensation of 1-anthracenecarbonyl chloride (2.0 g, 8.3 mmol) with *p*-xylene-α,α'-diol (0.2 g, 1.4 mmol) in chloroform (20 ml) in the presence of triethylamine (2 ml). Yield 0.46 g (58%). Mp 217 °C. Found: C, 83.57; H, 4.51%. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79%. ^{1}H NMR (CDCl$_3$) δ=5.5 (4H, s, -CH$_2$-), 7.4—8.5 (20H, m, Aromatic ring except for 10, 10′ of anthracene ring), 9.6 (2H, s, 10, 10′ of anthracene ring). IR (KBr) $\nu_{C=O}$ 1710 cm^{-1} (ester).

1,4-Phenylenebis(methylene) Bis(2-anthracenecarboxylate) (2). Compound **2** was prepared in the same manner as **1**, except for using 2-anthracenecarbonyl chloride instead of 1-anthracenecarbonyl choloride. Yield 0.15 g (19%). Mp 217 °C. Found: C, 83.28; H, 4.56%. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79%. ^{1}H NMR (CDCl$_3$) δ=5.5 (4H, s, -CH$_2$-), 7.4—9.0 (22H, m, Aromatic ring). IR (KBr) $\nu_{C=O}$ 1705 cm^{-1} (ester).

1,4-Phenylenebis(methylene) Bis(9-anthracenecarboxylate) (3). Compound **3** was prepared in the same manner as **1**, except for using 9-anthracenecarbonyl chloride instead of 1-anthracenecarbonyl chloride. Yield 0.40 g (51%). Mp 236 °C. Found: C, 83.97; H, 4.53%. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79%. ^{1}H NMR (CDCl$_3$) δ=5.5 (4H, s, -CH$_2$-), 7.4—8.1 (20H, m, Aromatic ring except for 10, 10′ of anthracene ring), 8.5 (2H, s, 10, 10′ of anthracene ring). IR

(KBr) $\nu_{C=O}$ 1710 cm^{-1} (ester).

Preparation of Membranes. PVC membranes containing compounds **1**—**3** were prepared by pouring a mixture of PVC (0.65 g), DEA (2.8 g), **1**, **2**, or **3** (2.5 mg), and THF (20 ml) onto a flat petri dish (7.7 cm diameter) and allowing the solvent to evaporate. The prepared membranes had a thickness of ca. 0.6 mm.

Photoirradiation. Photoirradiation was performed with a 500 W xenon lamp using a monochrometer at 20 °C. The intensity of the near-UV (390 nm) and UV (260 nm) irradiations were about 2.0×10^{-5} W mm^{-2} and 2.5×10^{-6} W mm^{-2}, respectively.

Claculation. To calculate a linear combination of atomic orbital (LCAO) coefficients from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the CNDO program in CHEMLAB-II (Molecular Design Ltd.) was used. In the present study, the relative distortion energy (ΔE) was defined as being the difference between the distortion energy at 25 °C of the most stable structure for **1**—**3** and those for the corresponding coupling product. These energies were caluculated using the MM program in CHEMLAB-II.

Results and Discussion

Photo-Coupling Reaction of 1—3. To examine the photo-coupling reaction of **1**—**3** in PVC membranes we measured the absorption spectra of the respective membranes before and after near-UV (390 nm) light irradiation. The absorption spectra of these membranes are shown in Fig. 2. Before near-UV irradiation, each PVC membrane shows an absorption band between 300—400 nm from the π–π* transition of the anthracene ring. This absorption intensity decreases after near-UV irradiation. This spectral change indicates that the photo-coupling reactions of **1**—**3** proceeded.[19–21] The amount of each coupling product was monitored using the decreased absorbance at 390 nm of **1** and **2** or 386 nm of **3**. After about 2 minutes of near-UV irradiation (a total light energy of 25 mJ mm^{-2}), the amounts of the coupling product derived from **1**, **2**, and **3** in the PVC membranes were 68, 42, and 29%, respectively. Under the same photoirradiation conditions, the amounts of the coupling products derived from ethyl 1-, 2-, and 9-anthracenecarboxylates in the PVC membranes were 6, 6, and 4%, respectively. Since ethyl 1-, 2-, and 9-anthracenecarboxylates have one anthracene moiety, the possible structures of the coupling products are of the intermolecular coupling type. If the photo-reaction of **1**, **2**, and **3** give intermolecular coupling products, the rates of these reactions are comparable to those of ethyl 1-, 2-, and 9-anthracenecarboxylates, respectively. However, the rates of the coupling reactions of **1**, **2**, and **3** are actually much faster than those of ethyl 1-, 2-, and 9-anthracenecarboxylates. We therefore believe that most of compounds **1**—**3** are converted into intramolecular coupling products by near-UV irradiation.

The absorbances of near-UV irradiated membranes are increased by UV (260 nm) irradiation. This spectral change indicates that each coupling product reverts to the respective *p*-xylylenebis(anthrylcarboxylate)s. Though the total UV irradiated energy was more than 10 mJ mm^{-2}, these absorbances did not increase. After all, these absorbances were not reached before near-UV irradiation. According to a study by Hida et al.,[20] not only cleavage, but also the coupling reaction of two anthracene moieties proceeded due to UV irradiation. These absorption changes thus suggest that an equilibrium state between cleavage and the coupling reaction are reached when the total energy of UV

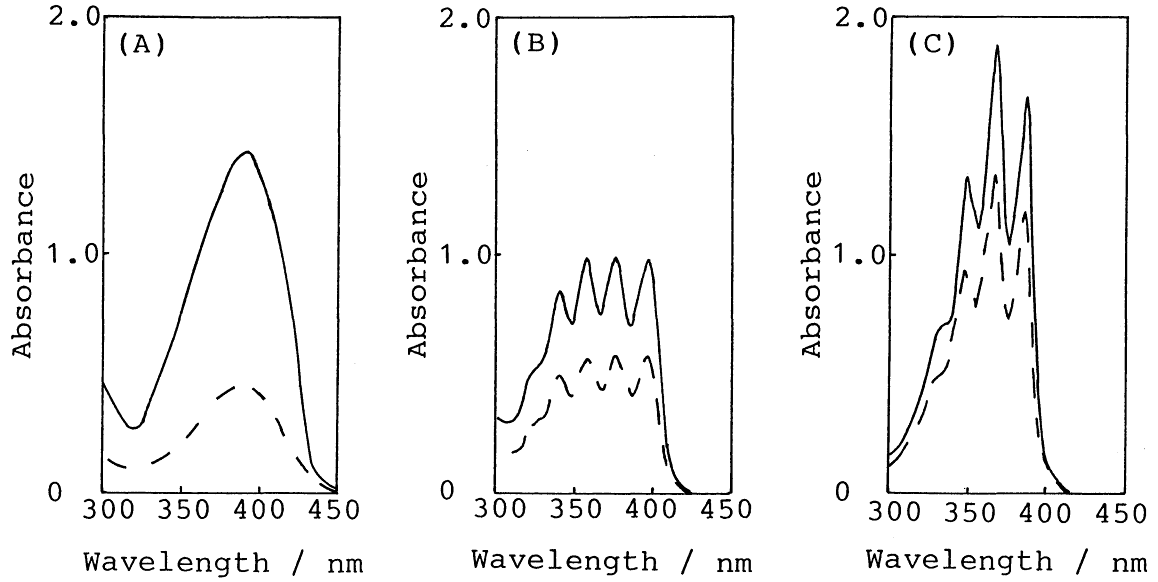

Fig. 2. Absorption spectra of **1**—**3** in PVC membrane before (——) and after (----) near-UV light irradiation for 2 min. (A) Absorption spectra of **1**, (B) Absorption spectra of **2**, (C) Absorption spectra of **3**.

irradiation is more than 10 mJ mm^{-2}.

Thermal Stability of the Coupling Products from 1—3. Figure 3 shows the changes in the absorbance of the near-UV irradiated PVC membrane under 60 °C. Most of the coupling products derived from anthracene derivatives change thermally into the anthracene derivatives, which have the same structures as those before near-UV irradiation;[20—22] also, the absorption intensity from the π–π^* transition of the anthracene increases. We therefore assume that the increase of the absorbance of the near-UV irradiated PVC membranes under 60 °C is due to a change from the coupling product to the anthracene derivative. The absorbances of membranes containing 3 gradually increase. However, they do not change for **1** and **2**. This means that the coupling products from **1** and **2** are thermostable, and thus the thermal stability of the coupling products would follow the order **1**, **2** > **3**.

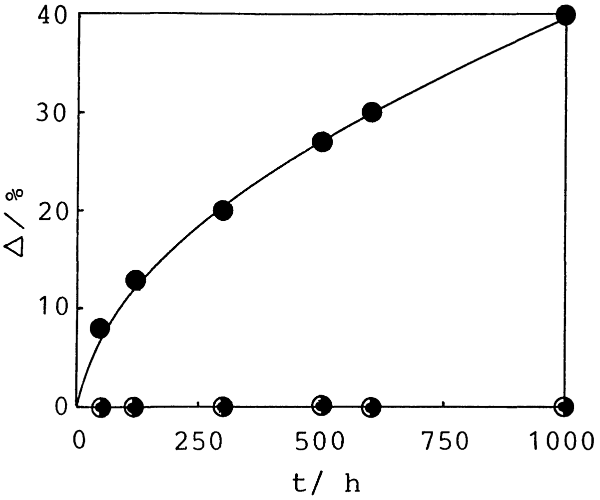

Fig. 3. Absorbance changes at 60 °C of a membrane irradiated with near-UV for 2 min. —◉—; **1**, —◑—; **2**, and —●—; 3. Δ/%; $(A_A - A_{A0})/(A_B - A_{A0})$. A_B; Absorbance before near-UV irradiation, A_{A0}; Absorbance after near-UV irradiation, A_A; Absorbance after near-UV irradiation at *t*.

It has been suggested that the thermal stability of the coupling products from anthracene derivatives might be related to their intramolecular structural strain.[19,20,22] We though that these structural strains could be estimated in terms of the relative distortion energy. However, there are several possible structures of the coupling products from **1**—**3**. We tried to identify the structures and to calculate the distortion energy of these coupling products.

Structures of Coupling Products from 1—3. The possible structures of the coupling product from **1**—**3** are 9–9′,10–10′- and 9–10′,10–9′-bianthracenes. Therefore, those from **1** are 1,1′- and 1,8′-substituted 9–9′,10–10′-bianthracenes, and 1,4′- and 1,5′-substituted 9–10′,10–9′-bianthracenes. Those from **2** are also 2,2′- and 2,7′-substituted 9–9′,10–10′-bianthracenes, and 2,3′- and 2,6′-substituted 9–10′,10–9′-bianthracenes. Those from **3** are also 9,9′-substituted 9–9′,10–10′-bianthracene, and 9,10′-substituted 9–10′,10–9′-bianthracene. We attempted to determine the number of coupling product isomers, and thus analyzed the extract (extracting solvent: $CHCl_3$) from a near-UV irradiated membrane by thin-layer chromatography (TLC). In each case, one spot originated from either compound **1**, **2**, or **3**, and another spot from the coupling product. This was due to the observation that the former spot was detected following irradiation at both 365 and 254 nm, though the latter spot was only detected under 254 nm irradiation. Although we changed the eluent polarity, the spot corresponding to the coupling product did not separate. We thus tried to identify each structure of the coupling product using the LCAO coefficients of HOMO and LUMO from the p_z orbital of anthracene rings, and ^{1}H NMR. We first calculated the LCAO coefficients. Since the number of atoms in **1**—**3** was greater than the capacity of our CNDO calculation system, we calculated ethyl 1-, 2-, and 9-anthracenecarboxylates instead of **1**, **2**, and **3**, respectively. Table 1 lists the results. The absolute values of the LCAO coefficients from 9- and 10-carbon atoms of each ethylanthracenecarboxylate are larger than those of the other carbon atoms in the anthracene

Table 1. P_z of LCAO Coefficients of Carbon Atoms in Anthracene Ring

Position of carbon atom anthracene ring	Substitutional position of ethoxycarbonyl moiety in anthracene ring					
	1		2		9	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
1	−0.32	0.31	0.29	0.37	−0.30	0.25
2	−0.20	−0.31	0.22	−0.26	−0.20	−0.24
3	0.22	−0.20	−0.22	−0.15	0.22	−0.18
4	0.28	0.37	−0.30	0.29	0.29	0.28
5	0.30	0.26	−0.31	0.27	0.27	0.28
6	0.22	−0.18	−0.22	−0.23	0.21	−0.17
7	−0.21	−0.22	0.22	−0.19	−0.19	−0.24
8	−0.30	0.25	0.30	0.29	−0.28	0.24
9	0.43	−0.37	−0.42	−0.44	0.44	−0.40
10	−0.41	−0.41	0.43	−0.39	−0.39	−0.44

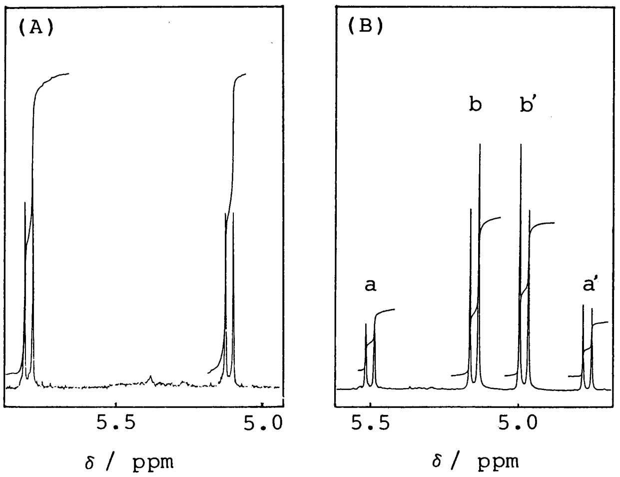

Fig. 4. ^{1}H NMR spectra of coupling products from **1**, **2**. (A) Coupling product from **1**, (B) Coupling product from **2**.

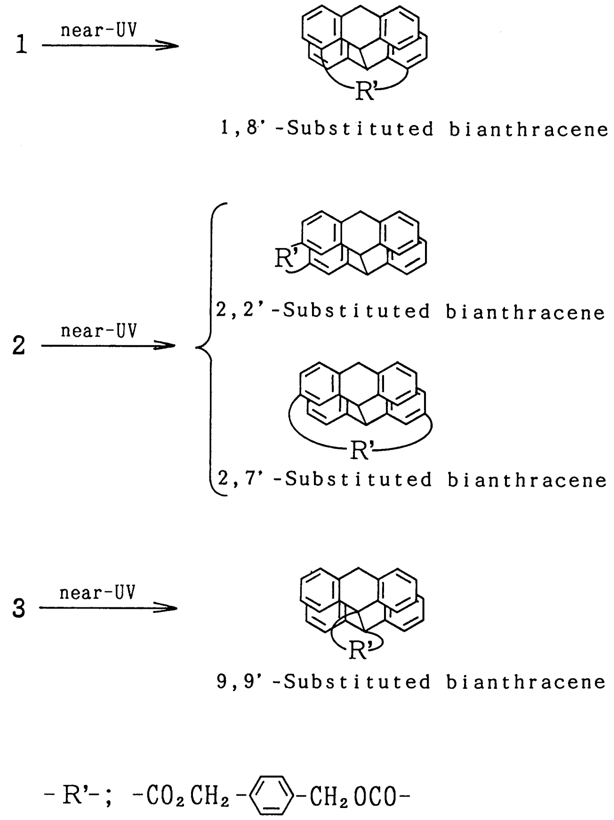

Fig. 5. Structures of the coupling products from **1**—**3**.

ring. This result shows that the 9- and 10-carbon atoms take part in the photo-coupling reaction. From the sign of the LCAO coefficients, the new C–C bonds, which result from photo-coupling reactions of the ethyl 1-, 2-, and 9-anthracenecarboxylates, are not derived from 9 and 10- or 10 and 9-carbons, but from the 9 and 9- or 10 and 10-carbons of the anthracene rings.[23] The coupling products from **1**—**3** are therefore 9–9′,10–10′-bianthracenes. The possible structures of the coupling products from **1** are thus 1,1′- and 1,8′-substituted; from **2**, 2,2′- and 2,7′-substituted; and from **3**, is 9,9′-substituted bianthracenes.

We now discuss each structure of the coupling product in terms of ^{1}H NMR. Each coupling product was extracted (solvent: $CHCl_3$) from the near-UV irradiated membrane and purified by TLC. After extraction we estimated the amount of residues in these membranes by measuring the absorbances at 260 nm. The amount of residue in each membrane was less than 10% of that before extraction. The ^{1}H NMR spectra of the coupling products from **1** and **2** are shown in Figs. 4 (A) and (B), respectively. When **1** and **2** are coupled, the NMR signals (doublet) from the 9, 10, 9′, 10′-protons of anthracene rings shifted from about 8.5—9.6 ppm to 4.5—5.9 ppm. Figure 4 (B) shows that the coupling product from **2** is a mixture (**a, a′** : **b, b′**≒1 : 3) of 2,2′- and 2,7′-substituted bianthracenes (as shown in Fig. 5). The proton signals of the 9 and 9′ positions of 2,7′-substituted bianthracene should appear in a higher magnetic field than those of 2,2′-substituted bianthracene, because of the shielding effect of the benzene ring, which links the two anthracene rings. The difference between the 9,9′- and 10,10′-proton signals of 2,7′-substituted bianthracene (0.73 ppm) is larger than those of the 2,2′-substituted bianthracene (0.17 ppm). Thus, the **a**, **a′** and **b**, **b′** signals are derived from 2,7′- and 2,2′-substituted bianthracene, respectively. Thus, the ratio of the coupling product from **2** is as follows: 2, 2′-substituted bianthracene : 2,7′-substituted bianthracene≒3 : 1. Figure 4 (A) shows that the coupling product from **1** is one species: 1,1′-or 1,8′-substituted bianthracene. The difference between the 9,9′- and 10,10′-proton signals (0.68 ppm) is approximately the same as that of 2,7′-substituted bianthracene. Furthermore, the 9 and 9′-protons of 1,8′-substituted bianthracene should appear in a higher magnetic field than those of 1,1′-substituted bianthracene, due to a shielding effect of the benzene ring which links the two anthracene rings. The coupling product from **1** should thus be 1,8′-substituted bianthracene, as shown in Fig. 5. After near-UV irradiation, the NMR signals for the 10,10′-protons of the coupling product from **3** are shifted from 8.5 ppm (singlet) to 4.5 ppm (doublet). The coupling product from **3** is thus 9,9′-substituted bianthracene, as shown in Fig. 5.

Δ*E* of the Coupling Products from 1—3. To investigate the the relationship between the degree of thermal stability and relative distortion energy (Δ*E*), we calculated Δ*E* of the coupling products from **1**—**3**. Table 2 lists the results. The values of Δ*E* of the coupling products from **1** and **2** are smaller than those from **3**. According to Fig. 3, although the coupling products from **1** and **2** are thermostable, those from **3** are not. Therefore, Fig. 3 and Table 2 show that the lower is Δ*E* of the coupling product, the greater is the thermostability of the coupling product; the coupling

Table 2. Relative Distortion Energy (ΔE) of the Intramolecular Coupling Product

Compound	Substitutional position of anthracene ring	ΔE kcal mol^{-1}
1	1, 8′	66.4
2	2, 2′	47.9
	2, 7′	102.9
3	9, 9′	128.9

products from **1** and **2** are therefore thermostable due to their low ΔE.

Conclusion

In this study we found that compounds **1** and **2** change into thermostable intramolecular coupling products. Based on the LCAO coefficients of HOMO and LUMO and ^{1}H NMR, the structures of these coupling products could be identified. Their thermal stability was explained based on the magnitude of the relative distortion energy.

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