CHEMISTRY LETTERS, pp. 419-422, 1990.

Intramolecular Photo- and Thermal Dimerizations of Diaza[3.3](9,10)anthracenophanes[1)]

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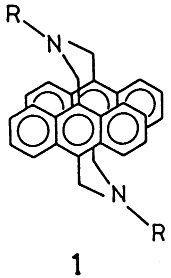
Intramolecular dimerizations of seven novel diazaanthracenophanes (1) were studied. Some of 1 underwent the novel thermal dimerization of anthracene rings. The reactivities of 1 were classified into three types according to the direction in the thermal reaction.

It is well-known that [2.2](9,10)-,[2)] [2.2](1,4)-,[3)] and [3.3](1,4)anthracenophanes[4)] similarly to anthracene derivatives,[5)] undergo the photodimerization of anthracene rings and that their photoproducts revert to the original compounds on heating. In this paper we report on the intramolecular photo- and thermal dimerizations of seven novel diaza[3.3](9,10)anthracenophanes (1a - 1g). Although some of 1 behaved normally, the others showed unusual behaviour of thermal dimerization of anthracene rings. The latter has not been yet known.



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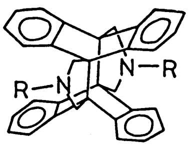

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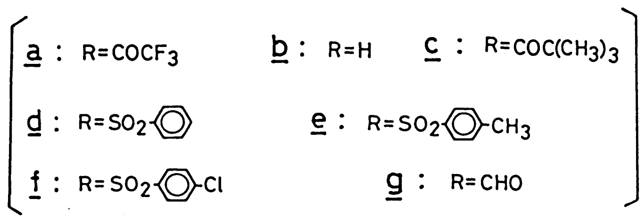


Compound 1a was synthesized by a high dilution coupling between 9,10-bis(chloromethyl)anthracene (3) and 9,10-bis(N-trifluoroacetylaminomethyl)anthracene (4) with sodium hydroxide in N,N-dimethylformamide (DMF) at 90 °C for 5 h in the dark in a 2% yield. Hydrolysis of 1a in alkaline water-ethanol at 70 °C for 5 h gave 1b in a 55% yield, and acylation of 1b with pivaloyl chloride in pyridine at 50 °C for 2.5 h gave 1c in a 44% yield. Formylation of 1b with formic acid in refluxing toluene for 8 h gave 1g almost quantitatively. The reaction between benzene-, p-toluene-, and p-chlorobenzenesulfonamide and 3 with sodium hydride in DMF at 60 °C for 5 h gave 1d, 1e, and 1f in 22%, 30%, and 26% yields, respectively. 1a and 1c were recrystallized from benzene, and 1b, 1d, 1e, and 1f were from pyridine. Recrystallization of 1g was not performed because of poor solubility in common solvent. 1a - 1g:[6] Orange crystals except 1g (orange powder); mp >300 °C except 1b (ca. 300 °C(dec)). These anthracenophanes gave satisfactory high resolution MS analyses.

Figure 1 shows the electronic spectra of 1a, 1b, 1c, 1e, and 4.[7] Characteristic features of the spectra of 1 are a new band in the long wavelength region and broadening of La band compared with that of the acyclic compound 4, suggesting layered structure.

Photoirradiations (λ>340 nm) of orange colored compounds 1a - 1g gave colorless intramolecular dimerization products 2a - 2g[8] in both the solid state and solution. Thermal reaction was investigated by means of IR spectra. Photoproducts 2d and 2g reverted quantitatively to the original compounds 1d and 1g, respectively, at 190 and 170 °C for 1 h in KBr pellets. 2b reverted to 1b on heating at 240 °C with partial decomposition. On the other hand 2a and 2c never reverted to 1a and 1c even on heating at 280 °C in KBr pellets, while 1a and 1c quantitatively gave 2a and 2c at 190 °C for 1 h, respectively. 2e and 2f were heated at 190 °C for 1 h in KBr pellets to revert partly to 1e and 1f, respectively. For example, IR spectral changes of 2f on heating and 1f on photoirradiation were shown in Fig. 2. The ratios of 1e to 2e and 1f to 2f after heating are obtained to be 1/4 and 1, respectively, by use of the absorbance of 1 at 900 cm^{-1} and that of 2 at 1000 cm^{-1}. The same ratios were also obtained by electronic spectra measurements in chloroform. Heating of 1e and 1f at 190 °C also gave the mixtures of the same ratios as that of 2e and 2f, respectively, and further, prolonged heating at the

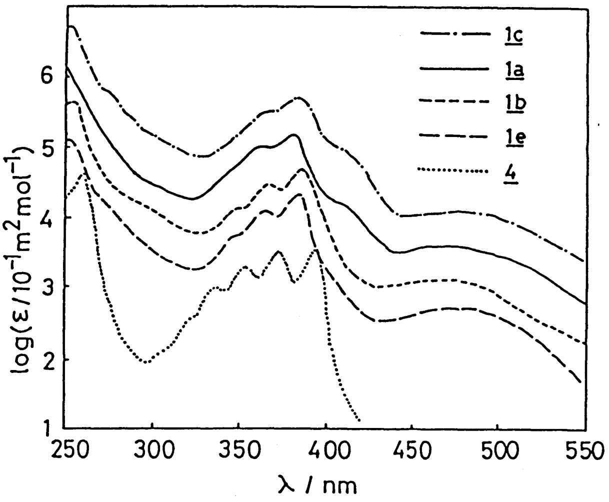


Fig. 1. Electronic spectra of anthracenophanes 1 and an acyclic compound 4 in chloroform.
The curves of 1b, 1a, 1c, and 4 are displaced upward by 0.5, 1.0, 1.5, and -0.5, respectively.

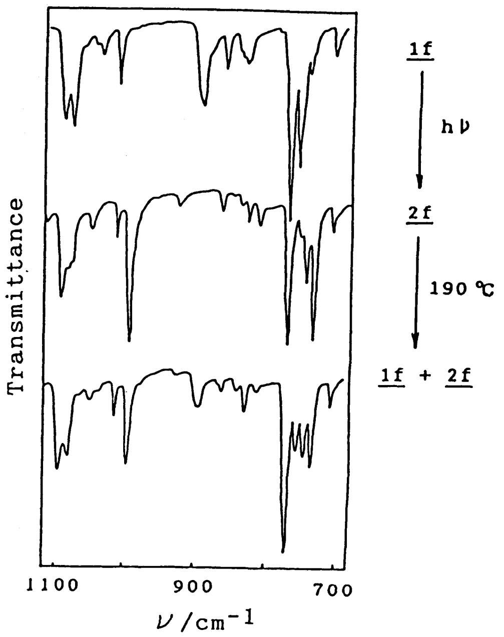
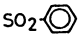
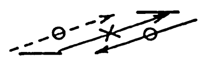
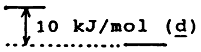
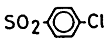
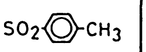
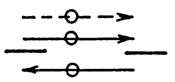
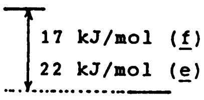
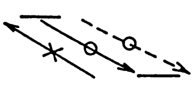
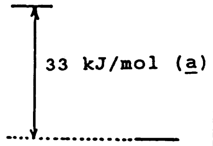


Fig. 2. IR spectral changes of 1f in a KBr pellet on irradiation (λ>340 nm) followed by heating at 190 °C.

same temperature did not change the ratios. These results indicate that these thermal reactions gave the thermal equiliblium mixture. These three types of reactivities can be understood by the difference in free energy of 1 and 2 as shown in Table 1. The anthracenophanes of type 1 undergo the photodimerization followed by the thermal reversion at 170 - 240 °C, since 1 is energetically more stable than 2. This is the typical reaction of anthracenophanes. On the other hand, those of type 3 undergo not only the photodimerization but also the thermal dimerization, and the thermal reversion does not occur, since 2 is energetically more stable than 1. When free energy of 1 is comparable to that of 2, the anthracenophanes undergo the reversible thermal dimerization (type 2). The thermal reaction of 1 in type 2 and 3 is, to our knowledge, the first example of the thermal dimerization of anthracene rings.

The ratios of 1e to 2e and 1f to 2f became large when 1 or 2 was heated at the higher temperatures than 190 °C, and became small when at the lower temperatures. These results implied that the processes of 1e to 2e and 1f to 2f were exothermic and the reverse ones were endothermic. Calorimetric measurements of 1e , 2e, 1f, 2f, 1a, and 2d were carried out by differential scanning calorimetry. Each compound showed an exo- or endothermic peak in the temperature range 170 - 230 °C. The apparent enthalpy changes of 1e to 2e and 1f to 2f were -18 and -7.5 kJ/mol (exothermic), and those of 2e to 1e and 2f to 1f were 4.6 and 9.5 kJ/mol (endothermic), respectively. These DSC results were consistent with the temperature dependence of the ratio of 1 to 2 as described above. The enthalpy changes of 1a to 2a and 2d to 1d were also determined to be -33 and 10 kJ/mol, respectively. The enthalpy gaps between 1 and 2 are also summarized in Table 1.$^{9)}$ The enthalpy of 1 is higher than that of 2 in these compounds. The gap between 1 and 2 increased in the order of d (type 1), f (type 2), e (type 2), and a (type 3). This order is the

Table 1. Energy diagrams and reactivities of diazaanthracenophanes

Type	R	Free energy a)		Enthalpy	
		1	2	1	2
1	g : CHO b : H d : 			 10 kJ/mol (d)	
2	f :  e : 			 17 kJ/mol (f) 22 kJ/mol (e)	
3	a : COCF$_3$ c : COC(CH$_3$)$_3$			 33 kJ/mol (a)	

a) - - → : Photoirradiation, ——→ : heating.
O : Reactive, x : unreactive.

same as that for the ease of thermal dimerization. Bulky substituents on the bridged chains accelerate the photocyclization and depress the thermal reversion in [3.3](1,4)naphthaleno(9,10)anthracenophanes10) and diaza[3.3]paracyclo(9,10)-anthracenophanes.11) The ring approach caused by the bulky substituents and the strain caused by the ring approach result in these reactivities.4,10,11) The distance between the faced rings in 1 of type 3 is probably shorter than that in the derivatives of the other types and 1 of type 3 is expected to have the higher strain energy. These characters of 1a seem responsible for the irreversible thermal dimerization and the greater enthalpy gap between 1 and 2. [2.2](9,10)-Anthracenophane has the shorter bridged chains than 1 but the enthalpy of its photodimer is higher than that of the original compound and the thermal dimerization does not occur.12) This is probably because cyclobutane rings in the photodimer of [2.2]phanes have higher strain energy than cyclopentane rings in that of [3.3]phanes.

The authors are indebted to Mr. Takao Uwabe of Tokyo Metropolitan Industrial Technology Center and Mr. Kouji Fujimoto of Seiko Instruments Inc. for DSC measurements, and to Mr. Yuichiro Arai, Mr. Hiroshi Ishihara, and Mr. Yasushige Kajikawa of Nihon University for the syntheses of these anthracenophanes.

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6) 1a: IR(KBr), 1681 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=5.84(s, 8H, CH$_2$), 6.8-8.1(m, 16H, arom). 1b: IR(KBr), 3230 cm^{-1}. 1c: IR(KBr), 1619 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.79(s, 18H, CH$_3$), 5.84(s, 8H, CH$_2$), 6.8-8.1(AA'BB', 16H, arom). 1d: IR(KBr), 1166 cm^{-1}. 1e: IR(KBr), 1167 cm^{-1}. 1f: IR(KBr), 1170 cm^{-1}. 1g: IR(KBr), 1662 cm^{-1}.
7) The spectra of 1d, 1f, and 1g were similar to those of 1b and 1e.
8) 2a: IR(KBr), 1690 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=4.83(s, 8H, CH$_2$), 6.7-7.3(m, 16H, arom), M$^+$, 630. 2b: IR(KBr), 3340 cm^{-1}, M$^+$, 438. 2c: IR(KBr), 1639 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.57(s, 18H, CH$_3$), 4.76(s, 8H, CH$_2$), 6.7-7.4(m, 16H, arom), M$^+$, 606. 2d: IR(KBr), 1171 cm^{-1}, M$^+$, 718. 2e: IR(KBr), 1173 cm^{-1}, M$^+$, 746. 2f: IR(KBr), 1175 cm^{-1}, M$^+$, 786. 2g: IR(KBr), 1666 cm^{-1}, M$^+$, 494.
9) Each enthalpy gap in e- and f derivative was obtained from the sum of apparent enthalpy gaps in the processes of 1 to 2 and 2 to 1.
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(Received December 9, 1989)