



## Syntheses and Reactions of Diazaanthracenophanes. Part 8: Syntheses and Photochromism of Diazaanthracenoparacyclophanes Having a Substituent on a Phenyl Ring

Masao Usui,\* Yoshio Shindo

Organic Chemistry Division, Tokyo Metropolitan Industrial Technology Center,  
Nishigaoka, Kita-ku, Tokyo, 115 Japan

Yoshiaki Suzuki

Research and Development Division, Victor Company of Japan, Ltd.,  
Yokosuka, Kanagawa, 239 Japan

&

Takamichi Yamagishi

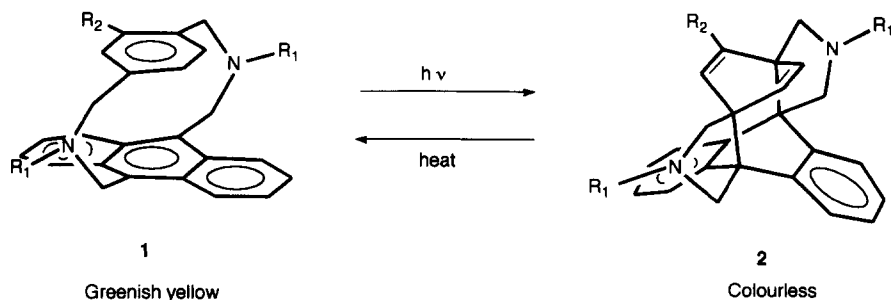
Department of Industrial Chemistry, Faculty of Technology,  
Tokyo Metropolitan University, Minamiosawa, Hachioji-shi, Tokyo, 192-03 Japan

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### ABSTRACT

Three diazaanthracenoparacyclophanes (**1b**, **1c** and **1d**) having various  $R_2$  substituents (chloro, methoxyl and cyano) on a phenyl ring were synthesized and their photochromic behaviour compared with those of the cyclophanes previously reported by us (**1a** and other derivatives) having various  $R_1$  substituents on the bridged chains. Photoirradiation of the greenish-yellow cyclophanes **1b–1d** gave colourless cycloadducts **2b–2d**, which reverted to the initial coloured cyclophanes on heating. Compounds **1b–1d** exhibited good reproducibilities after several irradiation-heating cycles, similarly to **1a**.  $R_2$  substituents accelerated both the photocycloaddition and thermal reversions in the order  $H < Cl \leq OCH_3 \leq CN$ , in contrast to the effect of  $R_1$  substituents with bulky substituents on the bridged chains, which accelerated the photocycloaddition and depressed the thermal reversion.

\* Corresponding author.



Compound	R <sub>1</sub>	R <sub>2</sub>
1a	COCF <sub>3</sub>	H
1b	COCF <sub>3</sub>	Cl
1c	COCF <sub>3</sub>	OCH <sub>3</sub>
1d	COCF <sub>3</sub>	CN

Scheme 1.

## 1 INTRODUCTION

Photochromic materials are attractive functional dyes in view of their reversible colour change and their potential applicability to high-density recording media.<sup>1,2</sup>

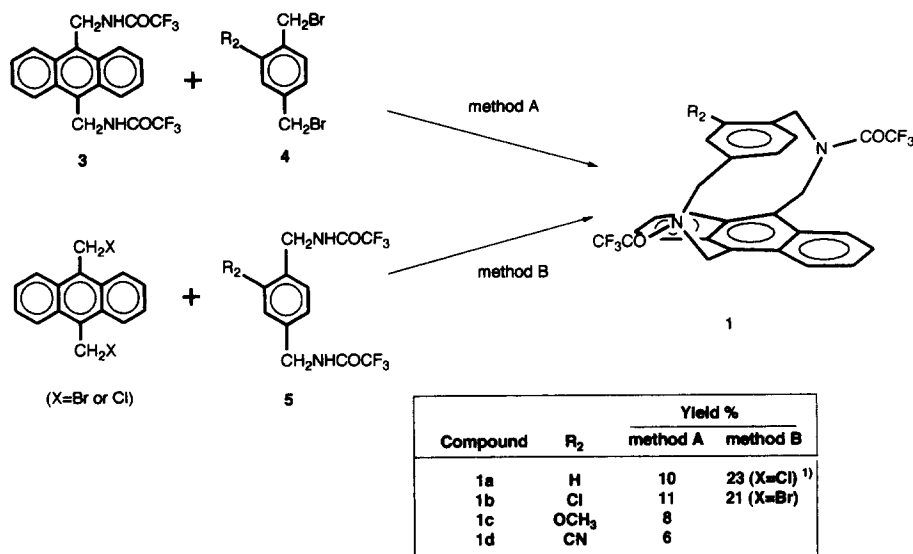
In our previous papers,<sup>3-5</sup> we have reported that diazaanthracenoparacyclophanes (**1**) show photochromism (Scheme 1), and, in this system, bulky R<sub>1</sub> substituents on the bridged chains accelerate the photocycloaddition and depress the thermal reversion. Similar steric effects by substituents on the bridged chains have been also reported in other cyclophanes with one or two anthracene rings,<sup>6-9</sup> but the effect of substituents in the aromatic rings of these cyclophanes has not yet been studied.

Three new diazaanthracenoparacyclophanes **1b**, **1c** and **1d** were synthesized to study the effect of the R<sub>2</sub> substituent in a phenyl ring on the thermal and photo reactions. The spectroscopic properties and reactivities of **1b**, **1c** and **1d** were compared with those of the previously reported **1a**.<sup>4,5</sup>

## 2 EXPERIMENTAL

### 2.1 Materials and apparatus

*N,N*-dimethylformamide (DMF) was dehydrated and distilled according to conventional methods. 9,10-Bis[(trifluoroacetyl amino)methyl] anthracene (**3**) and 9,10-bis(bromomethyl)anthracene were prepared as previously described.<sup>4,9</sup> Other materials were of analytical grade and were used without further purification.



1) Ref. 4.

Scheme 2.

Electronic and infrared spectra were recorded on an Otsuka Electronics SM-401 spectrophotometer and a JASCO DS-701G IR spectrophotometer, respectively. Mass and [<sup>1</sup>H] NMR spectra were obtained with a JEOL DX-300 mass spectrometer and a JEOL EX-400 (400 MHz) spectrometer, respectively. Elemental analyses were carried out on a Yanagimoto MT-3 CHN coder. Melting points were determined on a Yanagimoto micro-melting apparatus.

Photoirradiation was carried out using a 250-W high-pressure mercury lamp (Ushio) with a filter (Corning 0-52 λ > 340 nm), or a Hitachi MPF-4 spectrophotometer equipped with a 150-W Xenon lamp and a grating monochromator.

## 2.2 Syntheses

2-Substituted α,α'-dibromo-1,4-xylenes (**4b**, **4c** and **4d**) were prepared by bromination of the corresponding 2-substituted 1,4-xylene with *N*-bromo-succinimide. 2-Chloro- and 2-methoxy-α,α'-bis(trifluoroacetamino)-1,4-xylene (**5b** and **5c**) were prepared from the corresponding **4** and trifluoroacetamide, but the cyano compound (**5d**) could not be obtained.

**1b**, **1c** and **1d** were synthesized by reaction between **3** and the corresponding **4** (method A in Scheme 2); **1b** was also synthesized by method B in Scheme 2 for a comparison between these two methods. For the same reason, **1a** was also synthesized by method A. The yields of **1a** and **1b** by method B were superior to those by method A.

### 2.2.1 Synthesis of N,N'-bis(trifluoroacetyl)-2,19-diaza-22-chloro-[3](9,10)-anthraceno[3]paracyclophane (**1b**)

**Method A.** To a stirred suspension of powdered sodium hydroxide (150 mg, 3.75 mmol) in dry DMF (100 ml) was added **3** (644 mg, 1.50 mmol) at 90°C under a dry nitrogen atmosphere. After 2 h, **4b** (447 mg, 1.48 mmol) in dry DMF (100 ml) was added dropwise over 4 h to this reaction mixture in the dark, and the mixture was then maintained under the same conditions for 1 h. The reaction mixture was concentrated to about 10 ml *in vacuo*. Addition of distilled water (200 ml) and sodium chloride (4 g) gave a yellow precipitate, which was extracted with chloroform to give a reddish-brown solid. **1b** (93 mg, 0.164 mmol, yield 11.0%) was isolated from this solid by use of both thin-layer chromatography on silica gel and of gel permeation chromatography (Japan Analytical Ind. LC-08). Recrystallization from benzene–hexane gave greenish-yellow crystals, m.p.: 241.5–242.5°C.

IR(KBr)  $\text{cm}^{-1}$ : 1690 (C=O, s), 1210(s), 1138(s), 760(m). MS: (ionization voltage 70 V)  $m/z$  (relative intensity): 138(43), 313(100), 426(65), 564( $\text{M}^+$ , 84). Found: C 59.59% H 3.62% N 5.07%, Calcd for  $\text{C}_{28}\text{H}_{19}\text{ClF}_6\text{N}_2\text{O}_2$ : C 59.53% H 3.39% N 4.96%.

**Method B.** To a stirred suspension of powdered sodium hydroxide (147 mg, 3.68 mmol) in dry DMF (100 ml) was added **5b** (476 mg, 1.31 mmol) at 90°C under a dry nitrogen atmosphere. After 3 h, 9,10-bis(bromomethyl)-anthracene (475 mg, 1.30 mmol) was added to this reaction mixture in the dark in one portion because of the poor solubility of this bromo compound, and the mixture was then maintained under the same conditions for 4 h. **1b** (155 mg, 0.274 mmol, yield 21.1%) was isolated from the reaction mixture in the same manner as for method A.

### 2.2.2 Synthesis of N,N'-bis(trifluoroacetyl)-2,19-diaza-22-methoxy-[3](9,10)-anthraceno[3]paracyclophane (**1c**) by method A

Compound **4c** was reacted with **3**, following the general procedure for method A. Recrystallization from benzene–hexane gave greenish-yellow crystals, yield: 8.0%, m.p.: 246.1–247.2°C.

IR(KBr)  $\text{cm}^{-1}$ : 1677 (C=O, s), 1195(s), 1132(s), 755(m). MS: 134(100), 425(32), 560( $\text{M}^+$ , 52). Found: C 62.36% H 4.18% N 5.31%, Calcd for  $\text{C}_{29}\text{H}_{22}\text{F}_6\text{N}_2\text{O}_3$ : C 62.15% H 3.96% N 5.00%.

### 2.2.3 Synthesis of N,N'-bis(trifluoroacetyl)-2,19-diaza-22-cyano-[3](9,10)-anthraceno[3]paracyclophane (**1d**) by method A

Compound **4d** was reacted with **3** using method A. Recrystallization from benzene–hexane gave greenish-yellow prisms, yield: 6.3%, m.p.: 295.7–297.6°C.

IR(KBr)  $\text{cm}^{-1}$ : 2200 (CN, w), 1678–1691 (C=O, s), 1199(s), 1142(s), 761(m). MS: 129(20), 314(47), 426(100), 555( $\text{M}^+$ , 80). Found: C 62.80% H 3.66% N 7.69%, Calcd for  $\text{C}_{29}\text{H}_{19}\text{F}_6\text{N}_3\text{O}_2$ : C 62.71% H 3.45% N 7.56%.

## 2.3 Procedures

### 2.3.1 Reproducibility of spectral changes

When each chloroform solution (about  $45 \mu\text{mol litre}^{-1}$ , 3.5 ml) of **1b**, **1c** and **1d** was irradiated in a stoppered quartz cell with 413-nm, 419-nm and 408-nm monochromatic light respectively, the solution turned from greenish-yellow to colourless. The colourless solution was carefully evaporated *in vacuo*. When the colourless residue was heated for 20 min at  $150^\circ\text{C}$  in the dark and dissolved again in the same volume of chloroform (3.5 ml), the colour returned to the initial greenish-yellow. The reproducibility in this cycle was quantitatively evaluated by measuring the electronic absorbance recovery. The reproducibility in a KBr pellet was also checked with an infrared spectrophotometer.

### 2.3.2 Quantum yields and rates of thermal reversion

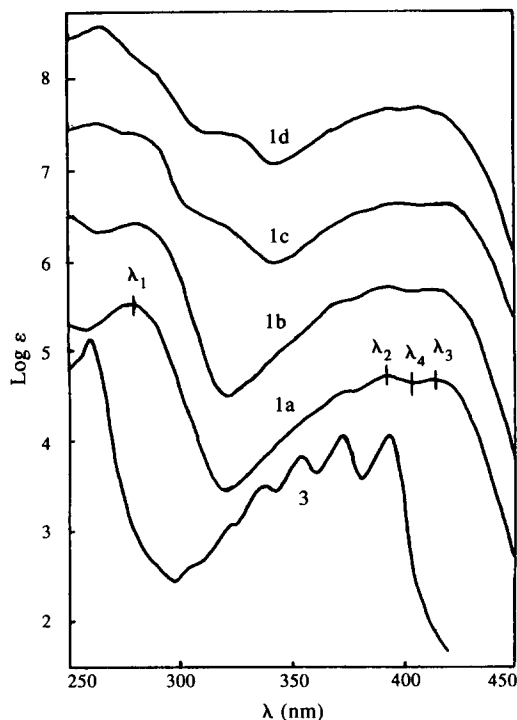
After each chloroform solution (about  $45 \mu\text{mol litre}^{-1}$ , 3.5 ml) of **1b–1d** had been bubbled in a reaction quartz cell with nitrogen, air or oxygen for 10 min, the cell was sealed and irradiated with monochromatic light. The quantum yield of the photocycloaddition was determined by measuring the decrease in the absorbance of **1** and simultaneously by determining the number of photons absorbed by **1** with a chemical actinometer of potassium tris(oxalato)ferrate(III).<sup>10</sup>

Each xylene solution of **1b–1d** was irradiated in a reaction quartz cell until it became colourless and then placed in an oil bath kept at  $70^\circ\text{C}$  in the dark. The rate of thermal reversion was determined by measuring the absorbance recovery of **1**. The rate constant was estimated by first-order kinetic analysis.

## 3 RESULTS AND DISCUSSION

### 3.1 Electronic spectra

The electronic spectra of **1b**, **1c** and **1d** are shown together with those of **1a** and **3**, in Fig. 1 and Table 1. E2 bands (320–450 nm) of **1b** and **1c** show apparent broadening and a bathochromic shift in comparison with those of the acyclic compound (**3**), similar to that of **1a**. The bands of **1c** and **1d** in the region of 300–340 nm are assigned to the substituted phenyl ring



**Fig. 1.** Electronic spectra of **1** and **3** in chloroform. The curves of **1a**, **1b**, **1c** and **1d** are displaced upward by 1, 2, 3 and 4, respectively.

bathochromically shifted, because **4c** and **4d** have bands in the 280–320 nm region, not present for **4a** and **4b**. Such characteristic features of these cyclophanes support the layered structure.<sup>11</sup> These features are due to the transannular  $\pi$ -electron effect and to the lack of planarity of the aromatic rings.<sup>11</sup>

The ratios of molar absorbance coefficient of the peak top to that of the peak bottom ( $\varepsilon(\lambda_2)/\varepsilon(\lambda_4)$ ,  $\varepsilon(\lambda_3)/\varepsilon(\lambda_4)$ ) were employed in the index of the

**TABLE 1**  
Electronic Spectra of **1** and **3** in Chloroform

Compound	$\lambda_1$ (nm) <sup>a</sup>	$\lambda_2$ (nm)	$\lambda_3$ (nm)	$\varepsilon(\lambda_2)/\varepsilon(\lambda_4)^b$	$\varepsilon(\lambda_3)/\varepsilon(\lambda_4)$
<b>1a</b>	280	394.2	415.6	1.19	1.12
<b>1b</b>	283	393.0	413.3	1.10	1.07
<b>1c</b>	280	398.1	419.2	1.08	1.08
<b>1d</b>	~280 (sh)	390.3	408.9	1.03	1.07
<b>3</b>	260	373.5	394.5	3.19	3.21

<sup>a</sup>  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are the wavelengths at peak tops and  $\lambda_4$  is that at a peak bottom as shown in Fig. 1.

<sup>b</sup>  $\varepsilon(\lambda)$  is the molar absorbance coefficient at wavelength  $\lambda$ .

broadening. The extent of the broadening increased in the order of **3**  $\ll$  **1a** < **1b**, **1c** < **1d**. Such an order in **1a–1d** will reflect the difference of the extent of the transannular effect and/or the ring distortion. This order, interestingly, agreed with that of the reactivities of **1** described later. Such an agreement is also known in the other anthracenoparacyclophanes<sup>4,5</sup> and anthracenophanes.<sup>8</sup>

### 3.2 NMR spectra

NMR spectra of **1b**, **1c** and **1d** were complicated because of their unsymmetrical structure. All signals, therefore, were fully assigned in conjunction with HH-COSY and NOESY spectra. Table 2 shows the NMR spectral data of **1b**, **1c** and **1d** together with those of **1a** and acyclic compounds.

A characteristic feature of a layered cyclophane is an upfield shift due to the anisotropic effect of a faced aromatic ring.<sup>12</sup> The phenyl protons  $a_1$ ,  $a_2$  and  $a_3$  of **1b** and **1c** absorb at 1.2–1.5 ppm higher fields than the corresponding protons of the acyclic compounds **5b** and **5c**, similar to proton  $a$  of **1a**, which does so by 1.37 ppm relative to that of **5a**. The phenyl protons of **1d** also absorb at the higher fields by 1.3–1.6 ppm than those of **4d**, instead of **5d**. These results support the layered structures. On the other hand, protons  $b$ ,  $c$ ,  $d$  and  $e$  absorb at similar fields to the corresponding protons of **5a**, **5b**, **5c** and **3** because these protons are not situated just above the faced ring.

### 3.3 Photochromic behaviour

#### 3.3.1 Photoproduct

No band of the anthracene ring (320–450 nm) was observed in the electronic spectra of the photoproducts of **1b**, **1c** and **1d**. In addition, on the basis of the following IR, [<sup>1</sup>H] NMR and MS spectral data, these photoproducts were identified as (4  $\pi$  + 4  $\pi$ ) intramolecular cycloadducts (**2b**, **2c** and **2d**) similarly to the photoproduct of **1a**.

##### **2b**

IR(KBr)  $\text{cm}^{-1}$ : 1700(C=O, s), 1470(m), 1139(s).

[<sup>1</sup>H] NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.85(2H, s,  $\text{CH}_2$ ), 4.15, 4.71, 4.71(6H, 3ABq,  $\text{CH}_2$ ), 5.62(2H, s,  $\text{CH}=\text{CH}$ ), 5.67(1H, s,  $\text{CH}=\text{C}$ ), 7.2–7.5 (8H, m, benzene ring).

MS: 564( $\text{M}^+$ ).

##### **2c**

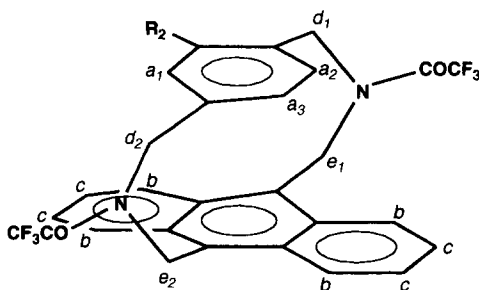
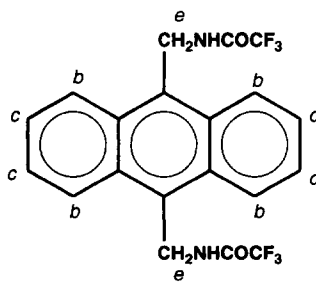
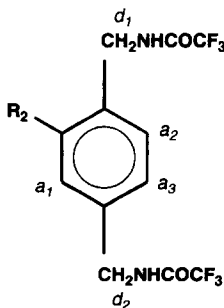
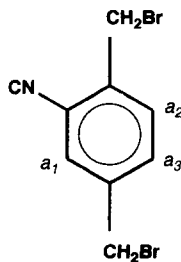
IR(KBr)  $\text{cm}^{-1}$ : 1690(C=O, s), 1468(m), 1135(s).

[<sup>1</sup>H] NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.90(3H, s,  $\text{OCH}_3$ ), 3.81, 4.03, 4.69, 4.69(8H, 4ABq,  $\text{CH}_2$ ), 5.49, 5.69(2H, AB,  $\text{CH}=\text{CH}$ ), 4.17(1H, s,  $\text{CH}=\text{C}$ ), 7.2–7.5 (8H, m, benzene ring).

MS: 560( $\text{M}^+$ ).

**TABLE 2**  
 $^1\text{H}$  NMR Spectra ( $\delta$  Value) of **1** and Acrylic Compounds in  $\text{CDCl}_3$

$R_2$	<b>1a</b> <i>H</i>	<b>1b</b> <i>Cl</i>	<b>1c</b> <i>OCH<sub>3</sub></i>	<b>1d</b> <i>CN</i>	<b>5a</b> <i>H</i>	<b>5b</b> <i>Cl</i>	<b>5c</b> <i>OCH<sub>3</sub></i>	<b>4d</b> <i>CN</i>	<b>3</b>
a	$a_1$	6.20 (s)	5.49 (s)	6.43 (s)		7.36 (s)	6.85 (s)	7.69 (d)	
	$a_2$	5.95 (s)	5.90 (d)	5.94 (d)	5.99 (s)	7.32 (s)	7.40 (d)	7.27 (d)	7.54 (d)
	$a_3$		5.68 (d)	5.48 (d)	5.99 (s)		7.21 (d)	6.87 (d)	7.61 (q)
b	8.30– 8.33 (m)	8.26– 8.44 (m)	8.25– 8.37 (m)	8.30– 8.52 (m)					8.32– 8.34 (m)
c	7.61– 7.64 (m)	7.55– 7.69 (m)	7.51– 7.65 (m)	7.67– 7.78 (m)					7.69– 7.71 (m)
d	$d_1$		4.74	4.59	4.84				
	$d_2$	4.52 (s)	(ABq)	(ABq)	(ABq)	4.54 (d)	4.62 (d)	4.51 (d)	
			4.51	4.49	4.58		4.52 (d)	4.52 (d)	
e	$e_1$		5.95	5.85	5.97				
	$e_2$	5.88 (s)	(AXq)	(AXq)	(AXq)				5.60 (d)
			5.90	5.90	5.90				
			(ABq)	(ABq)	(AXq)				

**1****3****5****4d**



**2d**

IR(KBr)  $\text{cm}^{-1}$ : 2224(CN, w), 1691–1703(C=O, s), 1476(m), 1136(s).

[ $^1\text{H}$ ] NMR ( $\text{CDCl}_3$ ):  $\delta$  = 3.92, 4.15, 4.74, 4.76 (8H, 4ABq,  $\text{CH}_2$ ), 5.59, 5.68(2H, AB,  $\text{CH}=\text{CH}$ ), 6.52(1H, s,  $\text{CH}=\text{C}$ ), 7.2–7.5 (8H, m, benzene ring).

MS: 555( $\text{M}^+$ ).

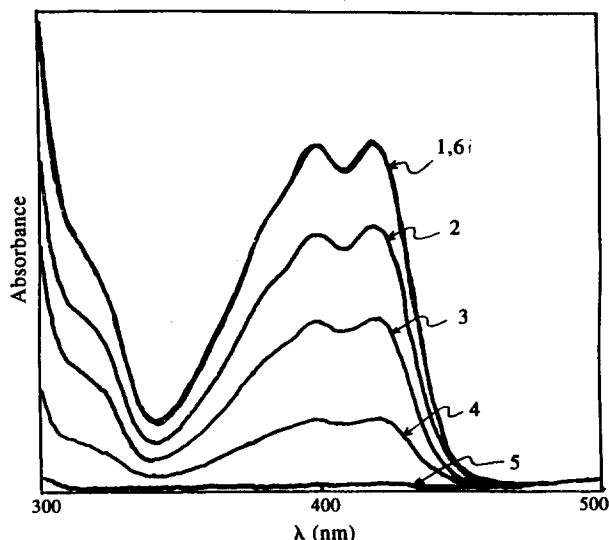
Other minor peaks of the conformational isomer due to the restricted rotation of the amide bond were observed in the NMR spectra of **2b–2d**. These peaks have also been observed in *N,N'*-diformyl-diazaanthracenoparacyclophane (**1**, where  $\text{R}_1 = \text{CHO}$  and  $\text{R}_2 = \text{H}$ ).<sup>4</sup>

**3.3.2 Reproducibility**

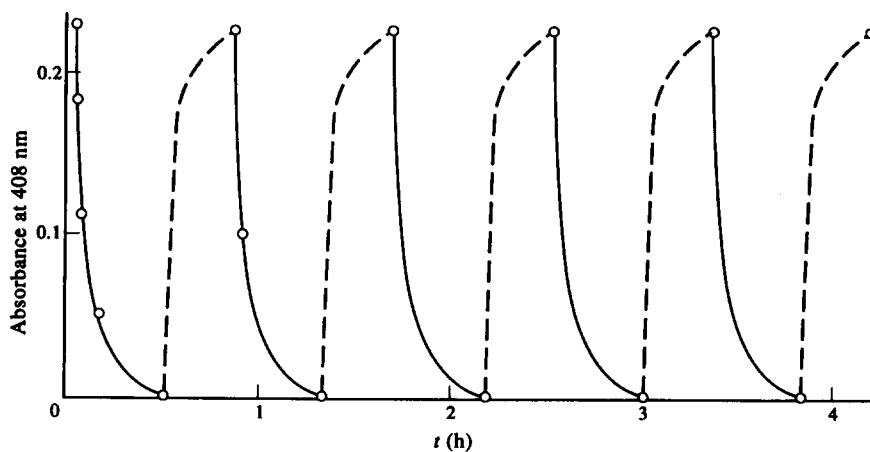
Compounds **1b**, **1c** and **1d** exhibited good reproducibilities after several ring closure-opening cycles. For example, Fig. 2 shows the electronic spectral changes of **1c** on photoirradiation and heating. Spectrum No. 6 for material recovered by heating, corresponds completely to the initial spectrum No. 1. Figure 3 shows the good reproducibility of the absorbance changes of **1d**. Figure 4 shows the reproducible IR spectral changes of **1b**, and the spectrum after four cycles is identical to that of the initial one.

**3.3.3 Kinetics of photocycloaddition and thermal reversion**

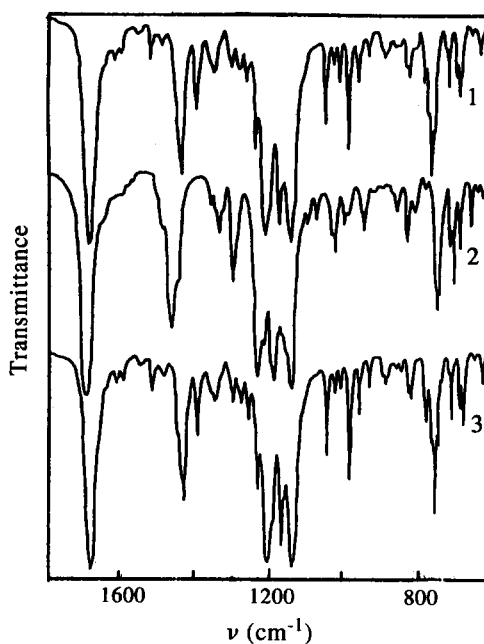
Table 3 shows the quantum yields ( $\Phi_r$ ) of photocycloaddition and the rate constants ( $k$ ) of the thermal reversion of **1b**, **1c** and **1d**, together with those of five derivatives<sup>5</sup> having various substituents ( $\text{R}_1$ ) on the bridged chains



**Fig. 2.** Electronic spectral changes of **1c** in chloroform on irradiation at 419 nm, followed by heating at 150°C in the solid state. 1, 2, 3, 4 and 5: Irradiated for 0, 1, 3, 10 and 30 min, respectively. 6: Heated for 20 min at 150°C.



**Fig. 3.** Reproducibility of absorbance changes of **1d** at 408 nm in chloroform (—) on irradiation at 408 nm, followed by (---) heating at 150°C in solid state.



**Fig. 4.** IR spectral changes of **1b** in a KBr pellet on irradiation ( $\lambda > 340$  nm), followed by heating at 150°C. (1): Initial compound (2): Irradiated compound (3): After irr.-heating procedure was repeated four times

**TABLE 3**  
Photo- and Thermochemical Reactivities

Compound	$R_1$	$R_2$	Quantum yield of photocycloaddition in chloroform <sup>a</sup>			Rate const. of thermal reversion in xylene at 70°C $k/10^{-6} \text{ s}^{-1}$	Ref. <sup>b</sup>
			$\Phi_r^{\text{N}_2}$	$\Phi_r^{\text{air}}$	$\Phi_r^{\text{O}_2}$		
	CHO	H	0.0076	0.0049	0.0019	200	a
	COCH <sub>3</sub>	H	0.18	0.13	0.062	5.7	a
	CO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	0.20	0.14	0.072	4.3	a
<b>1a</b>	COCF <sub>3</sub>	H	0.25	0.21	0.13	3.0	a, b
	COC(CH <sub>3</sub> ) <sub>3</sub>	H	0.46	0.46	0.39	0.35	a
<b>1b</b>	COCF <sub>3</sub>	Cl	0.49	0.47	0.46	3.8	b
<b>1c</b>	COCF <sub>3</sub>	OCH <sub>3</sub>	0.56	0.56	0.55	5.5	b
<b>1d</b>	COCF <sub>3</sub>	CN	0.61	0.59	0.59	7.2	b

<sup>a</sup>  $\Phi_r^{\text{N}_2}$ ,  $\Phi_r^{\text{air}}$ , and  $\Phi_r^{\text{O}_2}$  are the quantum yields of photocycloaddition under a nitrogen, air, and oxygen atmosphere, respectively.

<sup>b</sup> a: Ref. 5.

b: This work.

and no substituent ( $R_2 = \text{H}$ ) on a phenyl ring. As described in a previous paper,<sup>5</sup> the quantum yields  $\Phi_r$  increased and the rate constants  $k$  decreased with increasing bulkiness of the  $R_1$  substituent. This reaction mechanism was interpreted in terms of steric effects, viz., decrease of the C—N—C bond angle by bulky substituents facilitates the face-to-face orientation of the two aromatic rings and increases the strain of **1**. Consequently, the photocycloaddition is accelerated and the thermal reversion is depressed.

On the other hand, the  $R_2$  substituent effect evaluated in this present work is as follows: the quantum yields under a nitrogen atmosphere for **1b**, **1c** and **1d** are nearly twice as large as that of **1a**, and increase in the order **1a** < **1b** ≤ **1c** ≤ **1d**, similarly to that of the broadening in the electronic spectra. This similarity implies that the reactivities of **1** are related to electronic interaction between aromatic rings and/or molecular strain.

These photocycloadditions are scarcely affected by oxygen, suggesting that the lifetime of the excited state of the photoreaction is remarkably short. Such a short lifetime can be accounted for by fast decay through the cycloaddition pathway.

The rate constants of the thermal reversion of **1b**, **1c** and **1d** are greater than that of **1a**, and increase in the order **1a** < **1b** < **1c** < **1d**. This order agrees with that of the photocycloaddition.

As described above,  $R_2$  substituents on a phenyl ring, which accelerate both the photocycloaddition and the thermal reversion, are in contrast to  $R_1$  substituents on the bridged chains. The  $R_2$  substituent may bring about an electronic effect because of direct substitution into a phenyl ring, different

from an  $R_1$  substituent which is unconjugated with the aromatic rings. Furthermore, the  $R_2$  substituent may also bring about a steric effect, because it is located near the reaction centre and causes molecular strain. The effects of substituents on the aromatic ring on the ring closure-opening reaction have not been reported yet for paracyclophane-type compounds. However, these effects are known in methacyclophanes,<sup>13,14</sup> and the effects of a substituent at the reaction centre were interpreted in terms of steric effects, viz., acceleration of the reaction by the release of molecular strain. However, with the reactions of **1a–1d**, it is difficult to interpret their reactivities solely from a similar steric effect, because  $R_2$  substituents accelerate both the photoreaction and the thermal reversion.

These different effects between  $R_1$  and  $R_2$  substituents can therefore be utilised in the design of photochromic compounds having different reactivities.

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