The Preparation of Crown Ethers Containing Dicinnamoyl Groups and Their Complexing Abilities

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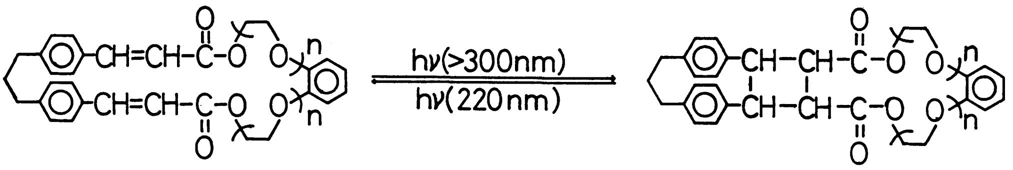
The reaction of 1, 10-bis[*p*-[2-(chloroformyl)vinyl]phenyl]-1,4,7,10-tetraoxadecane with the dipotassium salt of catechol in the presence of a catalytic amount of 18-crown-6 in benzene gave 5,6-benzo-4,7,17,20,23,29-hexaoxa[10.10]paracyclopha-1,5,9-triene-3,8-dione (**10a**) in 3.6% yield. Also, 24,25-benzo-1,4,7,10,13,23,26-heptaoxa[13.10]paracyclopha-20,24,28-triene-22,27-dione (**10b**) and 27,28-benzo-1,4,7,10,13,16,26,29-octaoxa-[16.10]paracyclopha-23,27,31-triene-25,30-dione (**10c**) were obtained by the same method in 3.1 and 3.0% yields, respectively. Irradiation of the acetonitrile solutions of the crown ethers, **10a**, **10b** and **10c**, by Pyrex-filtered UV light (>300 nm) gave the corresponding intramolecular [2+2]photocycloadducts, **11a**, **11b** and **11c**, in 95.8, 93.2 and 90.1% yields, respectively. The structures of **11a**, **11b** and **11c** were confirmed to be the β-form by their ^{1}H NMR spectra. The photoreversible cleavage of **11a**, **11b** and **11c** by 220 nm UV light gave the corresponding starting crown ethers, **10a**, **10b** and **10c**, in 30, 40 and 61% yields, together with their geometrical isomers in 30, 50 and 27% yields, respectively. Compound **10c** showed selective extraction abilities for K^+ and Rb^+ cations compared with **11c**.

While investigations of the crown ethers and their cation and/or anion complexes have been steadily gaining interest over the past two decades, most attention has so far been focused on the synthesis of a new type of ligand.[1] Recently, several kinds of photoresponsive crown ethers have been reported by several research groups.[2-4] For example, Shinkai et al. reported the controlling the complexing abilities of benzocrown ethers containing the azo group for alkali metal cations by UV light irradiation.[2] Furthermore, Mizuno et al. obtained cyclobutanocrown ethers (cyclobutacrown ethers) by intramolecular photocycloaddition of the bis(vinyloxy) compounds using a sensitizer.[5] The preparation of polymers having both a crown ether moiety as the cation binding site and a cinnamic acid ester moiety as the photodimerizable pendant group has been reported by Shirai et al.,[6] Hiratani,[7] and Kimura et al.[8] They also reported preparation of the dicinnamates of the polyethylene glycol derivatives. In connection with the abovementioned results, we have reported[9-12] on the synthesis of cyclobutacrown ethers such as **2**, **3** and **4** by the intramolecular [2+2]photocycloaddition of α,ω-dicinnamoyl polyethylene glycol derivatives and/or the corresponding crown ethers containing two cinnamoyl groups, and their properties.

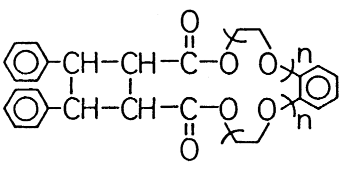
Results and Discussion

Synthesis. *p*-Hydroxycinnamic acid (**6**) was obtained in 32% yield by the reaction of *p*-hydroxybenzaldehyde (**5**) with malonic acid according to methods described in the literature.[13] The reaction of **6** with 1,8-dibromo-3,6-dioxaoctane (**7a**) in 70% ethanol gave 1,10-bis[*p*-(2-carboxyvinyl)phenyl]-1,4,7,10-tetraoxadecane (**8a**) in 23.0% yield. Also, **8b** and **8c** were obtained in 10.1 and 10.2% yields, respectively. The carboxyl



1a: n=0
1b: n=1
1c: n=2

2a: n=0
2b: n=1
2c: n=2



3a: n=0
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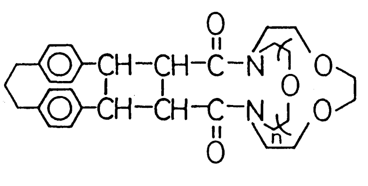


4a: n=1
4b: n=2

groups of **8a**—**8c** were chlorinated with thionyl chloride and used for the next reaction without further purification. Condensation of 1,10-bis[*p*-[2-(chloroformyl)vinyl]phenyl]-1,4,7,10-tetraoxadecane (**9a**) with the dipotassium salt of catechol in benzene in the presence of 18-crown-6 gave 5,6-benzo-4,7,17,20,23,29-hexaoxa[10.10]paracyclopha-1,5,9-triene-3,8-dione (**10a**) in 3.6% yield. Also, **10b** and **10c** were obtained in 3.1 and 3.0% yields, respectively. The structures of these products were established by their elemental analyses, mass spectral and ^{1}H NMR spectral data. As shown in Fig. 1, the ^{1}H NMR spectrum of **10b** showed the signals of the olefinic protons as a pair in the A_2B_2 pattern at $\delta=7.74$ (d, $J=15.9$ Hz, 2H) and 6.38 (d, $J=15.9$ Hz, 2H), the signals of the *p*-phenylene protons as a pair in the A_2B_2 pattern at $\delta=7.24$ (d, $J=8.7$ Hz, 4H) and 6.71 (d, $J=8.7$ Hz, 4H), the signal of the methylene protons as a multiplet at $\delta=3.75$—3.67 (8H), the signals of the *o*-phenylene protons as a pair in the A_2B_2 pattern at $\delta=7.39$—7.36 (m, 2H) and 7.32—7.29 (m, 2H) together with the signals of the methylene protons as a pair in the A_2B_2 pattern at $\delta=4.09$ (t, $J=4.7$ Hz, 2H) and 3.89 (t, $J=4.7$ Hz, 2H).

Intramolecular [2+2]Photocycloaddition of 10. Intramolecular [2+2]photocycloaddition of **10** was carried out according to a method as described in previous papers.[9–12] For example, irradiation of **10b** in acetonitrile for 2.0 h under nitrogen (Pyrex filter with a 450 W high-pressure mercury lamp) in the absence of any sensitizer gives the corresponding cyclobutacrown ether (**11b**) in 93.2% yield, as shown in Fig. 2. Also, **11a** and **11c** were obtained by the same method in 95.8 and 90.1% yields, respectively. As shown in Fig. 2, the rate of the ring closure reaction of **10** to **11** is in the order (half-life time): **10a**(99s) >**10b**(176s)>**10c**(179s). In this intramolecular [2+2]-photocycloaddition, no formation of by-products could be observed, although in case of **1** very tiny side reaction products were observed by means of TLC.[10] The respective configuration of the photoadducts (**11a**—**11c**) were elucidated by a comparative ^{1}H NMR study of **11a**—**11c** and the intramolecular [2+2]-photoadduct (**2b**) of 8,9-benzo-4,7,10,13-tetraoxa[16.3]-paracyclopha-1,8,15-triene-3,14-dione (**1b**), as described in a previous paper.[10] As shown in Fig. 1, the ^{1}H NMR spectrum of **11b** showed signals of the *p*-

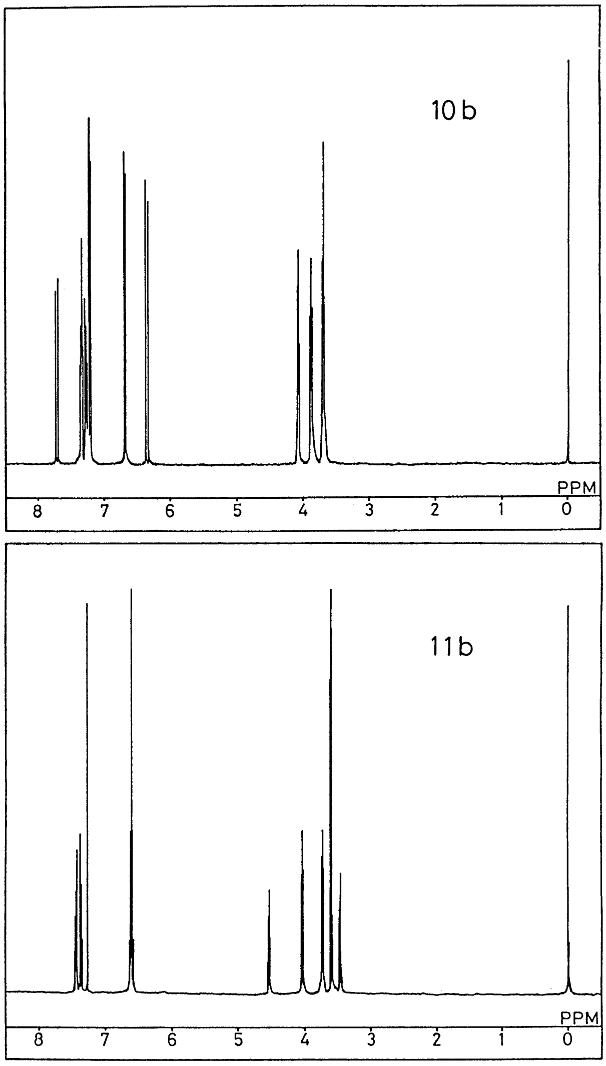
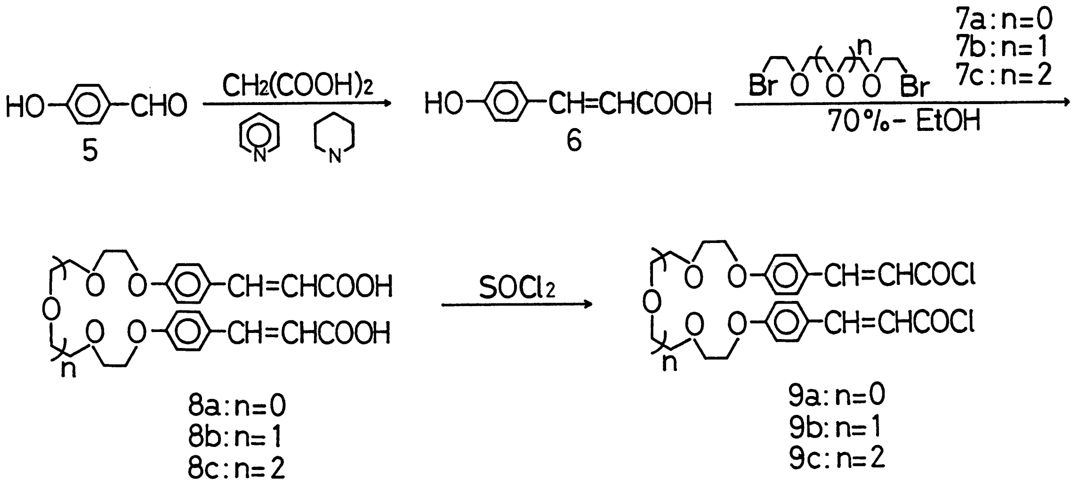
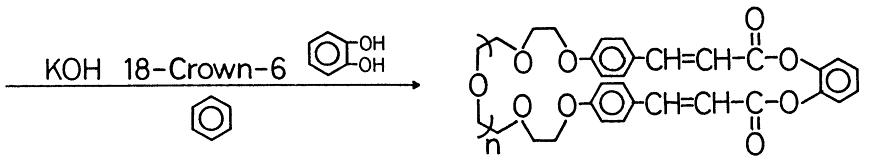
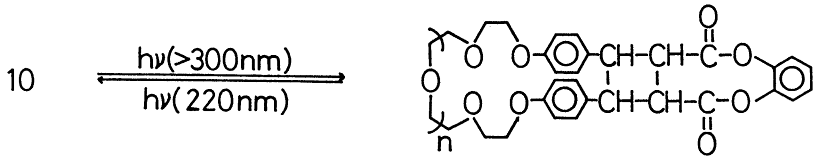


Fig. 1. 400 MHz ^{1}H NMR spectra of **10b** and **11b**.





10a: n=0
10b: n=1
10c: n=2



11a: n=0
11b: n=1
11c: n=2

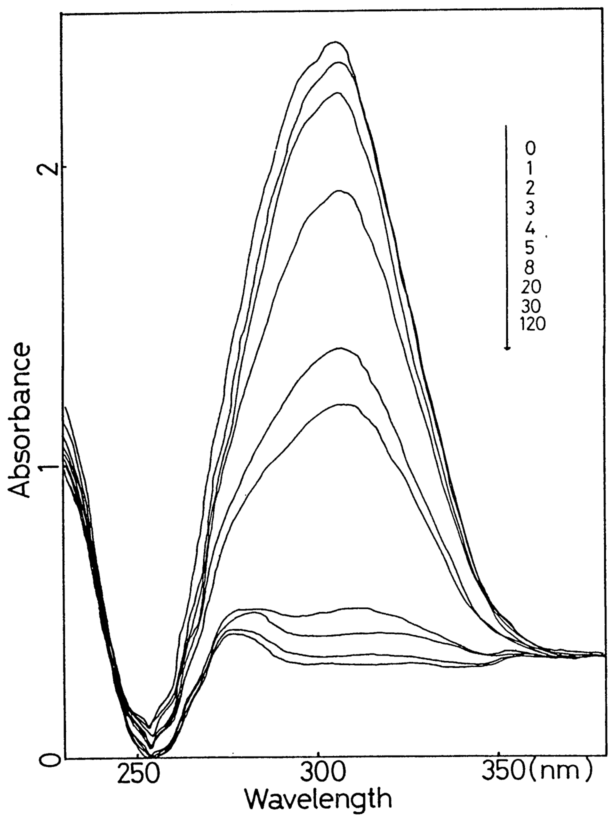


Fig. 2. Spectral changes of **10b** to **11b** in acetonitrile (4×10^{-5} M). The numbers beside the arrow are the elapse of irradiation time (min).

phenylene protons, as in the pair of the A_2B_2 pattern at δ=6.62—6.56 (m, 8H), the signals of *o*-phenylene protons at δ=7.44—7.34 (m, 4H), the signals of the methylene protons as in the pair of A_2B_2 pattern at δ=4.02 (t, J=4.4 Hz, 4H) and 3.72 (t, J=4.4 Hz, 4H) and the signal of the methylene protons as in the singlet at δ=3.58 (s, 8H) together with the methine protons in AA′BB′ pattern at δ=4.53—4.51 (m, 2H) and 3.46—3.45 (m, 2H). The aromatic protons of the *p*-phenylene groups shifted upfield (ca. 0.1—0.6 ppm) compared with those of the starting materials (**10b**). Furthermore, the split patterns and the chemical shifts of the methine protons of the cyclobutane ring are consistent with those of the β-isomer of **2b**,[10] the structures of which were confirmed by X-ray analysis. Therefore, the configuration of the cyclobutane ring of **11b** must be β-isomer. Similarly, the ^{1}H NMR spectra of **11a** and **11c** suggest that their cyclobutane rings also take the β-isomer configuration.

Photoreversible Cleavage of 11. Photoreversible cleavage of **11b** to **10b** in acetonitrile with 200—250 nm (10 nm interval) of UV light was investigated. As shown in Fig. 3, the rate of cleavage of the cyclobutane ring of **11b** to **10b** by UV light is in the order: 220>230>240>250>210>200 nm. Therefore, an acetonitrile solution of **11** was irradiated with 220 nm UV light in the following photocleavage reaction. As

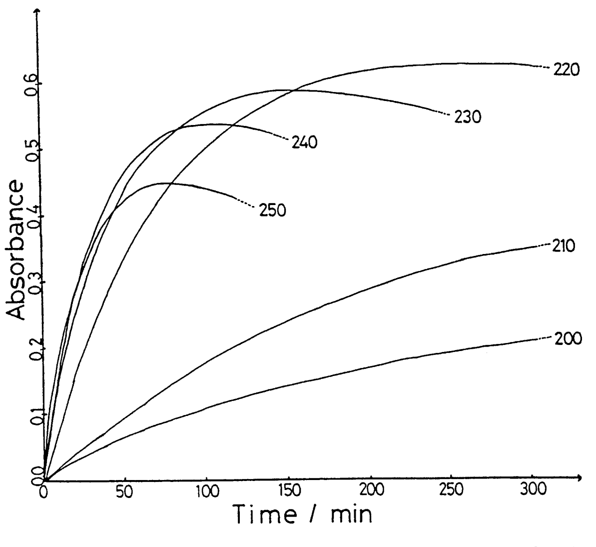


Fig. 3. The rate cleavage of cyclobutane ring of **11b** to **10b** by UV lights (200—250 nm: 10 nm interval).

shown in Fig. 4, the absorption band (308.5 nm) of **11b** (4.0×10^{-5} M) in acetonitrile increased with UV irradiation (M=mol dm^{-3}). The UV spectral change of **11a**, **11b** and **11c** (2.0×10^{-2} M) in acetonitrile attaining a steady state after, 60, 140 and 170 h, respectively. The irradiation of the acetonitrile solution of **11a** (2.0×10^{-2} M) gave **10a** and **10a′** (photoisomerized product of **10a**) in 30% yields, respectively, together with a starting material (**11a**) in 40% yield. Irradiation of **11b** and **11c** was carried out by the same method, producing **10b** and **10c** in 40 and 61% yields, respectively, together with **10b′** and **10c′** in 50 and 27% yields, respectively. Also, in the above-mentioned photoreactions the starting materials, **11b** and **11c**, were recovered in 10 and 12% yields, respectively. The structures of **10a′**—**10c′** were confirmed by elemental analysis, as well as mass and ^{1}H NMR spectral data. For example, in the ^{1}H NMR spectrum of **10b′**, the olefinic protons showed two sets of signals in the A_2B_2 pattern at δ=6.85 (d, J=13.2 Hz, 1H) and 6.03 (d, J=13.2 Hz, 1H), and at δ=7.62 (d, J=15.9 Hz, 1H) and 6.21 (d, J=15.9 Hz, 1H) due to the *cis* and *trans* C=C double bonds. The two kind of *p*-phenylene protons attached to *cis* and *trans* moieties of the C=C double bonds showed two sets of signals in A_2B_2 pattern at δ=7.87 (d, J=8.9 Hz, 2H) and 6.75 (d, J=8.9 Hz, 2H), and at δ=7.08 (d, J=8.7 Hz, 2H) and 6. 81 (d, J=8.7 Hz, 2H). As is shown in Fig. 5, no photocleavage (fashion B) of the cyclobutane ring of **11** with 220 nm UV light occurred, although the cleavage (fashion A) of the C-C bonds in the cyclobutane ring of **2a** and **2b** with 220 nm UV light occurred together with the cleavage (fashion B) of the C-C bonds.[10] However, in the case of **11**, the photoisomerized isomer (**10′**) of **10** was obtained in relatively high yield. The results suggest that irradiation of the cyclobutacrown ether (**11**) with 220 nm UV light first gave the corresponding open-ring crown ether (**10**); then, **10** was isomerized to **10′**, because irradiation of an acetonitrile solution of **10** with 220 nm UV light gave the corresponding **10′**.

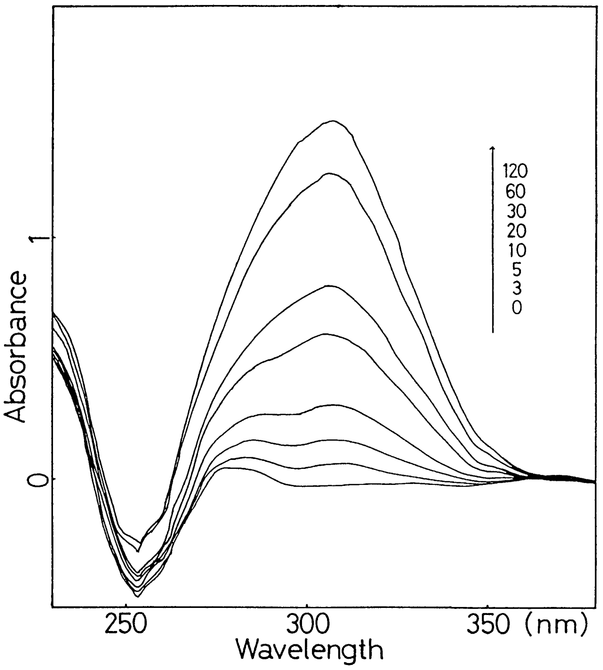


Fig. 4. Spectral changes of **11b** to **10b** in acetonitrile (4×10^{-5} M). The numbers beside the arrow are the elapse of irradiation time (min).

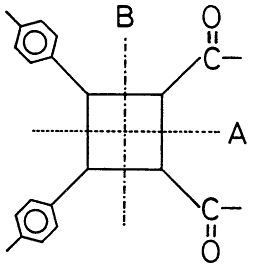


Fig. 5.

Extraction Abilities of 10 and 11. Measurement of the extraction abilities of **10** and **11** toward alkali and alkaline earth metal cations was carried out by a method described in a previous paper.[9,10] These results are summarized in Table 1, along with those of the benzocrown ethers. The extraction abilities of the crown ethers (**10a**, **10b**, **11a**, **11b**, and **11c**) were low in value, a tendency similar to that of **1** and **2**.[10] However, the present crown ethers showed relatively higher extraction abilities toward both alkali and alkaline earth metal cations compared with those of **1** and **2**, due to an absence of the ester moiety in the crown ether part. The most significant finding is the selective extraction abilities of **10c**, which contain six oxygen atoms, toward K^+ and Rb^+ cations. The corresponding cyclobutacrown ether (**11c**), however, showed low extraction abilities and no selectivity. The significant abilities of **10c** toward K^+ and Rb^+ cations may be attributed to the flexibility of the large crown ether moiety which can take a conformation favoring complexation. These results are consistent with those for benzo-18-crown-6, although **10c** showed lower extraction abilities for K^+ and Rb^+ cations

Table 1. Percentage of Metal Picrates Extracted from the Aqueous to Organic Phase[a)]

Compd	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
10a	3	3	4	4	4	4	4	4	4
11a	5	5	5	4	4	5	4	3	3
10b	4	4	4	5	5	5	5	5	4
11b	7	6	6	6	7	6	5	5	4
10c	6	8	33	30	19	5	5	8	5
11c	6	7	9	9	9	5	5	5	4
B15C5	3	10	17	10	4	1	1	0	0
B18C6	3	8	55	46	33	0	1	7	0

a) Solvent: water and dichloromethane (1 : 1). Concentration of crown ether: 7.0×10^{-4} M. Concentration of picric acid: 7.0×10^{-5} M. Concentration of metal nitrate: 1.0×10^{-1} M.

compared with those of 18-crown-6. Therefore, the conformation and shape of the crown ether moiety of **10c** in solution may be similar to those of benzo-18-crown-6. In contrast, the distance between the two ether oxygen atoms attached to the benzene rings of **11c** is further than that in **10c** due to an intramolecular [2+2]photocycloaddition of **10c** to **11c**. Therefore, the hole shape of the crown ether moiety of **11c** is deformed and can not adapt to incorporate the guest cation.

Experimental

All melting points are uncorrected. The IR spectra were measured on a JASCO IRA-2 diffraction grating infrared spectrometer. UV spectral data were obtained on a Hitachi 330 spectrometer and ^{1}H NMR spectra were obtained on JEOL GX400 and JEOL FX-90Q spectrometers with SiMe$_4$ as an internal standard. Mass spectra were taken on a Hitachi M80 spectrometer. For irradiation of 10 on a preparative scale, the solution was internally irradiated with an USIO high-pressure mercury lamp(HPL)(UM-452). The photocleavage of **11** to **10** was also carried out by means of 200—250 nm UV light using a grating monochromater (Model JASCO CT-10), with a 500 W xenon lamp (JASCO PS-X500) and a band width of 0.5 nm.

Solvent Extraction. Measurement of the extraction ability was carried out by a method described in a previous paper.[12]

Materials. Solvents were dried by appropriate methods and then purified by distillation under nitrogen. Other reagents employed were either commercial or prepared by the usual method. Benzo-18-crown-6 and benzo-15-crown-5 were also prepared by a method described in the literature.[14]

***p*-Hydroxycinnamic Acid (6).** A mixture of *p*-hydroxybenzaldehyde (100 g, 0.82 mol), malonic acid (128 g, 1.23 mol) and piperidine (15 cm^3) in dry pyridine (400 cm^3) was heated for 7 h at 100 °C. The mixture was cooled to room temperature and then poured into an ice-water containing concd hydrochloric acid. The resulting precipitate was filtered off and then resolved into aqueous sodium hydroxide solution. The insoluble material was removed by filtration. The filtrate was acidified with concd hydrochloric acid and the resulting precipitate was collected by filtration. The solid was recrystallized from water to give **6** in 32.1% yield as flesh colored crystals. Mp 215.0—217.0 °C (lit.[13] 207.0 °C).

1,13-Bis[*p*-(2-carboxyvinyl)phenyl]-1,4,7,10,13-pentaoxatridecane (8b). To a refluxing mixture of **6** (30.0 g, 183 mmol) and sodium hydroxide (14.7 g, 368 mol) in 70% aqueous ethanol **7b** (58.2 g, 182 mmol) was added dropwise for 1 h, after which refluxing was continued for 24 h; sodium hydroxide (22.0 g, 550 mmol) in water (50 cm^3) was then added and refluxed for 2 h. The mixture was concentrated in vacuo. After the concentrated solution was acidified with concd hydrochloric acid, the resulting precipitate was collected by filtration and resolved in hot chloroform. The insoluble solid was collected by filtration and then recrystallized from ethanol to give **8b** in 10.1% yield, mp 185.0—187.0 °C. Found: C, 63.90; H, 6.03%. Calcd for $C_{26}H_{30}O_9$; C, 64.19; H, 6.22%. MS (70 eV): m/z 486 (M$^+$). ^{1}H NMR (DMSO-d_6) δ=7.68 (d, J=9.0 Hz, 4H), 7.62 (d, J=16.2 Hz, 2H), 7.03 (d, J=9.0 Hz, 4H), 6.41 (d, J=16.2 Hz, 2H), 4.21 (t, J=4.8 Hz, 4H), 3.83 (t, J=4.8 Hz, 4H), 3.65 (s, 8H).

8a and **8c** were also obtained by a method similar to that described above.

1,10-Bis[*p*-(2-carboxyvinyl)phenyl]-1,4,7,10-tetraoxadecane (8a). Yield 23.0%, mp 224.0—226.0 °C. Found: C, 64.05; H, 6.06%. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.94%. MS (70 eV): m/z 442 (M$^+$). ^{1}H NMR (DMSO-d_6): δ=7.74 (d, J=8.8 Hz, 4H), 7.66 (d, J=16.3 Hz, 2H), 7.08 (d, J=8.8 Hz, 4H), 6.48 (d, J=16.3 Hz, 2H), 4.25 (t, J=4.8 Hz, 4H), 3.86 (t, J=4.8 Hz, 4H), 3.73 (s, 4H).

1,16-Bis[*p*-(2-carboxyvinyl)phenyl]-1,4,7,10,13,16-hexaoxahexadecane (8c). Yield 10.2%. Mp. 187.0—189.0 °C. Found: C, 62.87; H, 6.45%. Calcd for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46%. MS (70 eV): m/z 530 (M$^+$). ^{1}H NMR (DMSO-d_6): δ=7.71 (d, J=9.0 Hz, 4H), 7.65 (d, J=16.2 Hz, 2H), 7.06 (d, J=9.0 Hz, 4H), 6.43 (d, J=16.2 Hz, 2H), 4.25 (t, J=4.8 Hz, 2H), 3.85 (t, J=4.8 Hz, 2H), 3.65 (s, 12H).

1,13-Bis[*p*-[2-(chloroformyl)vinyl]phenyl]-1,4,7,10,13-pentaoxatridecane (9b). A mixture of thionyl cloride (65 cm^3) and **8b** (4.47 g, 9.19 mmol) was stirred for 5 h at 35 °C. The excess thionyl chloride was removed under reduced pressure and the residual solid used for the next reaction without further purification.

Compounds **9a** and **9c** were also obtained by a method similar to that described above and used for the next reaction without purification .

24,25-Benzo-1,4,7,10,13,23,26-heptaoxa[13.10]paracyclopha-20,24,28-triene-22,27-dione (10b). Compound **9b** (26.0 g,49.7 mmol) in benzene (150 cm^3) and catechol (5.46 g, 49.6 mmol) in benzene (150 cm^3) were added to a benzene solution (300 cm^3) containing potassium hydroxide (5.57 g, 99.3 mmol) and 18-crown-6 (catalytic amount) at the same rate over a period of 5 h and then refluxed further for 72 h. The reaction mixture was filtered and evaporated, and the residue was extracted with chloroform. The extract was washed with water, dried, and evaporated in vacuo. The residue was chromatographed on alumina using chloroform as the eluent. The second fraction was collected and concentrated. The recrystallization of the residual oil from benzene-hexane gave **10b** in 3.1% yield as colorless needles, mp 132.0—133.5 °C. Found: C, 68.61; H, 5.86%. Calcd for $C_{32}H_{32}O_9$: C, 68.56; H, 5.75%. MS (70 eV): m/z 560 (M$^+$). ^{1}H NMR (CDCl$_3$): δ=7.74 (d, J=15.9 Hz, 2H), 7.39—7.36 (m, 2H), 7.32—7.29 (m, 2H), 7.24 (d, J=8.7 Hz, 4H), 6.71 (d, J=8.7 Hz, 4H), 6.38 (d, J=15.9 Hz, 2H), 4.09 (t, J=4.7 Hz, 4H), 3.89 (t, J=4.7 Hz, 4H), 3.75—3.67 (m, 8H).

Compounds **10a** and **10c** were obtained by a method similar to that described above.

5,6-Benzo-4,7,17,20,23,29-hexaoxa[10.10]paracyclopha-1,5,9-triene-3,8-dione (10a). Yield 3.6%, mp 167.5—168.5 °C. Found: C, 69.73; H, 5.51%. Calcd for $C_{30}H_{28}O_8$: C, 69.76; H, 5.46%. MS (70 eV): m/z 516 (M$^+$). ^{1}H NMR (CDCl$_3$): δ=7.71 (d, J=16.0 Hz, 2H), 7.37—7.34 (m, 2H), 7.32—7.29 (m, 2H), 7.18 (d, J=8.7 Hz, 4H), 6.67 (d, J=8.7 Hz, 4H), 6.35 (d, J=16.0 Hz, 2H), 4.09 (t, J=4.8 Hz, 4H), 3.87 (t, J=4.8 Hz, 4H), 3.75 (s, 4H).

27,28-Benzo-1,4,7,10,13,16,26,29-octaoxa[16.10]paracyclopha-23,27,31-triene-25,30-dione (10c). Yield 3.0%, mp 113.0—114.0 °C. Found: C, 67.63; H, 6.19%. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54; H, 6.00%. MS (70 eV): m/z 604 (M$^+$). ^{1}H NMR (CDCl$_3$): δ=7.74 (d, J=15.9 Hz, 2H), 7.36—7.33 (m, 4H), 7.30 (d, J=8.7 Hz, 4H), 6.77 (d, J=8.7 Hz, 4H), 6.39 (d,

J=15.9 Hz, 2H), 4.11 (t, J=4.7 Hz, 4H), 3.88 (t, J=4.7 Hz, 4H), 3.74—3.67 (m, 12H).

Preparation of 11 by the Photoreaction of 10. A solution of **10b** in acetonitrile (4.0×10^{-2} M) was irradiated internally with a high-pressure mercury lamp (450 W) through a Pyrex filter at the temperature of running water for 2 h. The solvent was then evaporated, and the residue chromatographed on silica gel, using ethyl acetate as the eluent. The first fraction was concentrated and recrystallized from benzene-hexane to give **11b** as colorless needless in 93.2% yield, mp 138.5—139.0 °C. Found: C, 68.84, H, 5.94%. Calcd for $C_{32}H_{32}O_9$: C, 68.56; H, 5.75%. MS (70 eV): m/z 560 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.44—7.34 (m, 4H), 6.62—6.56 (m, 8H), 4.53—4.51 (m, 2H), 4.02 (t, J=4.4 Hz, 4H), 3.72 (t, J=4.4 Hz, 4H), 3.58 (s, 8H), 3.46—3.45(m, 2H).

11a and **11c** were also obtained by a method similar to that described above.

11a. Yield 95.8%, mp. 222.0—223.5 °C. Found: C, 70.61; H, 5.76%. Calcd for $C_{30}H_{28}O_8$: C, 69.76; H, 5.46%. MS (70 eV): m/z 516 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.44—7.36 (m, 4H), 6.60—6.53 (m, 8H), 4.53—4.51 (m, 2H), 4.10 (t, J=4.6 Hz, 4H), 3.64 (t, J=4.6 Hz, 4H), 3.53 (s, 4H), 3.49—3.47 (m, 2H).

11c. Yield 90.1%, mp 172.0—173.0 °C. Found: C, 67.54; H, 6.10%. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54; H, 6.00%. MS (70 eV): m/z 604 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.43-7.33 (m, 4H), 6.63—6.58 (m, 8H), 4.53—4.51 (m, 2H), 4.00 (t, J=4.6 Hz, 4H), 3.75 (t, J=4.6 Hz, 4H), 3.62 (s, 12H), 3.44—3.43 (m, 2H).

Photoreversible Cleavage of 11. An acetonitrile solution of **11** (4.0×10^{-5} M) was placed in a quartz cell (1×1×4 cm) and irradiated at room temperature with 200—250 nm (10 nm intervals) UV light using a grating monochromater with a xenon lamp (500 W). The UV spectral changes were recorded during irradiation. The rate of cleavage of **11** to **10** by UV light is in order: 220>230>240>250>210>200 nm. Therefore, the following photoreversible cleavage of **11** was performed using 220 nm UV light. The steady state of the acetonitrile solution of **11** (2.0×10^{-2} M) was determined by HPLC and those of **11a**, **11b**, and **11c** were obtained within 60, 140 and 170 h, respectively.

Isolation of Photocleavaged Products (10 and 10′). An acetonitrile solution of **11a** (2.0×10^{-2} M) was placed in a quartz cell (1×1×4 cm) and irradiated at room temperature with 220 nm UV light using a grating monochromater with a xenon lamp (500 W) for 60 h. The solution was then evaporated, and the residue was chromatographed on silica gel using ethyl acetate-hexane (5:4) as the eluent. The first fraction was concentrated and the residue was recrystallized from benzene-hexane to give **10a′** as colorless needles. Yield 30%, mp 134.0—136.0 °C. Found: C, 69.66, H, 5.65%. Calcd for $C_{30}H_{28}O_8$: C, 69.76, H, 5.46%. MS (70 eV): m/z 516 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.86 (d, J=8.9 Hz, 2H), 7.68 (d, J=14.6Hz, 1H), 7.40—7.19 (m, 4H), 7.11 (d, J=8.7 Hz, 2H), 6.89 (d, J=8.7 Hz, 2H), 6.85 (d, J=13.1 Hz, 1H), 6.70 (d, J=8.9 Hz, 2H), 6.25 (d, J=14.6 Hz, 1H), 6.01 (d, J=13.1 Hz, 1H), 4.28—3.66 (m, 12H).

The second fraction was concentrated and the residue recrystallized from hexane-benzene to give **10a** as colorless needles in 30% yield.

Isolation of photocleavage products of **11b** and **11c** was also carried out by a method similar to that described above.

Photocleavage Products of 11b. 10b′. Yield 50%, mp 122.0—124.0 °C. Found: C, 68.27, H, 5.93%. Calcd for $C_{32}H_{32}O_9$: C, 68.56, H, 5.75%. MS (70 eV): m/z 560 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.87 (d, J=8.9 Hz, 2H), 7.62 (d, J=15.9 Hz, 1H), 7.38—7.21 (m, 4H), 7.08 (d, J=8.7 Hz, 2H), 6.85 (d, J=13.1 Hz, 1H), 6.81 (d, J=8.7 Hz, 2H), 6.75 (d, J=8.9 Hz, 2H), 6.21 (d, J=15.9 Hz, 1H), 6.03 (d, J=13.1 Hz, 1H), 4.17—3.67 (m, 16H).

10b. Yield 40%.

Photocleavage Products of 11c. 10c′. Yield 27%, mp 103.0—105.0 °C. Found: C, 66.92, H, 6.05%. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54, H, 5.75%. MS (70 eV): m/z 604 (M^+). ^{1}H NMR ($CDCl_3$): δ=7.87 (d, J=8.9 Hz, 2H), 7.62 (d, J=15.9 Hz, 1H), 7.36—7.16 (m, 4H), 7.06 (d, J=8.7 Hz, 2H), 6.85 (d, 13.1 Hz, 1H), 6.76 (d, J=8.7 Hz, 2H), 6.70 (d, J=8.9 Hz, 2H), 6.20 (d, J=15.9 Hz, 1H), 6.03 (d, J=13.1 Hz, 1H), 4.20—3.64 (m, 20H).

10c. Yield 61%.

Photoisomerization of 10 to 10′. An acetonitrile solution of **10a** (2.0×10^{-2} M) was irradiated with 220 nm UV light for 60 h at room temperature. The solution was concentrated and the residue was chromatographed on silica gel using ethylacetate-hexane (5:4) as the eluent. The first fraction was concentrated and the residue was recrystallized from benzene-hexane giving **10a′** in 50% yield.

10b′ and **10c′** were also obtained from **10b** and **10c** in 50 and 30% yields, respectively, by a method similar to that described above.

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