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Highly Effective and Reversible Control of the Rocking Rates of Rotaxanes by Changes to the Size of Stimulus-Responsive Ring Components

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Abstract: We have designed and synthesized rotaxanes whose rates of rocking motion (pendular motion) were switched reversibly through changes to the size of the ring component in response to external stimuli. The ring molecules of the rotaxanes incorporate a metaphenylene unit, which swings like a pendulum, and a dianthrylethane unit, which undergoes reversible isomerization in response to photo- and thermal stimuli and changes the size of the ring component. The rocking rates were estimated quantitatively by variable-temperature (VT) NMR spectroscopy and saturation transfer experiments, which revealed substantial changes in the rates between the open and closed forms, particularly in the case of rotaxanes with an isopropoxy group attached to a phenylene unit.

Keywords: crown compounds · molecular devices · rotaxanes · supramolecular chemistry

Introduction

Rotaxanes[1] are thought to be prime candidates for the construction of artificial molecular machines[2] and fabrication of molecular electronic devices,[3] since the ring and dumbbell components of rotaxanes are capable of exchanging the position of one component relative to that of the other through motions, such as shuttling[4] (linear motion), circumrotation[5] (rotary motion), and rocking[6] (pendular motion). These motions can, in principle, be controlled by external impetus, such as chemical,[7] electrical,[8] or photochemical[9] stimuli. Of these motions, shuttling motions have been most extensively studied for their applications in molecular devices. In contrast with controlling the relative position of the ring component by the shuttling motion, control of its rocking mobility (oscillation frequency) has not been studied.[10]

If a ring component of a rotaxane has a large dipole moment and its direction or oscillation frequency is controlled, then the rotaxane can be applied to switching devices on a molecular scale. For example, it is reported that the efficiency of photoinduced electron transfer is changed substantially by changing the direction of the dipole moment of helical peptides immobilized on a substrate.[11] The tunneling current between an STM tip and an Au(111) substrate has been shown to oscillate in response to the rotation of a dipolar 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene rotor unit of a molecular machine placed under the tip.[12]

A hypothetical scheme for an impetus-responsive dipole-switching system based on the rocking motion of a rotaxane is shown in Scheme 1. The ring component in the rotaxane possesses a dipolar unit that undergoes pendular motion. When the dipolar moiety flips rapidly, the net dipole moment would be negligible (Scheme 1, situation A). By applying an external electric (E) or magnetic field (H) to this system (Scheme 1, process a), the rocking motion can be stopped or decelerated owing to the interaction of the dipole with the external field (Scheme 1, situation B).[12] At this stage, if the size of the ring component is contracted by an external stimulus (Scheme 1, process b),[13] the rocking motion would be frozen because of increased steric hindrance between the ring and axle components, thereby locking the dipole moment (Scheme 1, situation C). As a first step in constructing such switching systems, we report herein the reversible and effective switching of the rocking frequency of rotaxanes in response to physical stimuli.

Results and Discussion

Design of rotaxanes: The structures of rotaxanes **1a**,**b** and **2a**,**b** are shown Scheme 2. We planned to switch the rates of

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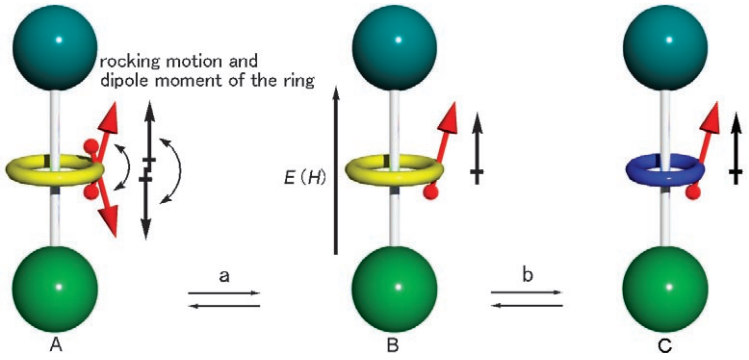
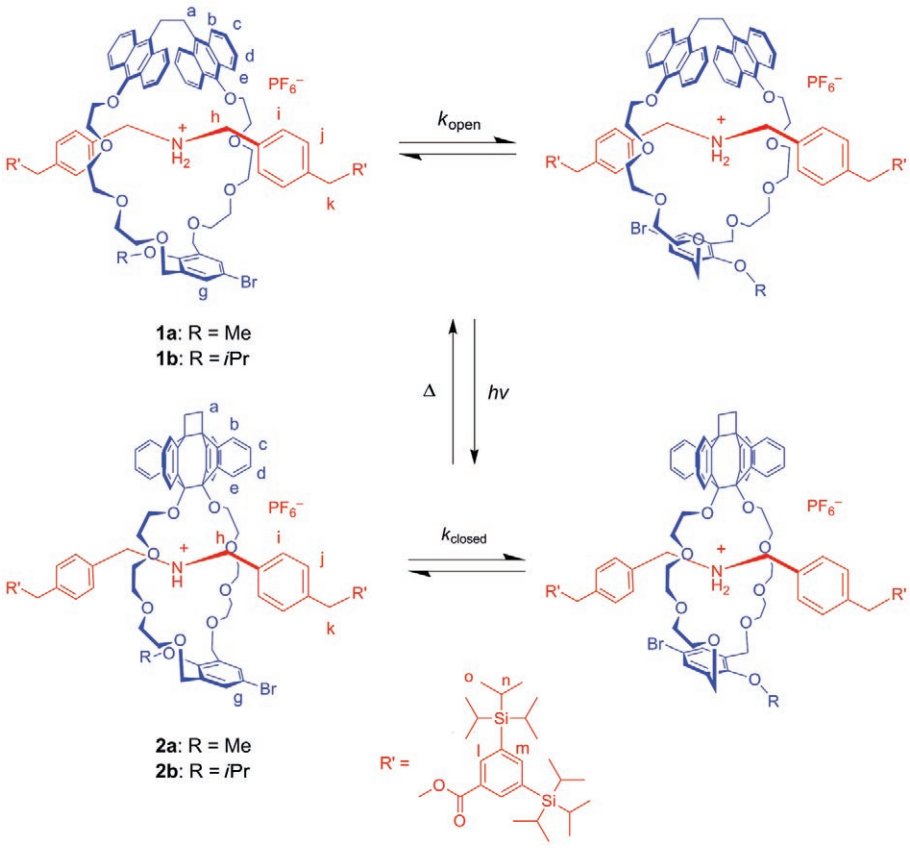


Scheme 1. Schematic model of the switching system using rocking motion. a) Application of an external electric (E) or magnetic field (H) results in alignment of the dipolar unit with the field. b) The ring moiety contracts to reduce the size of the ring, and thereby the rocking motion in the absence of the external field is fixed. Red arrow: dipolar moiety in the ring component.

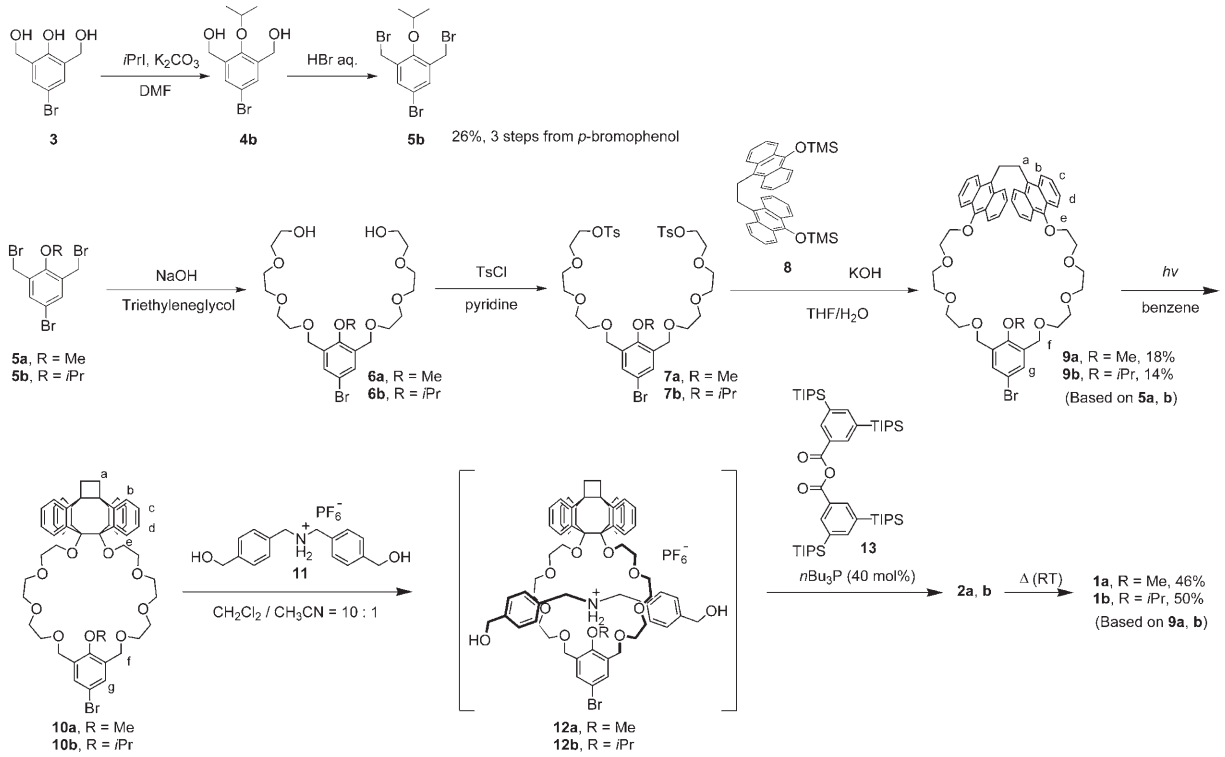


Scheme 2. Switching of the rocking rates (k) of rotaxanes **1a**,**b** and **2a**,**b** based on the change in the size of the ring component.

the rocking motion of the metaphenylene unit by changing the size of the ring component. We expected that the barrier to the pseudorotation of the phenylene moiety would change between the open (**1a**,**b**) and closed forms (**2a**,**b**) of the rotaxanes. To induce an appropriate steric barrier for switching the rocking frequencies between the open and closed forms, a methoxy or an isopropoxy group was attached at the *para* position of the bromometaphenylene unit. Because it is well known that dianthrylethane derivatives undergo reversible photodimerization and the thermal reverse reaction quantitatively,[14] the size of the ring molecules can be changed by employing this protocol. Indeed, we have previously demonstrated switching of the rates of slipping/deslipping and shuttling motions by using a size-variable ring component.[15] A dibenzyl ammonium cation was used as the station that interacts more strongly with the closed form of the ring molecule than the open form. Finally, a 3,5-bis(triisopropylsilyl)phenyl group was employed as the stopper component because it is bulky enough to prevent dethreading of the axle in the open form.[16]

Preparation of rotaxanes 1a,b: The synthetic route for the preparation of rotaxanes **1a**,**b** is shown in Scheme 3. In accordance with the literature,[17] 2,6-bis(bromomethyl)-4-bromoanisole (**5a**) was prepared from 4-bromophenol. The corresponding isopropyl derivative (**5b**) was prepared by using a similar procedure with **3** as the starting material, as shown in Scheme 3. Condensation of these halides (**5a**,**b**) with triethylene glycol (2 equiv) in the presence of NaOH gave **6a**,**b** and subsequent tosylation gave **7a**,**b**. On the other hand, 1,2-bis[10-(trimethylsiloxyl)-9-anthryl]ethane (**8**),[18] which was obtained from the corresponding diol by using *N*,*O*-bis(trimethylsilyl)acetamide (BSA), was deprotected in situ and coupled with ditosylates **7a**,**b** under high-dilution conditions to provide crown ethers **9a**,**b**, in yields of 18 and 14% from **5a**,**b**, respectively.

By photoirradiation of solutions of **9a**,**b** in benzene with a high-pressure mercury lamp, the corresponding closed forms (**10a**,**b**) were formed. After the solvent was changed to a mixture of dichloromethane and acetonitrile (10:1), pseudorotaxanes **12a**,**b** were formed by complexation of **10a**,**b** with secondary ammonium salt **11**[16] at −10°C. The acylation



Scheme 3. Syntheses of ring molecules **9a**,**b** and rotaxanes **1a**,**b**. TsCl = tosyl chloride.

capping reaction[19] of **12a**,**b** with anhydride **13**[16] catalyzed by nBu$_3$P afforded the corresponding rotaxanes **2a**,**b**, which then reverted to open-form rotaxanes **1a**,**b** during the workup and isolation procedures. The yields of rotaxanes **1a**,**b** from crown ethers **9a**,**b** (4 steps) were 46 and 50%, respectively.

Interconversion between open and closed crown ethers: The photoisomerization of the open ring molecule (**9a**) to the corresponding closed form (**10a**) proceeded quantitatively. A solution of **9a** in CD_3CN was placed in a Pyrex NMR tube and degassed by bubbling with dry argon, before subsequent irradiation with a 500 W high-pressure mercury lamp for 30 min in a water bath. After the photoirradiation procedure, the solution was kept below 273 K to avoid significant thermal conversion back to **9a**. In the ^{1}H NMR spectra, a sharp singlet signal assigned to the benzylic protons (H^a) of the anthracene unit of **9a** at $\delta = 4.10$ ppm disappeared and a singlet signal assigned to the aliphatic protons of **10a** appeared at $\delta = 2.95$ ppm after irradiation as shown in Figure 1. In the aromatic region, the characteristic anthracene signals at $\delta = 8.12$ and 7.55 ppm (H^e and H^b, respectively) shifted to $\delta = 7.23$ and 7.10 ppm, respectively, after irradiation. When the NMR sample of **10a** was left at room temperature overnight, the spectrum of **10a** reverted to that of **9a**, which implied that the thermal conversion of **10a** to **9a** proceeded quantitatively. Reversible transformations of isopropyl derivatives **9b** and **10b** were also observed as shown in Figure 2.

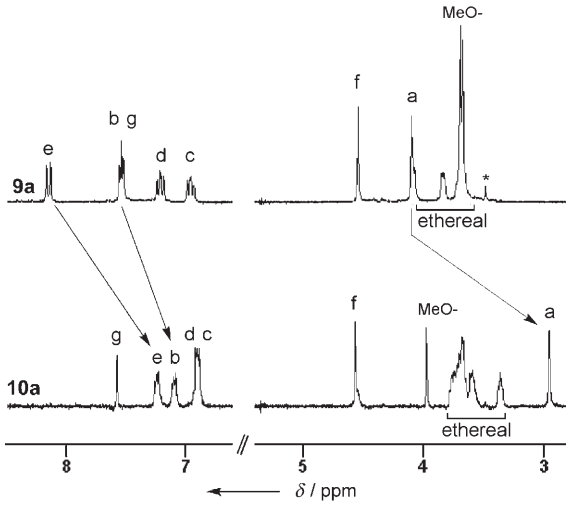


Figure 1. Partial ^{1}H NMR spectra (270 MHz, CD_3CN, 273 K) of **9a** (top) and **10a** (bottom). The assignments of the protons refer to those indicated in Scheme 3.

Interconversion between open and closed forms of the rotaxanes: The photochemical ring closure and the thermal conversion of the anthracene units took place reversibly between open-form rotaxanes **1a**,**b** and closed forms **2a**,**b**, respectively. As shown in Figure 3, the photoreaction of rotaxane **1a** in [D_8]THF was monitored by ^{1}H NMR spectroscopy in a similar manner to that used for ring molecules **9a**,**b**.

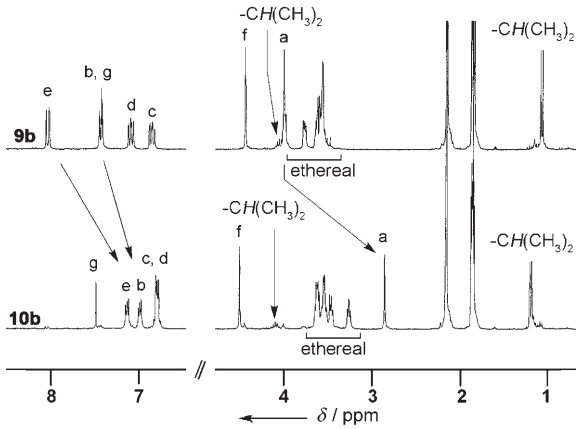


Figure 2. Partial ^{1}H NMR spectra (270 MHz, CD_3CN, 273 K) of **9b** (top) and **10b** (bottom). The assignments of the protons refer to those indicated in Scheme 3.

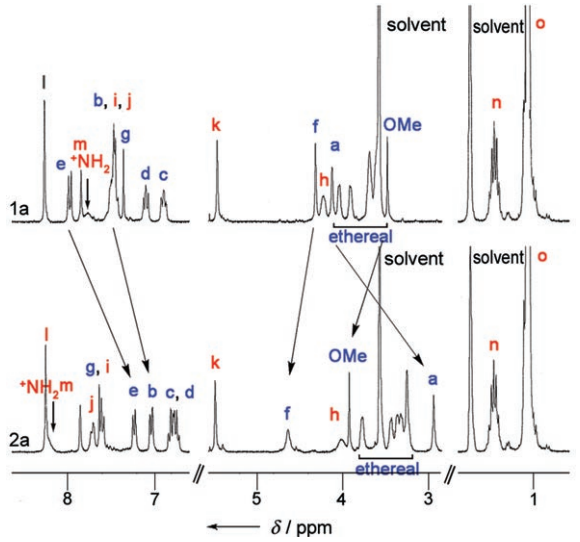


Figure 3. Partial ^{1}H NMR spectra (270 MHz, [D_8]THF, 273 K) of **1a** (top) and **2a** (bottom). The assignments of the protons refer to those indicated in Scheme 2.

Upon irradiation, the singlet peak at $\delta = 4.12$ ppm assigned to the ethylene protons (H^a) of the dianthrylethane unit of **1a** disappeared and a characteristic signal of the cyclobutane protons of **2a** appeared at $\delta = 2.94$ ppm, which indicated that ring closure proceeded efficiently. In contrast with the photoisomerization of crown ether **9a**, the signal of the benzyl protons of the ring component (H^f) shifted downfield and appeared as a broad singlet (from $\delta = 4.31$ to 4.64 ppm). The signals assigned to the protons of the terminal part of the axle component (H^l, H^k) did not shift significantly by photoisomerization (from $\delta = 8.27$ and 5.45 ppm to 8.25 and 5.48 ppm, respectively), as shown in Figure 3. These results indicate that ring contraction did not significantly affect the magnetic environment of the terminal part of the axle component. The spectrum of **2a** reverted to that of **1a** when the NMR sample of **2a** was left at room temperature overnight; this implied that the thermal conversion of **2a** to **1a** also proceeded quantitatively.

The reversible transformation of isopropyl derivatives **1b** and **2b** was also observed, as shown in Figure 4. In contrast with the photoisomerization of rotaxane **1a**, photoirradiation of corresponding isopropyl rotaxane **1b** gave rise to additional differences in the appearance of the ^{1}H NMR spectra. For example, the signals assigned to the protons of the axle component of **2b** appeared as a pairs of singlets (H^l: $\delta = 8.26$ and 8.24 ppm, H^k: 5.51 and 5.45 ppm). Moreover, the benzylic protons (H^f) of the ring component appeared as a double doublet at $\delta = 4.97$ and 4.37 ppm. These results indicate that the rate of the rocking motion of isopropyl derivative **2b** is slower than the NMR timescale.

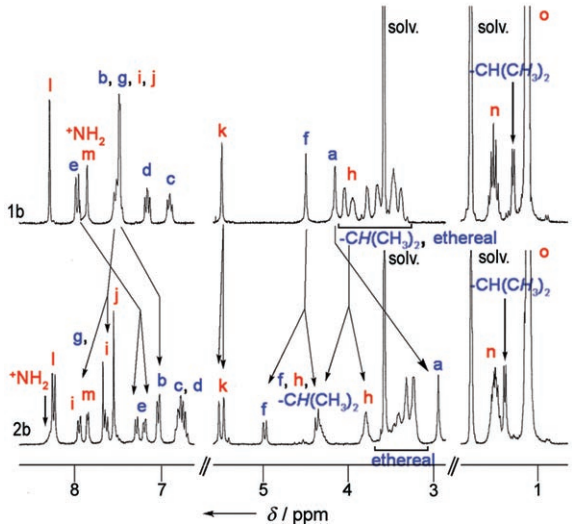


Figure 4. Partial ^{1}H NMR spectra (270 MHz, [D_8]THF, 273 K) of **1b** (top) and **2b** (bottom). The assignments of the protons refer to those indicated in Scheme 2.

Rates of thermal conversions of crown ethers 10a,b and rotaxanes 2a,b: The thermal conversion of closed forms **10a**, **10b**, **2a**, and **2b** into the corresponding open forms **9a**, **9b**, **1a**, and **1b**, respectively, gave rise to remarkable spectral changes in the UV-visible spectra in CH_3CN (Figure 5). Based on the increase in the absorbance at $\lambda = 383$ nm, the first-order rate constants of the thermal conversion were determined. The rate constants of the thermal conversions of **10a**, **10b**, **2a**, and **2b** at 303 K were 1.36×10^{-3}, 1.33×10^{-3}, 4.97×10^{-4}, and 2.85×10^{-4} s^{-1}, respectively (the corresponding half-lives were 9, 9, 23, and 41 min). As shown in Table 1, the rates of conversion of **2a**,**b** were slower than those of the corresponding crown ethers **10a**,**b**. These results indicate that the closed-form rotaxanes **2a**,**b** are more stabilized than crown ethers **10a**,**b** by the ion–dipole interactions between the crown ether ring and the secondary ammonium ion. In addition, it should be noted that the rates for **10a** and **10b** were almost identical, whereas that of **2b** was twice

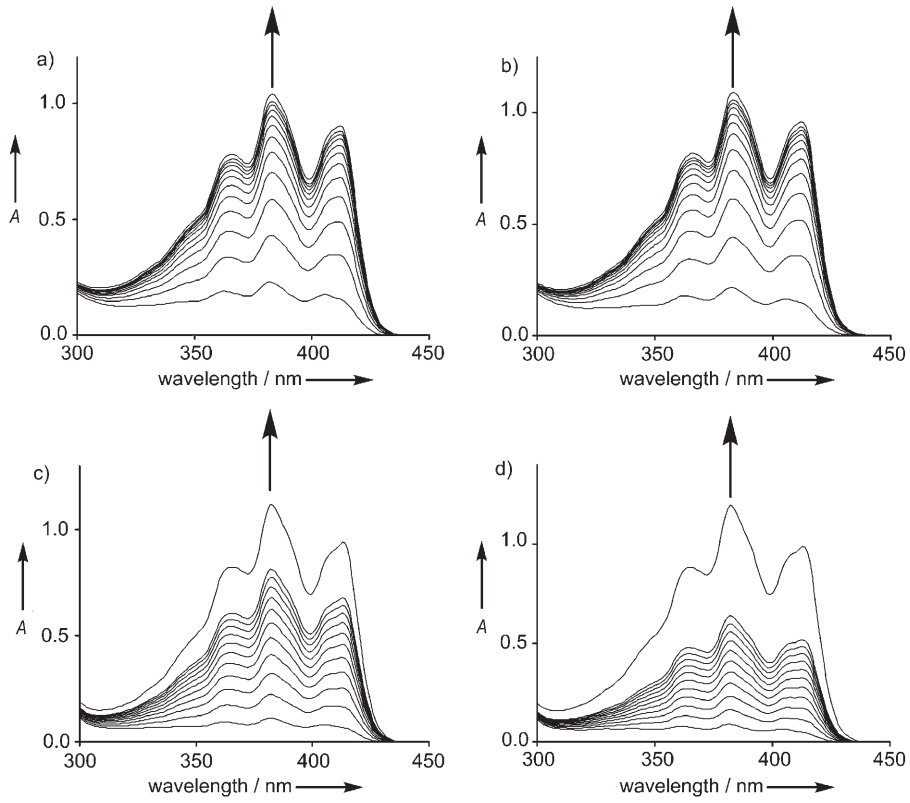


Figure 5. UV/Vis absorption spectra (in CH_3CN, ≈0.1 M, 303 K) of a) **10a**, b) **10b**, c) **2a**, and d) **2b**. UV spectra were measured at intervals of four minutes. The top spectrum in each graph was measured when the thermal conversion was completed.

Table 1. Reverse rate constants and half-lives of **10a**,**b** and **2a**,**b**.[a]

	k [10^{-5} s^{-1}]		$\tau_{1/2}$ [min]	
	T=283 [K]	T=303 [K]	T=283 [K]	T=303 [K]
10a	9.50	136	121	9
10b	9.33	133	124	9
2a	3.00	49.7	385	23
2b	1.47	28.5	784	41

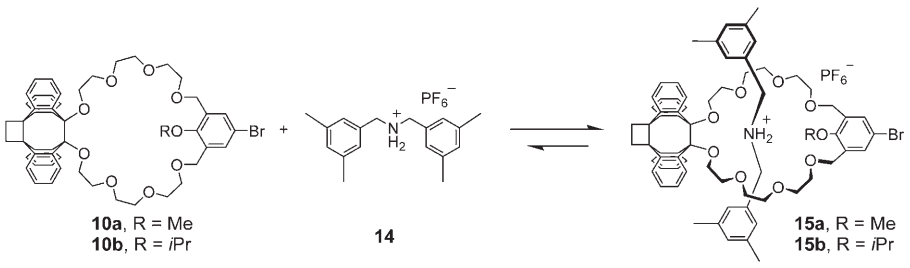
[a] Reactions performed in CH_3CN.

as large as that of **2a** in spite of the greater steric hindrance in **2b**. This result suggests that the ion–dipole interactions in **2b** are stronger than those in **2a** owing to the stronger basicity of the isopropoxy group than that of the methoxy group.[20]

Complexation constants of crown ethers 10a,b with bis(3,5-dimethylbenzyl)ammonium hexafluorophosphate (14): The relative strength of the ion–dipole interactions of closed-form crown ethers **10a**,**b** with a secondary ammonium ion were estimated by determining their complexation constants with bis(3,5-dimethylbenzyl)ammonium hexafluorophosphate (**14**) by using ^{1}H NMR spectroscopy in a mixture of CD_2Cl_2/CD_3CN (2:1), as shown in Scheme 4. Because of the lability of the closed form of the ring molecules, the titration method could not be used. Instead, the complexation constants were determined by the relative integration of the signals of the free and complexed ring components in the ^{1}H NMR spectra. Slightly bulky **14** was employed as a guest molecule because the slipping/deslipping rates between **10a**,**b** and **14** were slow enough to observe the respective signals of the components.[20] As a result, compound **10b**, which has an isopropoxy substituent, exhibits complexation constants that are about five times larger than those of **10a**, which has a methoxy substituent.[21] This result is consistent with the observed rate reduction of the thermal conversion of closed-form rotaxanes **2a**,**b** (Table 2).

Evaluation of the rates of rocking motions: The rates of the rocking motions of **1b** and **2b** were determined by line-shape analysis of their variable-temperature (VT) NMR spectra in [D_8]THF. Figure 6a shows partial experimental ^{1}H NMR spectra of H^k on the axle component of **1b** between 178 and 188 K and the simulated spectra assuming the rate constants shown. Similarly, the rates of rocking of **2a** were estimated on the basis of the line-shape analysis[22] of the VT-NMR spectra for H^f as shown in Figure 6b. The kinetic parameters were determined from the Eyring plots and are listed in Table 3.

In contrast with **1b**, the room temperature spectrum of **1a** indicates that the rocking motion of the phenylene unit is



Scheme 4. Complexation process of **10a**,**b** with **14** (CD_2Cl_2/CD_3CN 2:1).

Table 2. Complexation constants of **10a**,**b** with **14**, respectively.[a]

	K [M^{-1}]	
T_c [K]	**10a**	**10b**
273	30	150
263	40	250
253	100	440
243	150	750
233	350	1200

[a] It was confirmed that the complexation abilities of open-form crown ethers **9a**,**b** were negligible by ^{1}H NMR spectroscopy. Reactions performed in CD_2Cl_2/CD_3CN 2:1.

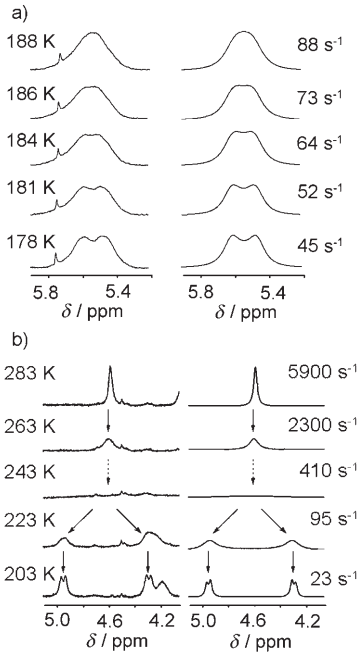


Figure 6. Experimental (left) and simulated (right) partial VT-NMR spectra (270 MHz, [D$_8$]THF) of a) H^k of **1b** and b) H^f of **2a**.

Table 3. Rocking rates and kinetic parameters of **1a**,**b** and **2a**,**b**.[a]

	T_c [K]	ΔH [kJ mol^{-1}]	ΔS [J K^{-1} mol^{-1}]	k_{303}[b] [s^{-1}]
1a	n.d.	n.d.	n.d.	$>4.0\times10^4$[c]
1b	186	17 ± 3.0	-113 ± 15	8.9×10^3[d]
2a	241	32 ± 5.0	-59 ± 21	1.0×10^4[d]
2b	n.d.	n.d.	n.d.	<3.5[e]

[a] Reactions performed in [D$_8$]THF; n.d. = not determined. [b] Rocking rate at 303 K. [c] Minimum estimate (see text). [d] Estimated by extrapolation of the Eyring plot. [e] Maximum value estimated on the basis of the saturation transfer experiment.

rapid on the NMR timescale and the spectrum did not change even when the solution was cooled to 165 K. Therefore, the minimum rate of rocking (k_{303}) of **1a** was estimated to be 4.0×10^4 s^{-1} by assuming that the rocking frequency of **1a** at the coalescence temperature is same as that of **1b**, and that the temperature dependence of their rocking frequencies is also identical. In contrast, the ^{1}H NMR spectrum of **2b** at 273 K indicates that the rocking motion is slow on the NMR timescale. In contrast with **2a**, coalescence of the signals, however, was not observed when the temperature was elevated to 303 K, which indicated that the rocking rate of **2b** is much slower than that of **2a**.

The rate of rocking of closed-form rotaxane **2b** was also estimated by saturation transfer experiments.[23] The saturation transfer experiment indicated that the rocking rate (k_{303}) of **2b** was slower than 3.5 s^{-1}. Table 3 summarizes the kinetic parameters and the rocking frequencies at 303 K of rotaxanes **1a**,**b** and **2a**,**b**.[24]

For rotaxanes **1a** and **2a** with a methoxy substituent, the rate of rocking of open-form **1a** ($k_{303}>4.0\times10^4$ s^{-1}) should be at least four times faster than that of closed-form **2a** ($k_{303}=1.0\times10^4$ s^{-1}). On the other hand, for rotaxanes **1b** and **2b**, which contain the isopropoxy substituent, the difference between the rocking rates should be more than 10^3 times (**1b**: $k_{303}=8.9\times10^3$ s^{-1}, **2b**: $k_{303}<3.5$ s^{-1}). These results clearly demonstrate that the rocking rate is switched by the external stimuli. Moreover, the remarkable difference observed in the ratio of the rocking frequencies between the open and closed forms of the rotaxanes (**1a**/**2a** vs. **1b**/**2b**) is ascribed to the small rocking rate of **2b** (Table 3). The reason for the slow rocking rate can be attributed to the destabilization of the transition state for rocking due to large steric hindrance of the bulkier isopropoxy substituent. On the other hand, it can also be attributed to the stabilization of the ground state because the crown ether unit of **2b** with an isopropoxy substituent has a larger interaction with the secondary ammonium cation than that of **1b** with a methoxy substituent due to the stronger electron-donating ability of the isopropyl group. These two effects may contribute to increase the activation energy of the rocking motion of **2b**, thereby decelerating the rocking rate substantially.

Conclusion

We synthesized rotaxanes with a dianthrylethane moiety in the ring unit, of which the ring size was changed reversibly by photochemical cycloaddition and thermal interconversion. The rates of the rocking motion of the rotaxanes were determined on the basis of NMR spectroscopy experiments. Fair to substantial differences between the rocking rates of the open and closed forms of the rotaxanes were observed, and demonstrated that the rocking motions were switched by the external stimuli. Moreover, it was found that the difference of the rocking frequencies between the open and closed forms of the rotaxanes varies considerably depending on the steric and electronic properties of the substituent attached to the ring component.

Experimental Section

General procedure: ^{1}H (270, 300, or 400 MHz) and ^{13}C NMR (67.5, 75.0, or 100 MHz) spectra were recorded on a JEOL JNM-AL-400, a Varian Mercury 300, or a JEOL JNM-GSX-270 spectrometer. The chemical shifts of ^{1}H and ^{13}C NMR signals are quoted relative to tetramethylsilane

or residual solvent. IR spectra were recorded as KBr disks on a JASCO FTIR-410 spectrometer. Mass spectral analyses were performed on a JEOL JMS-DX303HF. Elemental analyses were carried out with a Perkin–Elmer 2400II analyzer. UV/Vis spectra were recorded on a Hitachi U-3310 spectrometer in acetonitrile. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as the eluent. Solvents were dried (drying agent in parentheses) and distilled prior to use: THF (sodium benzophenone ketyl), CH_3CN (CaH_2), CH_2Cl_2 (CaH_2). Compounds **8**, **11**, and **13** were prepared according to literature procedures.[16,17]

Compound 4b: A solution of **3b**[17] (crude product obtained from *p*-bromophenol; 20.0 g, 85.8 mmol), K_2CO_3 (15.4 g, 112 mmol), and 2-iodopropane (9.40 mL, 94.4 mmol) in acetone (420 mL) was stirred at reflux for 43 h. The mixture was cooled to RT and diluted with H_2O (120 mL). Acetone was removed under reduced pressure. The precipitate was collected by filtration and washed with a small amount of water. This solid (**4b**: 16.3 g, 69%) was used for subsequent reactions without any purification. An analytical sample of **4b** was obtained after isolation by chromatography on silica gel (eluent: $CHCl_3$/EtOH 9:1) and subsequent recrystallization from ethyl acetate/hexane. M.p. 125–126 °C; ^{1}H NMR (270 MHz, [D$_6$]DMSO): $\delta = 7.44$ (s, 2H), 5.20 (t, $J = 5.7$ Hz, 2H), 4.48 (d, $J = 5.7$ Hz, 4H), 4.12 (septet, $J = 5.9$ Hz, 1H), 1.18 ppm (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (67.5 MHz, [D$_6$]DMSO): $\delta = 150.5$, 137.9, 128.8, 115.3, 75.7, 57.6, 22.1 ppm; MS (EI): m/z: 274 [M^+]; IR (KBr): $\tilde{\nu} = 3265$, 3167, 2971, 2930, 1443, 1385, 1351, 1196, 1103, 1067, 935, 867, 827, 734 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{15}O_3Br$: C 48.02, H 5.50; found: C 48.29, H 5.33.

Compound 5b: A suspended solution of **4b** (16.0 g, 58.2 mmol) in 48% hydrobromic acid (450 mL) was stirred at 70 °C for 3 h. The mixture was cooled to RT and the precipitate was collected by filtration. The precipitate was dissolved in $CHCl_3$ and the solution was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent, chromatography on silica gel (eluent: $CHCl_3$) gave **5b** as a pale yellow solid (7.00 g, 26% in 3 steps from *p*-bromophenol). M.p. 88–89 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.51$ (s, 2H), 4.49 (septet, $J = 5.9$ Hz, 1H), 4.47 (s, 4H), 1.37 ppm (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta =$ 152.7, 134.8, 134.0, 116.7, 77.3, 27.3, 22.6 ppm; MS (FAB): m/z: 400 [M^+]; IR (KBr): $\tilde{\nu} = 3052$, 2968, 2927, 1451, 1385, 1371, 1240, 1210, 1194, 1171, 1099, 934, 874, 829, 780, 613, 543 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{13}Br_3$: C 32.95, H 3.27; found: C 33.18, H 3.28.

Compound 6b: Compound **5b** (3.00 g, 7.48 mmol) was added to a solution of sodium hydroxide (761 mg, 19.0 mmol) in triethylene glycol (21.7 g, 144 mmol) and the mixture was stirred at 110 °C for 40 min. The solution was cooled to RT and diluted with water. The mixture was extracted with $CHCl_3$ and the extract was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, chromatography on silica gel (eluent: $CHCl_3$/EtOH = 9/1) gave **6b** as a colorless oil (3.49 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.52$ (s, 2H), 4.55 (s, 4H), 4.13 (septet, $J = 6.0$ Hz 1H), 3.72–3.59 (m, 24H), 2.63 (brs, 2H), 1.25 ppm (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 152.3$, 133.8, 131.2, 116.6, 77.0, 72.5, 70.7, 70.6, 70.4, 69.9, 67.7, 61.7, 22.4 ppm; MS (FAB): m/z: 541, 539 [M^++H]; IR (neat): $\tilde{\nu} = 3302$ (br), 2988, 2941, 2788, 2710, 1560, 1414, 1041, 840, 809 561 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{39}O_9Br$: C 51.21, H 7.29; found: C 51.24, H 7.43.

Compound 7b: Tosyl chloride (4.25 g, 22.3 mmol) was added portionwise to a solution of **6b** (4.00 g, 7.41 mmol) in pyridine (60 mL) with stirring at 0 °C. After stirring at 0 °C for 10 h, the solution was diluted with 6 N HCl. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, chromatography on silica gel (eluent: $CHCl_3$) gave **7b** as a pale yellow oil (5.60 g, 89%). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.79$ (d, $J = 8.4$ Hz, 4H), 7.49 (s, 2H), 7.33 (d, $J = 8.4$ Hz, 4H), 4.54 (s, 4H), 4.18–4.06 (m, 5H), 3.71–3.59 (m, 20H), 2.43 (s, 6H), 1.24 ppm (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.4$, 144.6, 134.0, 133.0, 131.2, 129.7, 127.8, 116.6, 76.9, 70.7, 70.6, 70.5, 69.9, 69.2, 68.7, 67.6, 22.3, 21.6 ppm; MS (FAB): m/z: 869 [M^++Na]; IR (neat): $\tilde{\nu} = 3066$, 2972, 2872, 1598, 1451, 1357, 1292, 1246, 1190, 1177, 1101, 1018, 925, 817, 775, 664, 554 cm^{-1}; elemental analysis calcd (%) for $C_{37}H_{51}O_{13}S_2Br$: C 52.42, H 6.06; found: C 52.22, H 6.03.

Crown ether 9b. A solution of **13** (2.20 g, 3.94 mmol) and **12b** (3.36 g, 3.96 mmol) in degassed THF (80 mL) through a Hershberg dropping funnel over 18.5 h was added to a solution of KOH (40 g, 71 mmol) in water (14 mL) and THF (480 mL) at reflux. After stirring for an additional 0.5 h under reflux, the reaction mixture was cooled in an ice bath. The resulting reddish suspension was neutralized with 6 N HCl in an ice bath. The solvent was removed by evaporation and the residue was extracted with CH_2Cl_2. The extract was washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, chromatography on silica gel (eluent: hexane/ethyl acetate 1/1) followed by preparative HPLC gave **9b** as a yellow foam (713 mg, 18%). M.p. 44–45 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 8.15$ (d, $J = 8.7$ Hz, 4H), 7.55 (d, $J = 8.9$ Hz, 4H), 7.54 (s, 2H), 7.20–7.15 (m, 4H), 7.00–6.94 (m, 4H), 4.55 (s, 4H), 4.17–4.03 (m, 9H), 3.98–3.94 (m, 4H), 3.83–3.63 (m, 16H), 1.18 ppm (d, $J =$ 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.4$, 150.0, 134.1, 131.1, 130.7, 129.1, 124.7, 124.1, 124.0, 123.9, 122.6, 116.8, 76.9, 74.9, 71.2, 71.1, 70.83, 70.81, 70.0, 67.6, 27.6, 22.4 ppm; MS (FAB): m/z: 917 [M^++H]; IR (KBr): $\tilde{\nu} = 3067$, 2921, 2870, 1439, 1349, 1281, 1199, 1100, 933, 772, 683, 618 cm^{-1}; elemental analysis calcd (%) for $C_{53}H_{57}O_9Br$: C 69.35, H 6.26; found: C 69.24, H 6.24.

Closed crown ether 10b: A solution of **9b** (2.7 μmol) in CD_3CN (750 μL) in a Pyrex NMR tube was thoroughly degassed by bubbling dry argon for 30 min. Then, the solution was irradiated by using a 500 W high-pressure mercury lamp for 30 min in a water bath. After irradiation the solution was maintained below 0 °C to avoid thermal reversion. The structure of **10b** was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR (270 MHz, CD_3CN, 0 °C): $\delta = 7.50$ (s, 2H), 7.17–7.13 (m, 4H), 7.03–6.98 (m, 4H), 6.83–6.79 (m, 8H), 4.51 (s, 4H), 4.10 (septet, $J = 6.1$ Hz, 1H), 3.66–3.24 (m, 24H), 2.86 (s, 4H), 1.21 ppm (d, $J = 6.1$ Hz, 6H).

Rotaxane 1b. A solution of **9b** (200 mg, 218 μmol) in benzene (20 mL) was placed in a Pyrex glass tube and thoroughly degassed by bubbling dry argon for 30 min. The solution was irradiated with a 500 W high-pressure mercury lamp for 15 min in an ice bath. After irradiation, the solvent was evaporated with cooling to give **10b**. A solution of **5** (88 mg, 218 μmol) in dry CH_3CN (250 μL), a solution of **7** (377 mg, 442 μmol) in dry CH_3CN (1.9 mL), and nBu$_3$P (27 μL, 109 μmol) were added to the residue. The mixture was stirred in an ice/salt bath for 3 h and at RT for 20 min. Evaporation of the solvent followed with isolation by preparative HPLC separation gave **1b** as a yellow foam (235 mg, 50%). M.p. 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.23$ (d, $J = 1.0$ Hz, 4H), 7.90–7.84 (m, 8H), 7.53–7.49 (m, 8H), 7.34–7.32 (m, 6H), 7.10–7.07 (m, 4H), 6.90–6.86 (m, 4H), 5.47 (s, 4H), 4.37 (s, 4H), 4.07 (brs, 4H), 4.02 (septet, $J =$ 6.1 Hz, 1H), 3.72 (brs, 8H), 3.62–3.57 (m, 8H), 3.46 (brs, 8H), 1.43 (septet, $J = 7.3$ Hz, 12H), 1.17 (d, $J = 6.1$ Hz, 6H), 1.07 ppm (d, $J = 7.3$ Hz, 72H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.0$, 153.0, 149.0, 147.1, 138.4, 136.4, 134.2, 133.8, 132.7, 130.7, 129.8, 129.5, 129.1, 128.4, 128.0, 124.7, 124.5, 124.1, 123.6, 122.0, 116.4, 77.2, 74.7, 71.3, 71.0, 70.5, 70.4, 70.1, 68.7, 65.8, 52.3, 27.2, 22.4, 18.6, 10.8 ppm; MS (FAB): m/z: 2010 [M^+–PF_6^-]; IR (KBr): $\tilde{\nu} = 3054$, 2921, 2870, 1439, 1349, 1281, 1199, 1100, 933, 772 cm^{-1}; elemental analysis calcd (%) for $C_{119}H_{165}O_{13}NF_6Si_4PBr$: C 66.33, H 7.72, N 0.65; found: C 66.29, H 7.80, N 0.79.

Closed form rotaxane 2b: A solution of **1b** (3.5 μmol) in CD_3CN (750 μL) was placed in a Pyrex NMR tube and thoroughly degassed by bubbling dry argon for 30 min. Then, the solution was irradiated by using a 500 W high-pressure mercury lamp for 30 min in an ice bath. After irradiation, the solution was maintained below 0 °C to avoid the thermal reverse reaction. The structures of **2b** were confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR (270 MHz, [D$_8$]THF, 0 °C): $\delta = 8.25$ (d, $J = 7.3$ Hz, 6H), 7.95 (d, $J = 7.9$ Hz, 2H), 7.85 (d, $J = 4.5$ Hz, 2H), 7.67–7.62 (m, 4H), 7.55 (s, 4H), 7.28–7.19 (m, 4H), 7.30 (d, $J = 7.1$ Hz, 4H), 6.80–6.69 (m, 8H), 5.48 (d, $J = 15$ Hz, 4H), 4.97 (d, $J = 9.7$ Hz, 2H), 4.38–4.35 (m, 5H), 3.79 (brs, 4H), 3.57–3.23 (m, 24H), 2.95 (s, 4H), 1.48–1.39 (m, 12H), 1.33 (d, $J = 5.9$ Hz, 4H), 1.08–1.04 ppm (m, 72H).

Determination of complexation constants: A solution of **9a** or **9b** (8.0 μmol) in CD_2Cl_2 (0.60 mL) and a solution of **8** (8.0 μmol) in CD_3CN (0.30 mL) in an NMR tube was degassed by bubbling argon in an EtOH-

dry ice bath for 30 min, before it was irradiated using a 500 W high-pressure mercury lamp. A small amount of CD_3CN was added to this solution to readjust the volume back to the original level owing to evaporation of the solvent as a result of bubbling argon through it. The ^1H NMR spectra were measured at 10 °C intervals from 0 to −40 °C.

Determination of rates of thermal reversion: A solution of an open-form compound (ca. 0.1 mM) in CH_3CN was charged into a UV/Vis cuvette equipped with a side neck for degassing. The solution was degassed by bubbling argon, followed by five freeze-pump-thaw cycles, and then sealed. The solution was irradiated for 15 min with a 500 W high-pressure mercury lamp in a water bath. After irradiation, the UV spectral change was followed at 10 and 30 °C for **6a**,**b** and **2a**,**b**, from which the rates of the reverse reaction and the half-lives were determined.

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[23] One of the signals of H^k which appeared at higher field was irradiated at 303 K. However, no change in the signal intensity of the other H^k signal was observed, which suggests that the relaxation time (T_1) of H^k is longer than the lifetime of the conformation. T_1 was determined by the null point method. Details of the saturation transfer experiment are given in the Supporting Information.

[24] From the VT-NMR spectroscopy study of open-form rotaxanes **1a**,**b**, it turned out that the shape of the anthracene protons, especially H^c and H^d, changed dramatically as shown in Figures S4 and S5 in the Supporting Information. This spectral change can be resulted from restriction of the quasi-rotation of the dianthrylethane unit shown below. The rates of this twist motion of the dianthrylethane unit were also determined by using VT-NMR spectroscopy. From the coalescence temperature and the rough estimate of $\Delta\nu$ for anthracene proton H^c or H^d, the twisting frequency was estimated to be ca. 10^3 Hz at 213–203 K. The rates of rocking motion of **1b** at the same temperature range vary from 270 to 510 Hz, which indicates that the rocking motion of the metaphenylene unit and the twisting motion of the dianthrylethane unit are independent.

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