

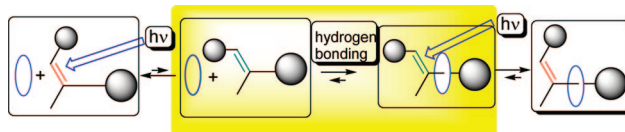
Using Photoresponsive End-Closing and End-Opening Reactions for the Synthesis and Disassembly of [2]Rotaxanes: Implications for Dynamic Covalent Chemistry

Yuji Tokunaga,^{*,†} Koichiro Akasaka,[†] Nobuharu Hashimoto,[†] Shou Yamanaka,[‡]
Kenji Hisada,[‡] Youji Shimomura,[†] and Suzuka Kakuchi[†]

Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui,
Fukui, 910-8507, Japan, and Department of Fiber Amenity Engineering, Faculty of Engineering,
University of Fukui, Fukui, 910-8507, Japan

tokunaga@matse.u-fukui.ac.jp

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We have synthesized two [2]rotaxanes, each possessing a (*Z*)- α -methylstilbene unit as one of its stoppers, in good yield through the photoisomerization of terminal (*E*)- α -methylstilbene units of dialkylammonium salts in the presence of the crown ether dibenzo[24]crown-8 (DB24C8). The synthesis relies on the formation of pseudorotaxane intermediates through hydrogen bond-guided self-assembly and subsequent end-closing photoisomerization. An (*E*)- α -methylstilbene unit is not sufficiently bulky to prevent dissociation of the DB24C8 unit, whereas a (*Z*)- α -methylstilbene unit acts as a true stopper. We also synthesized these [2]rotaxanes from the (*Z*)- α -methylstilbene-terminated axle-like salts though thermodynamic covalent chemistry by taking advantage of the reversibility of the photoisomerization. To dissociate the components of the [2]rotaxanes, we performed the reverse end-opening process under UV irradiation (i.e., *Z*-to-*E* isomerization of the α -methylstilbene termini) in a polar solvent. These rotaxanes are stable at room temperature, but dissociate slowly to their two components at elevated temperatures.

Introduction

Artificial molecular switches based on photoreactions rely on differences in the chemical properties of organic and organometallic compounds in response to irradiation.¹ Several rotaxanes function as switchable systems based on photocontrolled translational motion (molecular shuttling).² Such rotax-

anes possess two or more stations that interact noncovalently to varying degrees with the macrocyclic component; photoirradiation alters the strength of these interactions. Other photoresponsive systems possessing rotaxane-like structures function through the association or dissociation of pseudorotaxanes in response to photoirradiation. Copper(I),³ anthracene,^{4,5} cycloheptatriene,⁶ bipyridinium/hydroquinone systems,⁷ 1,8-naphthalimide,⁸ and transition metal complexes^{9,10} have all been used as key photoactive units in reversible switching systems that

[†] Department of Materials Science and Engineering.

[‡] Department of Fiber Amenity Engineering.

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function through photoresponsive reactions and their reversal under orthogonal conditions.

Photochemical reactions that afford a change in the three-dimensional structure of a molecule can be considered as the signaling of a molecular switch.¹ For example, the *Z*-to-*E* isomerization of a carbon–carbon double bond in the retinylidene chromophore in rhodopsin plays an important role in the principal visual process of the eye. The activity of rhodopsins is triggered by the photoinduced isomerization of the corresponding chromophores. The conformational change that occurs upon isomerization is usually referred to as the primary event of the protein photocycle.¹¹ Rotaxane switching systems have been developed to take advantage of structural changes arising from photoisomerization reactions; in these systems, the geometrical changes of carbon–carbon¹² or nitrogen–nitrogen^{12e,13,14} double bonds affect the molecular shuttling or association/dissociation reactions between the ring-shaped and axle-like components.¹⁵

Stilbene is one of the most widely investigated molecules in organic photochemistry and photophysics.¹⁶ (*E*)-Stilbene isomerizes to its *Z* isomer upon exposure to UV light in the presence of an approximate sensitizer. Upon irradiation in the presence of an alternative sensitizer, the *Z* isomer reverts back to its *E* isomer. Both reactions proceed reversibly under these irradiation

conditions: i.e., the *Z* (or *E*) isomer slowly isomerizes to the *E* (or *Z*) isomer under the conditions that predominantly afford the *Z* (or *E*) isomer. The *E* isomer possesses a planar conformation because of its extended π conjugation, whereas the two benzene rings of the *Z* isomer are slightly twisted about the olefinic bond because of the steric repulsion between the protons at the 2 and 2' positions. Accordingly, a stilbene unit is “thicker” (less flat) after isomerization of the *E* isomer to the *Z* isomer. Recently Leigh and co-workers reported a molecular information ratchet using the rotaxane system, which consists of asymmetric ammonium stations and the photoresponsive α -methylstilbene “gate” in the axle and of a crown ether possessing the photosensitizer part.^{12f}

In this paper we report (1) the synthesis of two [2]rotaxanes through the photoisomerization of terminal (*E*)-stilbene units to their *Z* isomers in the presence of dibenzo[24]crown-8 (DB24C8) in an aprotic solvent (a so-called “end-closing” process), (2) the synthesis of a rotaxane through UV irradiation of a terminal (*Z*)-stilbene unit in the presence of DB24C8 under thermodynamic control,^{17–21} and (3) the degradation of these rotaxanes (a) through photoisomerization of the (*Z*)-stilbene unit to its *E* isomer on the rotaxane axle (a so-called “end-opening” process) and (b) under thermal conditions in a polar solvent (Figure 1).²²

Results and Discussion

Design Principle. For this study, we selected the well-established self-assembly of dialkylammonium ions and DB24C8²³ because of the strong hydrogen bonding between the components and the adequate size of the DB24C8 cavity with respect to a stilbene unit. Rotaxanes possessing stilbene units on their axle moieties have been reported previously by the Stoddart group, but these nonsubstituted (*E*)- and (*Z*)-stilbene units were not sufficiently large to prevent disassembly of the components.²⁴ Computer simulation revealed that introduction of a methyl group at the α position of stilbene increases its

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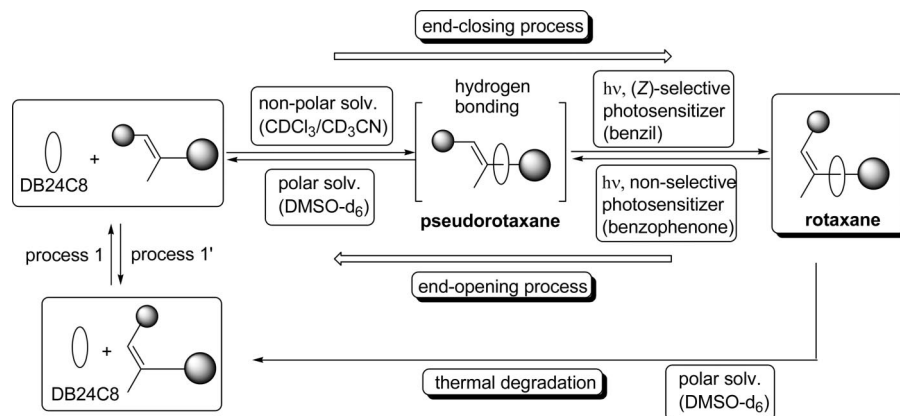


FIGURE 1. Outline of the end-closing synthesis of a [2]rotaxane, its end-opening degradation through photoisomerization, and thermal degradation.

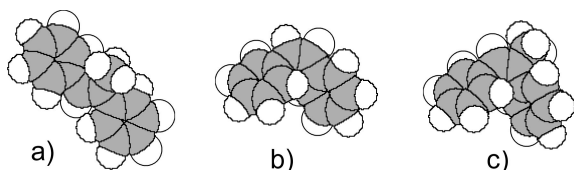


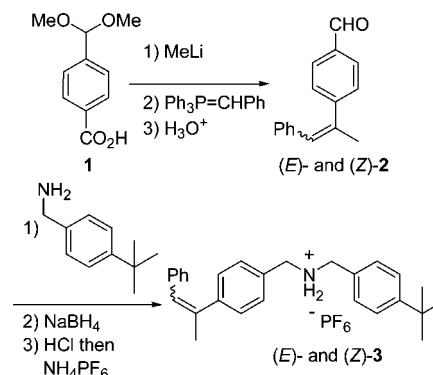
FIGURE 2. Space-filling representations of the energy-minimized structures of (a) (*E*)- α -methylstilbene, (b) (*Z*)-stilbene, and (c) (*Z*)- α -methylstilbene.

bulk and causes a dramatic difference between the sizes of the (*E*)- and (*Z*)- α -methylstilbenes (Figure 2). Because the isopropylphenyl group permits slippage of DB24C8,²⁵ we expected this macrocycle to have little trouble passing over the linear and flat (*E*)- α -methylstilbene terminus (Figure 2a), i.e., through a mechanism involving (i) passage over the *p*-phenylene unit, (ii) “slippage” over the isopropylene unit, and (iii) dissociation over the terminal phenyl group. In contrast, molecular modeling of the (*Z*)- α -methylstilbene terminus (Figure 2c) suggested that a DB24C8 unit would dissociate through a different mechanism: hovering over the *p*-phenylene unit (but not passing over it completely), stretching to overcome the α -methyl group, and then passing over the phenyl group. The need to pass over the methyl and phenylene groups simultaneously would make the (*Z*)- α -methylstilbene unit a much bulkier stopper unit for a rotaxane possessing DB24C8 as its ring-shaped component.

Synthesis of Axle Components. We synthesized the key axle components **3** using a previously reported procedure (Scheme 1).²² 4-Carboxybenzaldehyde dimethyl acetal **1** was first methylated and then subjected to a Wittig reaction; deprotection of the acetal provided a separable mixture of the (*E*)- and (*Z*)-stilbene derivatives **2** in 45% and 43% yields, respectively. Condensation of these isomers with 4-*tert*-butylbenzylamine and subsequent reduction of the imines produced the corresponding secondary amines, which we converted into the dialkylammonium salts (*E*)- and (*Z*)-**3** through protonation and counterion exchange.

Rotaxane Synthesis. We found that the (*E*)- α -methylstilbene terminus was sufficiently small to allow its passage through the cavity of DB24C8. The solubility of (*E*)-**3** in CDCl₃/CD₃CN was poor; the addition of DB24C8 improved its solubility, suggesting the immediate formation of pseudorotaxane (*E*)-**4**. A ¹H NMR spectrum of a mixture of (*E*)-**3** and DB24C8 in

SCHEME 1



CDCl₃/CD₃CN (1:1) revealed the presence of (*E*)-**4** through the appearance of signals for the CH₂N⁺CH₂ protons at 4.67 and 4.77 ppm and for the aliphatic and aromatic protons of the DB24C8 component at 3.59–3.63 and 6.83–6.93 ppm, respectively. Such chemical shifts are typical for these types of rotaxanes.²³ In contrast, we observed no new signals in the ¹H NMR spectrum of a mixture of (*Z*)-**3** and DB24C8 in CDCl₃/CD₃CN, suggesting that the (*Z*)- α -methylstilbene unit is an impassable stopper. Next, we examined the feasibility of forming a rotaxane through photoisomerization of (*E*)-**4**. UV irradiation of a CDCl₃/CD₃CN (1:1) mixture of (*E*)-**3** (272 mM) and DB24C8 (408 mM), in the presence of benzil¹⁶ (272 mM) as a sensitizer, led to efficient *E*-to-*Z* isomerization of the stilbene unit of the pseudorotaxane (Figure 1 end-closing process: (*E*)-**3** + DB24C8 \rightarrow (*Z*)-**4**), resulting in the formation of the [2]rotaxane (*Z*)-**4** in a 73% isolated yield (NMR yield: 87%).^{26,27} The (*Z*)- α -methylstilbene moiety was sufficiently bulky to prevent unthreading at room temperature in polar solvents in the dark. We characterized the [2]rotaxane (*Z*)-**4** using ¹H and ¹³C NMR spectroscopy, FAB mass spectrometry, and IR spectroscopy; the ¹H NMR spectrum was fully assigned by using ¹H–¹H COSY and ROESY techniques. The shifts to higher field for the signals of the crown ether and to lower field for those of the benzylic protons of the axle support the presence of the components in a rotaxane structure. In the FAB mass spectrum,

(26) The use of 9-fluorenone, duroquinone, and pyrene as photosensitizers provided the [2]rotaxane (*Z*)-**4** in 54% (NMR yield: 79%), 71% (79%), and 58% (77%) yields, respectively.

(27) The geometry ratio of the α -methylstilbene was similar to Leigh's results in indirect photoisomerization reaction with benzil as a sensitizer (*Z*:*E* = 80:20).¹²⁷

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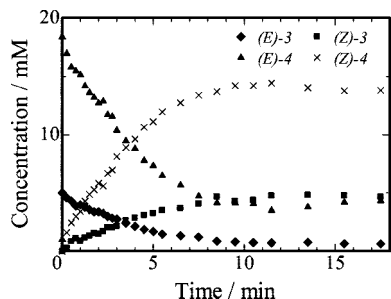


FIGURE 3. Plots of the concentrations of (*E*)-3, (*Z*)-3, (*E*)-4, and (*Z*)-4 over time during the irradiation of a $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) solution of (*E*)-3 and DB24C8 in the presence of benzil at 0 °C. The photoreaction was performed in an NMR tube under nitrogen with light from a high-pressure mercury lamp.

the presence of an intense peak at m/z 818, corresponding to the molecular weight of the [2]rotaxane in the absence of its counterion, confirmed the structural assignment.

We used ^1H NMR spectroscopy to monitor the progress of the photochemical isomerization of (*E*)-3 leading to the [2]rotaxane.²⁸ After irradiating a solution containing equimolar (23 mM) quantities of (*E*)-3, DB24C8, and benzil in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) at 0 °C, we observed over time the appearance and disappearance of resonances assigned to (*Z*)-4, (*Z*)-3, (*E*)-4, and (*E*)-3. The decreases in intensity of the signals of the protons of the *E* isomers were concomitant with the increases in the intensities of the signals associated with the *Z* isomers during the course of the reaction (Figure 3). On the basis of integration of pertinent signals in these spectra, we determined the association constant for the formation of the [2]pseudorotaxane (*E*)-4 to be $900 \pm 110 \text{ M}^{-1}$.²⁹

There was a significant difference between the ^1H NMR spectra of the crude products obtained at high (272 mM) and moderate (23 mM) concentrations. At high concentration, we identified only the signals of the substrates, expected products, and sensitizer; in contrast, we observed signals for some unidentified products when performing the reaction at moderate concentration, where the percentage of products decreased after 12 min (Figure 3). It is likely that the ca. 20% of axle-like species that existed in the uncomplexed form at moderate concentration decomposed under UV irradiation.^{14a,30} Indeed, long-term irradiation of a solution of the axle in the absence of DB24C8 afforded complex mixtures.

Rotaxane Formation through Dynamic Covalent Chemistry. The salt (*Z*)-3 is only partially soluble in $\text{CDCl}_3/\text{CD}_3\text{CN}$ at high concentrations, even when DB24C8 is present, because the species cannot form a [2]pseudorotaxane. We used ^1H NMR spectroscopy to monitor the progress (Figure 4) of the UV irradiation of a $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) solution of (*Z*)-3 (23 mM) and DB24C8 (23 mM) in the presence of benzil (23 mM).²⁸ Three equilibrating reactions occurred (Figure 1 process 1 and

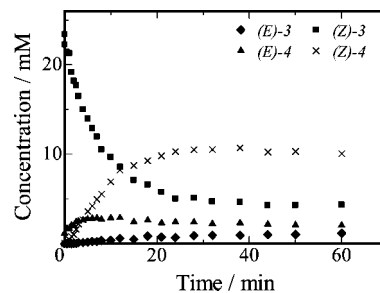


FIGURE 4. Plots of the concentrations of (*E*)-3, (*Z*)-3, (*E*)-4, and (*Z*)-4 over time during the irradiation of a $\text{CDCl}_3/\text{CD}_3\text{CN}$ solution (1:1) of (*Z*)-3 and DB24C8 in the presence of benzil at 0 °C. The photoreaction was performed in an NMR tube under nitrogen with light from a high-pressure mercury lamp.

end-closing process: (*Z*)-3 + DB24C8 \rightarrow (*Z*)-4): (i) (*Z*)-3 isomerized under UV irradiation to afford (*E*)-3; (ii) DB24C8 and (*E*)-3 self-assembled to produce the [2]pseudorotaxane (*E*)-4 through hydrogen bonding between the NH_2^+ unit and the crown ether; and (iii) (*Z*)-4 was produced through isomerization of (*E*)-4. As a result, the thermodynamically stable and photoisomerizationally predominant [2]rotaxane (*Z*)-4 was afforded through a sequence of end-opening and end-closing processes.

The final compositions of the [2]rotaxane mixtures formed after irradiation of the *E* and *Z* isomers in Figures 3 and 4 were similar. The ratio of compounds (*E*)-3, (*Z*)-3, (*E*)-4, and (*Z*)-4 was 3:20:18:59 after irradiation of (*E*)-3 in the presence of DB24C8 and benzil for 930 s; it was 6:24:12:58 after irradiation of (*Z*)-3 in the presence of DB24C8 and benzil for 3600 s. Note that the synthesis with the *Z* isomer required a longer reaction time, despite the otherwise identical reaction conditions. This finding suggests that the reaction rate for the isomerization of (*Z*)-3 is slower than that of its *E* isomer. In addition, the longer UV irradiation time results in decomposition of the axle-like units, thereby decreasing the yield of the [2]rotaxane in this case. The photoreactions of the *E* and *Z* isomers generated ca. 14 and 11 mM solutions, respectively, of the rotaxane (*Z*)-4 after irradiating moderate initial concentrations of the precursors for 10 (Figure 3) and 30 min (Figure 4), respectively.

Furthermore, we also prepared (Scheme 2) the dialkylammonium salts **5**, obtained as a 2:1 mixture of the *E* and *Z* regioisomers, possessing 3,5-dimethylphenyl groups as bulky stoppers on one end; we used the same photoisomerization reaction to convert these isomers into the corresponding [2]rotaxane (*Z*)-6. Thus, irradiating a suspension of the dialkylammonium salts **5** in the presence of DB24C8 and benzil for 330 min gave the corresponding [2]rotaxane (*Z*)-6 in 71% isolated yield (NMR yield: 76%).

Degradation of [2]Rotaxane through Photochemical and Thermal Reactions. We examined the rate of the end-opening reaction of the [2]rotaxane (*Z*)-4. Irradiation of a solution of (*Z*)-4 (8.5 mM) and benzophenone (8.5 mM)—a nonselective sensitizer¹⁶—in $\text{DMSO}-d_6$, which disrupts hydrogen bonding between the axle- and wheel-like components, led to the production of (*E*)-3, (*Z*)-3, and DB24C8. Monitoring this process with ^1H NMR spectroscopy revealed that the photodegradation of (*Z*)-4 fitted a first-order curve; the half-life was 103 min ((Figure 1 end-opening process and process 1': (*Z*)-4 \rightarrow (*E*)-3 and (*Z*)-3 + DB24C8, Figure 5).²⁸

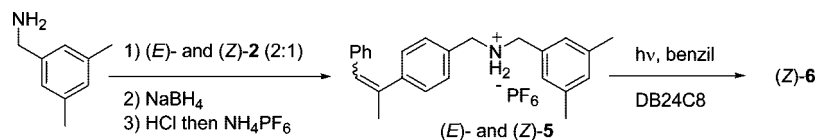
Next, we investigated the thermal degradation of the [2]rotaxane (*Z*)-6 (stopper unit: 3,5-dimethylphenyl group) (Figure 1 thermal degradation: (*Z*)-6 \rightarrow (*Z*)-5 + DB24C8 and (*Z*)-4 \rightarrow

(28) See the Supporting Information.

(29) The association constant was measured at 25 °C with the following equation: $K = [\text{pseudorotaxane}]/[\text{ammonium ion} + \text{ammonium salt}][\text{DB24C8}]$.

(30) Rotaxane-encapsulation can enhance the stability of the axle's components; for examples, see: (a) Parham, A. H.; Windisch, B.; Vögtle, F. *Eur. J. Org. Chem.* **1999**, 1233–1238. (b) Buston, J. E. H.; Young, J. R.; Anderson, H. L. *Chem. Commun.* **2000**, 905–906. (c) Craig, M. R.; Hutchings, M. G.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1071–1074. (d) Ghosh, P.; Mermagen, O.; Schalley, C. A. *Chem. Commun.* **2002**, 2628–2629. (e) Choi, S.; Park, S. H.; Ziganshina, A. Y.; Ko, Y. H.; Lee, J. W.; Kim, K. *Chem. Commun.* **2003**, 2176–2177. (f) Arunkumar, E.; Forbes, C. C.; Noll, B. C.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 3288–3289. (g) Hsueh, S.-Y.; Lai, C.-C.; Liu, Y.-H.; Wang, Y.; Peng, S.-M.; Chiu, S.-H. *Org. Lett.* **2007**, *9*, 4523–4526.

SCHEME 2



(Z)-3 + DB24C8). We heated a solution of (Z)-6 and 3,5-*tert*-butylphenol (a radical scavenger) in DMSO-*d*₆ in the dark at 80–110 °C.³¹ Plots of the concentration of rotaxane (Z)-6, monitored with ¹H NMR spectroscopy,²⁸ gave first-order curves; we obtained the values of *k*_{deg} from the slope of the straight line of the plot of ln{[(Z)-6]_{*t*}/[(Z)-6]₀} against *t*, where [(Z)-6]₀ and [(Z)-6]_{*t*} correspond to the initial concentration of (Z)-6 and the concentration of (Z)-6 at time *t*, respectively (Figure 6). On the basis of transition state theory, we estimated the activation enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger), and free energy (ΔG^\ddagger) at 25 °C to be 56.5 kJ/mol, –210 J/mol K, and 119 kJ/mol, respectively.³² We also obtained kinetic parameters of degradation of (Z)-4: $\Delta H^\ddagger = 60.3$ kJ/mol, $\Delta S^\ddagger = -199$ J/mol K, and $\Delta G^\ddagger = 120$ kJ/mol at 25 °C.²⁸ These kinetic parameters are close in value

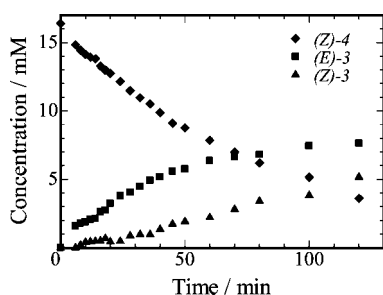


FIGURE 5. Plots of the concentrations of (E)-3, (Z)-3, and (Z)-4 over time during the photodegradation of the [2]rotaxane (Z)-4. The reactions were performed in an NMR tube under nitrogen with light from a high-pressure mercury lamp.

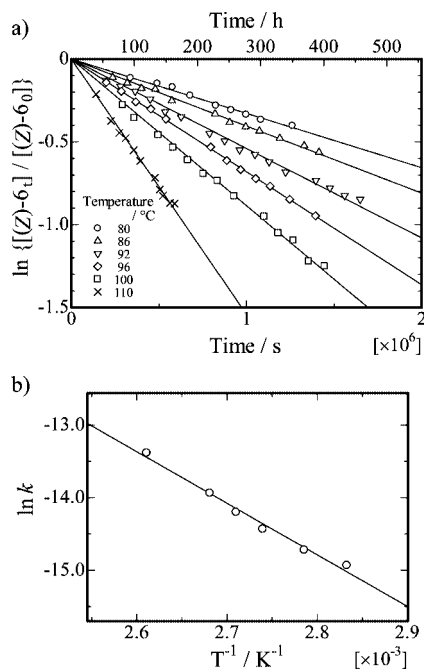


FIGURE 6. (a) Plots of ln{[(Z)-6]_{*t*}/[(Z)-6]₀} over time at 80 °C (○), 86 °C (△), 92 °C (▽), 96 °C (◇), 100 °C (□), and 110 °C (×). (b) Plots of ln *k* versus 1/*T*.

to those previously reported for the decomplexation of a rotaxane consisting of a mono-*meta*-fused dibenzo[25]crown-8 unit and a *tert*-butyl stopper in methanol ($\Delta H^\ddagger = 60.2$ kJ/mol; $\Delta S^\ddagger = -144$ J/mol K; $\Delta G^\ddagger = 103$ kJ/mol).³³ In our system, however, entropy contributes more strongly to the stability of the transition state than it did in the previous case. We suspect that several factors are responsible for this phenomenon: (1) the α -methylstilbene stopper may be strongly restricted by DB24C8 in the transition state; (2) differences of stoppers; and (3) differences in solvation.

Conclusion

It is possible to synthesize [2]rotaxanes comprising DB24C8 and secondary dialkylammonium ion units through the end-closing isomerization of (*E*)- α -methylstilbene termini to their *Z* isomer counterparts. The end-closing process, which includes [2]pseudorotaxane formation and photoisomerization reactions, forms [2]rotaxanes predominantly in aprotic, nonpolar solvents in the presence of an appropriate sensitizer. We also succeeded in constructing these [2]rotaxanes from the dialkylammonium ions possessing (*Z*)- α -methylstilbene termini, taking advantage of the reversible *Z*-to-*E* isomerization reactions. This process consisted of three reversible reactions: isomerization of the (*Z*)- α -methylstilbene unit of the dialkylammonium ion, [2]pseudorotaxane formation, and isomerization of the (*E*)- α -methylstilbene unit in the [2]pseudorotaxane. UV irradiation of the (*Z*)- α -methylstilbene under appropriate conditions shifts the equilibria to favor the formation of the [2]rotaxane. The photoinduced end-opening reaction fits a first-order curve to afford the axle- and wheel-like components when the [2]rotaxane is dissolved in a polar solvent in the presence of an appropriate sensitizer. We also investigated the thermal stability of [2]rotaxanes, monitoring the slow dissociation of DB24C8 from the NH₂⁺ center at high temperature to afford the kinetic parameters.

Experimental Section

(E)- and (Z)-4-(1-Methyl-2-phenylvinyl)benzaldehyde [(E)- and (Z)-2]. Butyllithium (1.59 M in hexane; 8.17 mL, 13.0 mmol) was added to a stirred suspension of benzylphosphonium chloride (5.56 g, 14.3 mmol) in THF (55 mL) at 0 °C and then the resulting mixture was stirred at 0 °C for 30 min. At this point, a solution of 4-acetylbenzaldehyde dimethylacetal (1.26 g, 6.49 mmol) in THF (13 mL) was added dropwise at 0 °C. After being stirred at room temperature overnight, the reaction mixture was quenched with 10% HCl, the organic solvent was evaporated off, and the residue was extracted with EtOAc. The extracts were washed with saturated brine and the residue obtained upon workup was chromatographed (100:1) to afford the (*E*)-2 (0.648 g, 45%) as colorless needles after recrystallization (hexane). Mp 77–78 °C. IR ν_{max} (KBr) 2976, 2939, 2895, 1701, 1599 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 10.03 (s, 1H), 7.91–7.87 (m, 2H), 7.71–7.66 (m, 2H), 7.43–7.36 (m, 4H), 7.32–7.25 (m, 1H), 6.97 (br s, 1H), 2.32 (br s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.4, 149.6, 137.4, 136.0, 134.9, 130.0, 129.6, 129.0, 128.1, 126.8, 126.2, 17.0. Anal. Calcd for C₁₆H₁₄O: C; 86.45, H; 6.35. Found: C; 86.57, H; 6.50. MS (FAB) *m/z* for C₁₆H₁₄O [M + H]⁺ calcd 223, found 223. Further elution (SiO₂;

hexane/EtOAc, 20:1) yielded (*Z*)-**2** (0.615 g, 43%) as a powder. Mp 38–40 °C. IR ν_{\max} (KBr) cm^{-1} 2976, 2939, 2895, 1732, 1522. ^1H NMR (300 MHz, CDCl_3) δ 9.98 (s, 1H), 7.81–7.77 (m, 2H), 7.37–7.33 (m, 2H), 7.14–7.08 (m, 3H), 6.95–6.90 (m, 2H), 6.58 (br s, 1H), 2.23 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.7, 148.7, 137.2, 136.9, 134.9, 129.8, 129.0, 128.9, 128.2, 127.9, 126.5, 26.3. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.45, H, 6.35. Found: C, 86.34, H, 6.60. MS (FAB) m/z for $\text{C}_{16}\text{H}_{14}\text{O} [\text{M} + \text{H}]^+$ calcd 223, found 223.

(*E*)-*N*-(4-*tert*-Butylbenzyl)-4-(1-methyl-2-phenylvinyl)benzylammonium Hexafluorophosphate [(*E*)-**3**]. A suspension of the aldehyde (*E*)-**2** (0.300 g, 1.35 mmol), 4-*tert*-butylbenzylammonium chloride (0.268 g, 1.35 mmol), potassium carbonate (0.934 g, 6.76 mmol), and magnesium sulfate (3.25 g, 27.0 mmol) in THF was stirred at room temperature for 4 h. The reaction mixture was filtered and the filtrate concentrated. The residue (0.464 g) obtained upon workup was taken up into THF/ethanol [1:1 (v/v), 4 mL] and cooled to 0 °C; sodium borohydride (76.6 mg, 2.03 mmol) was added and the mixture was stirred at room temperature for 16 h. The resulting mixture was treated with 10% HCl and then the solvent was evaporated off to give a residue; 10% NaOH was added and the mixture extracted with chloroform. The extracts were washed with saturated brine, dried, and evaporated to give a residue; 10% HCl was added at 0 °C and then the water was evaporated. The residue was washed with diisopropyl ether to provide the hydrochloride salt (0.430 g). Saturated aqueous ammonium hexafluorophosphate (1 mL) was added to a suspension of the hydrochloride salt (0.350 g) in water/acetone [1:1 (v/v), 30 mL] at 0 °C and then the mixture was stirred for 1 h at 0 °C. After evaporation of the solvent, the solid was filtered off and washed with water and benzene to afford (*E*)-**3** (0.361 g, 64% from (*E*)-**2**). Mp >230 °C. IR ν_{\max} (KBr) 3251, 2961, 2787, 1600, 1411, 837, 559 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.40–9.04 (br, 2H), 7.75–7.71 (m, 2H), 7.59–7.51 (m, 4H), 7.51–7.44 (m, 6H), 7.38–7.32 (m, 1H), 7.04–7.01 (m, 1H), 4.31–4.17 (m, 4H), 2.33–2.29 (m, 3H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 151.7, 143.7, 137.5, 135.9, 130.6, 130.0, 129.7, 129.0, 128.9, 128.2, 127.8, 126.7, 126.0, 125.5, 49.77, 49.76, 34.4, 31.0, 17.0. HR-MS (FAB) m/z for $\text{C}_{27}\text{H}_{32}\text{N}^+ [\text{M} - \text{PF}_6]^+$ calcd 370.2535, found 370.2533.

(*Z*)-*N*-(4-*tert*-Butylbenzyl)-4-(1-methyl-2-phenylvinyl)benzylammonium Hexafluorophosphate [(*Z*)-**3**]. Imine formation of (*Z*)-**2** (0.153 g, 0.689 mmol) followed by reduction and salt formation was performed as described above to give (*Z*)-**3** (0.171 g, 48%) as a powder. Mp >200 °C. IR ν_{\max} (KBr) 3250, 2964, 2789, 1585, 840, 559 cm^{-1} . ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.35–9.04 (br, 2H), 7.56–7.44 (m, 6H), 7.34–7.27 (m, 2H), 7.21–7.12 (m, 3H), 7.04–6.97 (m, 2H), 6.63 (br s, 1H), 4.27–4.16 (m, 4H), 2.23 (br s, 3H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 151.7, 142.4, 137.7, 137.0, 130.5, 130.2, 129.7, 128.9, 128.6, 128.2, 127.9, 126.7, 126.3, 125.4, 49.9, 49.8, 34.4, 31.0, 26.6. Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{F}_6\text{NP}$: C, 62.91, H, 6.26, N, 2.72. Found: C, 62.64, H, 6.20, N, 2.75. MS (FAB) m/z for $\text{C}_{27}\text{H}_{32}\text{N}^+ [\text{M} - \text{PF}_6]^+$ calcd 370, found 370.

[2]-{[(*Z*)-*N*-(4-*tert*-Butylbenzyl)-4-(1-methyl-2-phenylvinyl)benzylammonium]-(dibenzo[24]crown-8)}rotaxane Hexafluorophosphate [(*Z*)-**4**]. A solution of the ammonium salt (*E*)-**3** (70.0 mg, 0.136 mmol), DB24C8 (91.3 mg, 0.204 mmol), and benzil (28.6 mg, 0.136 mmol) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ [1:1 (v/v), 0.5 mL] was irradiated at 0 °C for 1.5 h with light from a 250-W high-pressure mercury lamp passed through a Pyrex filter. Evaporation of the solvent gave a residue;

hexane and toluene [1:1 (v/v), 8 mL] were added and then the mixture was stirred for 1 day at room temperature. The solid was filtered off and then purified through chromatography (SiO_2 ; hexane/EtOAc, 1:2) to yield crude (*Z*)-**4**, which was washed with toluene and hexane to afford (*Z*)-**4** (95.1 mg, 73%) as a solid. Mp 123–125 °C. IR ν_{\max} (KBr) 3161, 2934, 2876, 1506, 1456, 1254, 1124, 1055, 840, 557 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.75–7.40 (br s, 2H), 7.30–7.20 (m, 2H), 7.20–7.10 (m, 4H), 7.10–7.02 (m, 5H), 6.95–6.83 (m, 6H), 6.80–6.73 (m, 4H), 6.50 (br s, 1H), 4.65–4.56 (m, 2H), 4.53–4.42 (m, 2H), 4.18–4.02 (m, 8H), 3.83–3.68 (m, 8H), 3.55–3.37 (m, 8H), 2.50 (d, $J = 1.5$ Hz, 3H), 1.23 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.5, 147.5, 143.0, 137.7, 137.6, 130.5, 129.3, 129.1, 129.0, 128.7, 128.3, 127.9, 127.3, 126.3, 125.5, 121.8, 112.7, 70.6, 70.2, 68.2, 52.4, 52.2, 34.6, 31.2, 26.8. Anal. Calcd for $\text{C}_{51}\text{H}_{64}\text{F}_6\text{NO}_8\text{P} \cdot 0.5\text{H}_2\text{O}$: C, 62.95; H, 6.73; N, 1.44. Found: C, 62.85; H, 6.57; N, 1.59. MS (FAB) m/z for $\text{C}_{51}\text{H}_{64}\text{NO}_8^+ [\text{M} - \text{PF}_6]^+$ calcd 818, found 818.

(*E*)- and (*Z*)-*N*-(3,5-Dimethylbenzyl)-4-(1-methyl-2-phenylvinyl)benzylammonium Hexafluorophosphate [(*E*- and (*Z*)-**5**]. Imine formation from a mixture of aldehydes (*E*:*Z* = 2:1; 1.11 g, 5.00 mmol), reduction, and salt formation were performed as described above, yielding (*E*- and (*Z*)-**5** (1.50 g, 3.08 mmol, 65%, three steps; *E*:*Z* = 2:1) as a powder. Mp 173–175 °C. IR ν_{\max} (KBr) 3250, 3229, 2949, 2920, 1611, 842, 559 cm^{-1} . ^1H NMR (300 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1:1) δ 7.66–7.61 (m, 4/3H), 7.53–7.23 (m, 6H), 7.14–7.00 (m, 4H), 6.94–6.88 (m, 4/3H), 6.53–6.54 (br s, 1/3H), 4.24–4.08 (m, 4H), 2.34 (s, 6H), 2.28 (d, $J = 1.5$ Hz, 2H), 2.21 (d, $J = 1.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.7, 142.4, 137.81, 137.78, 137.7, 137.5, 137.0, 135.9, 131.7, 131.6, 130.7, 130.5, 130.30, 130.28, 130.2, 130.1, 129.1, 128.6, 128.3, 128.2, 128.0, 127.8, 127.6, 126.8, 126.7, 126.3, 126.0, 50.14, 50.06, 49.9, 49.8, 26.7, 20.81, 20.79, 17.1. Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{F}_6\text{NP}$: C, 61.60; H, 5.79; N, 2.87. Found: C, 61.64; H, 5.87; N, 2.73. MS (FAB) m/z for $\text{C}_{25}\text{H}_{28}\text{N}^+ [\text{M} - \text{PF}_6]^+$ calcd 342, found 342.

[2]-{(Dibenzo[24]crown-8)-[(*Z*)-*N*-(3,5-dimethylbenzyl)-4-(1-methyl-2-phenylvinyl)benzylammonium]}rotaxane Hexafluorophosphate [(*Z*)-**6**]. The isomerization of the ammonium salts (*Z*- and (*E*)-**5** (*E*:*Z* = 2:1; 65.8 mg, 0.135 mmol, 270 mM) in the presence of DB24C8 (90.8 mg, 0.203 mmol, 405 mM) and benzil (28.4 mg, 0.135 mmol, 270 mM) was performed as described above to give (*Z*)-**6** (44.4 mg, 71%) as a powder. Mp 138.5–140.0 °C. IR ν_{\max} (KBr) 3293, 3145, 2923, 2853, 1505, 1256, 1122, 841, 558 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.68–7.48 (br, 2H), 7.32–7.27 (m, 2H), 7.13–7.09 (m, 2H), 7.08–7.03 (m, 4H), 6.96–6.86 (m, 5H), 6.84–6.74 (m, 7H), 6.52–6.49 (m, 1H), 4.64–4.57 (m, 2H), 4.42–4.35 (m, 2H), 4.17–4.03 (m, 8H), 3.82–3.70 (m, 8H), 3.53–3.35 (m, 8H), 2.16 (d, $J = 1.2$ Hz, 3H), 2.12 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 147.5, 143.0, 138.3, 137.63, 137.57, 131.1, 130.7, 130.4, 129.4, 129.0, 128.7, 127.8, 127.3, 126.8, 126.3, 121.8, 112.7, 70.6, 70.1, 68.3, 52.8, 52.2, 26.7, 21.1. Anal. Calcd for $\text{C}_{49}\text{H}_{60}\text{F}_6\text{NO}_8\text{P}$: C, 62.88; H, 6.46; N, 1.50. Found: C, 62.62; H, 6.45; N, 1.36. MS (FAB) m/z for $\text{C}_{49}\text{H}_{60}\text{NO}_8^+ [\text{M} - \text{PF}_6]^+$ calcd 790, found 790.

General Procedure for the Decomplexation of Rotaxane (*Z*)-6**.** A solution of the [2]rotaxane (*Z*)-**6** (4 mM) and 2,6-di-*tert*-butylphenol (4.8 mM) in $\text{DMSO}-d_6$ was heated at 80–110 °C. ^1H NMR spectra were recorded at various time intervals.

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Supporting Information Available: ^1H NMR data on the progress of the formation of rotaxane ((*Z*)-**4**) and degradation of rotaxanes ((*Z*)-**4** and (*Z*)-**6**) and ^1H and ^{13}C NMR spectra of (*E*)-**2**, (*Z*)-**2**, (*E*)-**3**, (*Z*)-**3**, (*Z*)-**4**, (*E*)-**5**, (*Z*)-**5**, and (*Z*)-**6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(31) A *Z* to *E* isomerization reaction proceeded in the absence of the radical scavenger.

(32) The transition state theory is described by using the following equation: $k_{\text{deg}} = (kT/h) \exp(-\Delta G^\ddagger/RT)$, where R , h , and k correspond to the gas, Planck, and Boltzmann constants, respectively, k_{deg} is the rate constant of the thermal degradation reaction, and ΔG^\ddagger is the activation free energy, given by the activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger) as $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

(33) Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Glink, P. T.; Garrell, R. L.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3631–3634.