Effect of Steric Barrier on the Shuttling of Rotaxane Having Crown Ether Wheel

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Rotaxanes comprising dibenzo-24-crown-8 and a symmetrical ammonium salt were desymmetrized by N-acylation. The shuttling behavior was investigated in detail. For the *N*,*N*-di-*n*-alkyl-type axle, the propionyl group was necessary to stop shuttling, whereas the acetyl group was bulky enough for the *N*,*N*-dibenzyl-type axle. According to the $\Delta S^{\ddagger}$ term of the shuttling, the *N*-formyl and *N*-acetyl rotaxanes with an *N*,*N*-di-*n*-alkyl-type axle showed similar shuttling frequencies at room temperature.

Rotaxanes exhibit the interesting property of to-and-fro motion of the wheel on the axle, which is termed as shuttling.[1] On the basis of the shuttling behavior of the rotaxane, various molecular devices such as molecular switches have been proposed.[2] The rate of shuttling and stability of the on–off states of the molecular switch can be regulated by the structure and bulkiness of the barrier on the axle that determines the activation energy ($\Delta G^{\ddagger}$) of shuttling (Figure 1).[3] Although various rotaxanes have been prepared using dibenzo-24-crown-8 (DB24C8) as the wheel component,[4] the steric effect of the axle on the cavity of DB24C8 has been studied only for the system with strong intercomponent interaction.[3f] We studied the quantitative analyses to investigate how the bulkiness of the barrier on the axle attenuates the shuttling speed of the DB24C8 wheel using intercomponent interaction-free system and observed the unusual effect of the barrier on the shuttling behavior of DB24C8.

Symmetrical rotaxanes **1** and **2** were prepared from the corresponding aminoalcohols via the trifluoromethanesulfonic acid-catalyzed acylation method (Scheme 1).[5] The desymmetrization of **1** and **2** was carried out by *N*-acylation using acid anhydride in the presence of triethylamine to obtain rotaxanes **3** and **4**, respectively.[6] For the formylation reaction, mixed anhydride **5** was used as the acylation agent.[7]

Since the system becomes unstable when the wheel crown ether is situated on the central amide group, the wheel is located

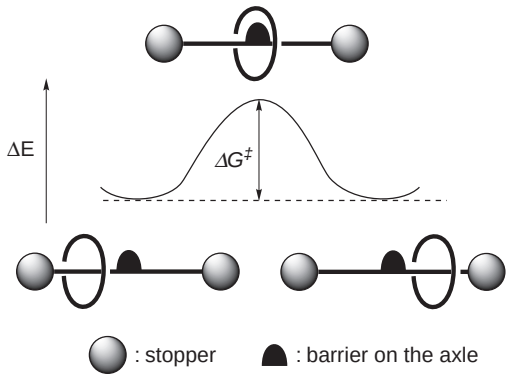
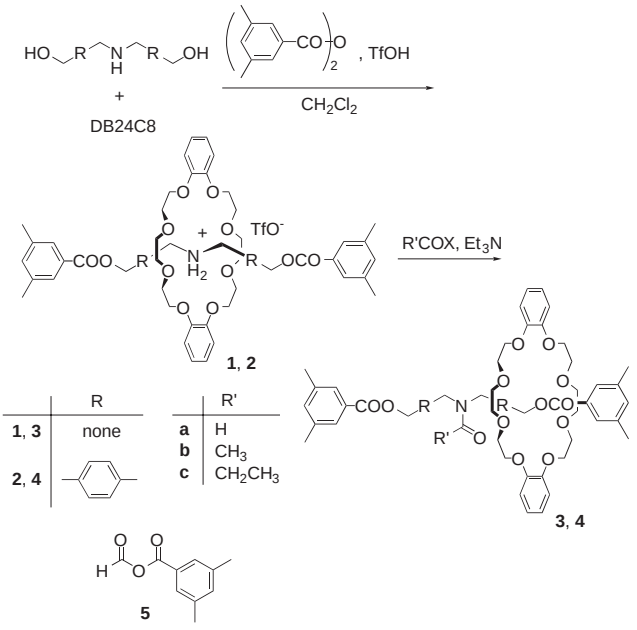


Figure 1. Energy diagram of shuttling.



Scheme 1.

at one of the two split sides of the axle to desymmetrize the axle component. Therefore, every ^{1}H NMR signal of the axle component was observed as a pair of signals with equal integration at lower temperature.[8] Above the coalescence temperature (T_c), the split signals coalesced with each other; this is because the two sides of the axle could not be distinguished from each other due to rapid shuttling. The $\Delta G^{\ddagger}$ values for **3** and **4** were estimated from the T_c value of the methyl group at the axle terminal.[9] The results are listed in Table 1. Although T_c values were observed for **3a**, **3b**, and **4a**, no coalescence or peak broadening was observed for **3c** and **4b**, indicating that the propionyl group in **3c** and acetyl group in **4b** strongly prevent shuttling ($\Delta G^{\ddagger} > 23$ kcal/mol). The value of $\Delta G^{\ddagger}$ depends not only on the bulkiness of the amide group but also on the structure of

Table 1. Thermodynamic parameters of the shuttling of **3** and **4** evaluated by ^{1}H NMR using peak coalescence method[a]

Rotaxane	270 MHz T_c/K	$\Delta G^{\ddagger}$/kcal mol^{-1}	400 MHz T_c/K	$\Delta G^{\ddagger}$/kcal mol^{-1}
3a	419	21.8	431	22.4
3b	420	21.5	432	21.7
3c	none	—	none	—
4a	391	19.8	402	20.1
4b	none	—	none	—

[a]Coalescence behavior was observed for the terminal methyl group in DMSO-d_6. none: no coalescence was observed below 452 K.

Table 2. Thermodynamic parameters of shuttling of **3** and **4** evaluated by ^{1}H NMR using SPT-SIR method[a]

Rotaxane	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$/kcal mol^{-1}
3a	2.84	−49.1	17.5
3b	12.9	−18.6	18.4
3c	—[b]	—[b]	—[b]
4a	7.60	−31.2	16.9
4b	—[b]	—[b]	—[b]

[a]Spin polarization of the terminal methyl groups was observed in DMSO-d_6. [b]No shuttling was detected.

the axle. For example, the acetamide group was bulkier in **4b** than in **3b**. Interestingly, the $\Delta G^{\ddagger}$ value of **3b** is slightly smaller than that of **3a** in spite of the fact that the acetamide group is evidently bulkier than the formamide group. This observation indicates that thermodynamic analyses are necessary over a wide range of the temperatures.

To determine the thermodynamic parameters of shuttling at the desired temperature, we employed the SPT-SIR method[10] that has recently been used to examine the thermodynamic behavior of supramolecular systems.[11] The rate of shuttling was determined at a specific temperature, and the $\Delta G^{\ddagger}$ value was calculated from Eyring's equation. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were evaluated from the relationship between the temperature and $\Delta G^{\ddagger}$. The results are listed in Table 2. The $\Delta G^{\ddagger}$ values calculated at 298 K are also listed in Table 2.

No shuttling was detected for **3c** and **4b** even at 180 °C because the $\Delta G^{\ddagger}$ values are too large for these rotaxanes to bring about shuttling.[12] When the *N*,*N*-di-*n*-alkyl-type axle is used, the propionyl group is necessary to stop the shuttling, whereas the acetyl group is bulky enough when the *N*,*N*-dibenzyl-type axle is used. The term $\Delta H^{\ddagger}$ reflects the bulkiness of the barrier: the $\Delta H^{\ddagger}$ value of **4a** is greater than that of **3a**, and the $\Delta H^{\ddagger}$ value of **3b** is considerably greater than that of **3a** (Table 2). However, the $\Delta S^{\ddagger}$ values for the formamide barrier are surprisingly small, resulting in a small difference in the $\Delta G^{\ddagger}$ values among **3a**, **3b**, and **4a**. Although the difference increases at lower temperatures, the difference in the $\Delta G^{\ddagger}$ values between **3a** and **3b** is less than 1 kcal/mol at 298 K. At higher temperatures, the formamide group acts as a bulkier barrier than the acetamide group according to the contribution of $\Delta S^{\ddagger}$. At present, the reason for such small $\Delta S^{\ddagger}$ values of formamide is unclear.

In summary, we have demonstrated how the bulky barriers introduced on the axle component attenuate the frequency of shuttling. The attenuation was affected by not only the steric bulkiness of the barrier but also the structure of the axle. Further, the bulky substituent on the axle did not always effectively attenuate shuttling because the $\Delta S^{\ddagger}$ term played an important role in the rate of switching.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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